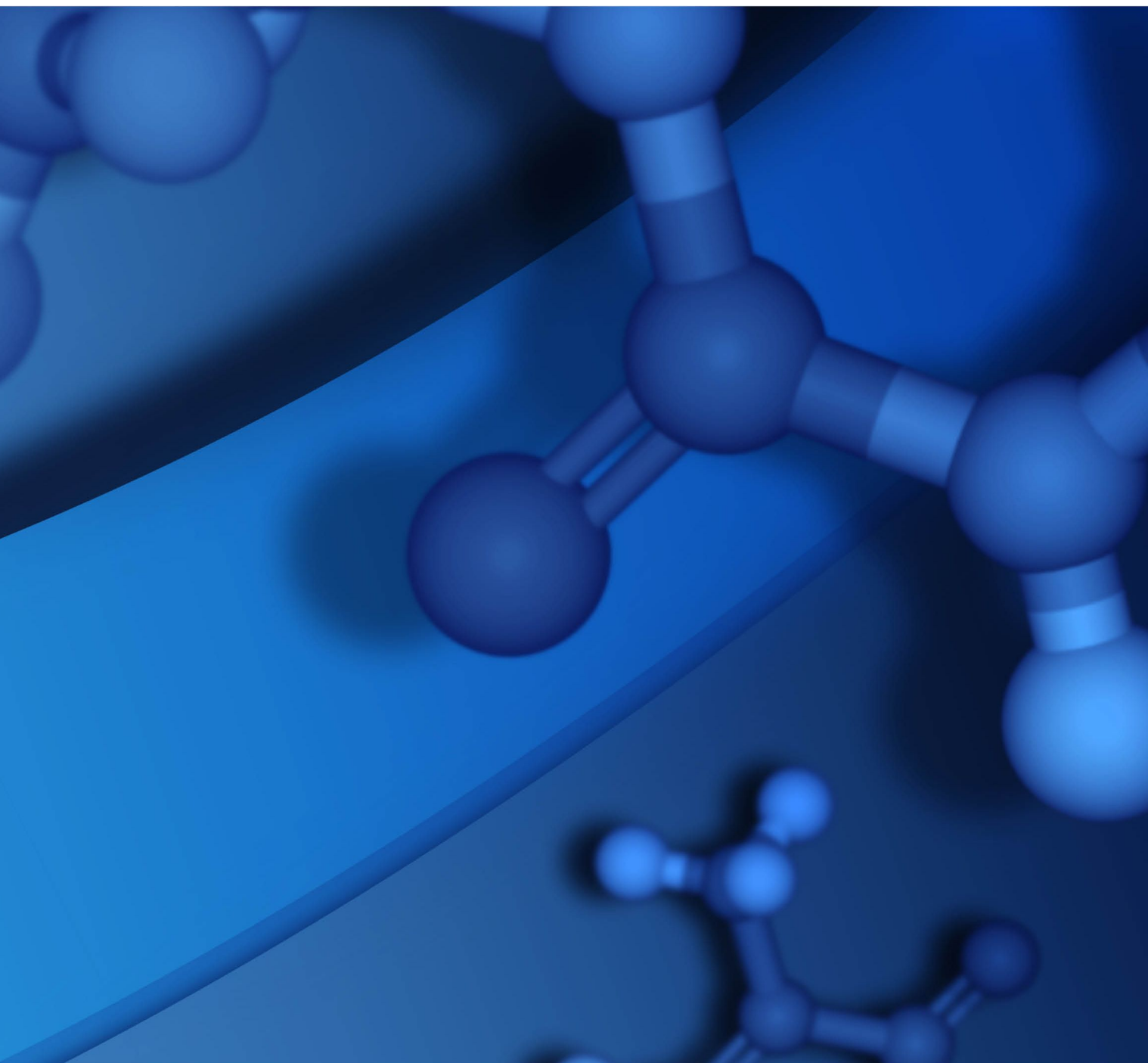


MODULES TUTORIALS

MATERIALS STUDIO 2017



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Tutorials

This section contains tutorials for the products you have installed.

Note: Numbers in the tutorials are shown in American English format. If your system is configured for a different locale, you should "translate" the numbers to the format appropriate to your locale before entering them.

For example, if your system is configured for the German locale, and a tutorial asks you to enter a value of 5,000 (five thousand), you should enter 5.000.

Adsorption Locator tutorials

The following tutorials illustrate how to utilize the Adsorption Locator's capabilities.

- [Determining the location of SO₂ on the Ni\(111\) surface with Adsorption Locator](#)
- [Modeling inhibitor adsorption onto a Pigment Red crystal face](#)

Determining the location of SO₂ on the Ni(111) surface with Adsorption Locator

Purpose: Introduces the use of Adsorption Locator to study the adsorption of different types of adsorbates onto substrates of different nature.

Modules: Materials Visualizer, Adsorption Locator, Forcite

Time: 

Prerequisites: Sketching a benzamide molecule Visualizer Tutorial

Background

This tutorial is inspired by a paper on "Density functional theory investigation of the structure of SO₂ and SO₃ on Cu(111) and Ni(111)" by Harrison et al. ([2006](#)). The importance of the adsorption of SO₂ and SO₃ molecules relates to the necessity of scrubbing such environmental pollutants from power station emissions. The paper presents DFT calculations on a number of geometries of the adsorbed SO₂ molecules.

Adsorption Locator can be used as a preparatory and screening tool in two ways:

- to generate adsorbed configurations automatically, which can subsequently be used as starting points for further DFT studies such as in the above paper.
- to use the forcefield method to obtain a ranking of the energies for each generated configuration, thereby indicating the preferred adsorption sites.

This tutorial will concentrate on the case of SO₂ on Ni(111), and covers:

- [Getting started](#)
- [To prepare the structures](#)
- [To set up the Adsorption Locator calculation](#)
- [To analyze the results](#)
- [Summary](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

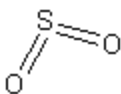
Begin by starting Materials Studio and creating a new project.


Open the **New Project** dialog and enter **Ni_SO2** as the project name, click the **OK** button.

The new project is created with *Ni_SO2* listed in the Project Explorer.

2. To prepare the structures

In this section of the tutorial you will prepare the structures of the Ni(111) surface and the SO₂ adsorbate. First prepare the SO₂ molecule.



Select **File | New...** from the menu bar to open the New Document dialog, double-click on **3D Atomistic**. Using the sketching tools, **build an SO₂ molecule** defining both S-O bonds as double bonds, click the **Clean** button . Select **File | Save** from the menu bar and save the structure as **SO2.xsd**.

The SO₂ molecule should be optimized before adsorbing it onto the Ni surface you will construct.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog. On the **Setup** tab, change the *Task* to **Geometry Optimization** and the *Quality* to **Fine**.

Select the **Energy** tab and change the *Forcefield* to **COMPASS**. Click the **Run** button.

When the job has completed the optimized structure is created in SO2 Forcite GeomOpt/SO2.xsd. Now you will construct a Ni(111) surface.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Structures/metals/pure-metals** and import **Ni.msi**.

Select **Build | Surfaces | Cleave Surface** from the menu bar to open the Cleave Surface dialog. Change the *Cleave plane (h k l)* to **1 1 1** and press the **TAB** key. Increase the *Fractional Thickness* to **6.0** and press the **TAB** key. Click the **Cleave** button and close the dialog.

The number of layers in the structure should be chosen so that the depth of the surface is greater than the non-bond cutoff used in the calculation. The choice of the cutoff will always be a trade off between the accuracy and the time required for the calculation. Using 6 layers of Ni atoms gives a sufficient depth that the SO₂ molecule will only be involved in non-bond interactions with Ni atoms in the layers of the surface, without increasing the calculation time unreasonably.

Next you will build a 2x2 supercell in order to expose a more realistic surface area for docking the SO₂ molecules.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase the values of **U** and **V** to **2** and click the **Create Supercell** button. **Close** the dialog.

This structure should be converted to have 3D periodicity. As 3D periodic boundary conditions are used, it is important that the size of the vacuum is great enough that the non-bond calculation for the sorbate does not interact with the periodic image of the bottom layer of atoms in the surface. The vacuum depth should be based on the non-bond cutoff and the shape of sorbate molecule. This should generally be over-estimated to ensure that the sorbate interacts only with the surface.

In this case, a distance of 15 Å between the Ni surface layer and the next layer beyond the vacuum is sufficient to prevent any non-bond interactions between the next repeat unit and either the Ni surface or the SO₂ molecule.


Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. Set the value of **Vacuum thickness** to **15.0** and click the **Build** button.

To display the Ni atoms more clearly the ball and stick display style should be used.

Select **View | Display style** from the menu bar to open the Display Style dialog. On the **Atom** tab, change the *Display style* to **Ball and stick**, then close the dialog.

3. To set up the Adsorption Locator calculation

You are now ready to set up the Adsorption Locator calculation, you will define the settings for the quality and the forcefield and the method for selecting the location of the sites that the calculation will probe.

Click the **Adsorption Locator** arrow  on the **Modules** toolbar and select **Calculation** from the dropdown list to open the Adsorption Locator Calculation dialog. Ensure that **Ni(1 1 1).xsd** is the active document.

On the **Setup** tab set the *Quality* to **Fine**. Select **SO2 Forcite GeomOpt/SO2.xsd** from the **Adsorbate** dropdown list. Set the value of **Loading** to **1**.

On the **Energy** tab select **COMPASS** from the **Forcefield** dropdown list.

On the **Location** tab check the **Surface region defined by atom set** checkbox.

When the *Quality* of the calculation is set to **Fine** many simulated annealing cycles with many steps per cycle will be used, so that good statistics are obtained.

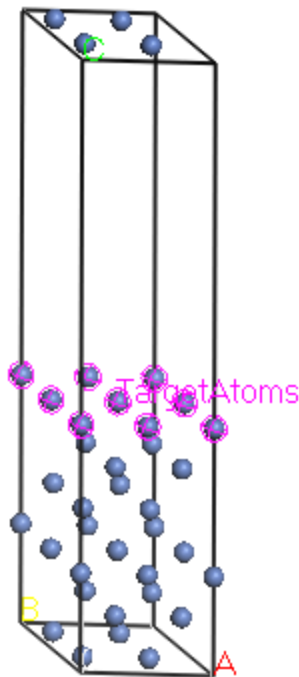
Now you need to select the atoms that define the surface region.

Select the **top layer of Ni atoms**, this will display them in yellow.

Tip: If you are not familiar with selecting atoms refer to the Opening and viewing 3D documents visualizer tutorial.

On the **Location** tab of the Adsorption Locator Calculation dialog, click the **Add** button to include the selected atoms in the *TargetAtoms* set for the adsorption calculation. Check the **Set maximum adsorption distance** checkbox, and enter a value of **5.0**.

The region defined by the specified maximum distance from the selected target atoms will be sampled for adsorbate inclusion. A value of **5.0** allows the system to develop new configurations of SO₂ adsorbed onto the Ni surface. If the maximum adsorption distance is too short some configurations will not be accessible, and if it is too long no new configurations will be added.



Ni(111) after defining the TargetAtoms set

The fixed energy window is used to select which configurations are reported, so all configurations which differ from the lowest configuration by less than 100 kcal/mol will be returned. In initial calculations it is useful to use a wider energy window, as this ensures that no significant configurations are missed.

On the **Properties** tab check the checkboxes for **all properties**. Select the radio button for **Fixed energy window** and enter a value of **100 kcal/mol**.

You are now ready to run the calculation.

Click the **Run** button and close the dialog.

4. To analyze the results

When the calculation begins Materials Studio will create a new folder called *Ni (1 1 1) Adsorption Anneal*. Once the calculation has completed, all results will be returned to this folder.

Open the 3D Atomistic document **Ni (1 1 1) Fields.xsd**.

This file displays a field of adsorption sites, higher density of points showing more likely locations.

Right-click in the document and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Field** tab click the **Color by field values** radio button and select the **Volume** display style. Close the dialog.

Now the more likely adsorption areas are shown in green and less likely sites appear red.

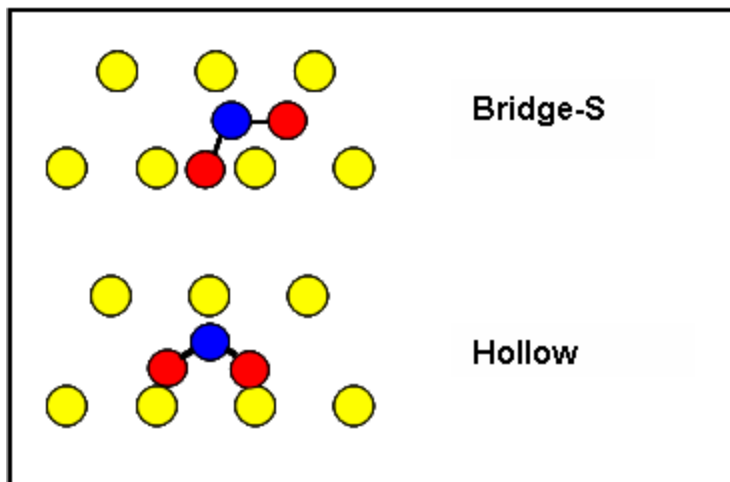
Open the study table **Ni(1 1 1).std**.

This contains the structures and energies of the lowest energy configurations. Compare the one found here with the lowest one found in the paper.

Repeat the Adsorption Locator calculation using Cu in place of Ni.

5. Summary

Your Adsorption Locator calculations should yield results similar to the following.



Schematic view of two possible bonding sites

Tip: To improve the view of the energy fields over the Ni surface, select all of the non-surface Ni atoms and, on the *Atom* tab of the Display Style dialog, set their display style to *None*.

Because the Monte-Carlo approach has a statistical component your results may be slightly different. To obtain results that are consistent between repeated calculations, it is necessary to run longer, more accurate simulations.

For SO_2 on Ni, the bridge site was found to be the lowest one in energy, in agreement with the [paper](#) by Harrison et al. They also reported no appreciable difference in energy between the bridge and the hollow sites for SO_2 on Cu.

This is the end of the tutorial.

"Density functional theory investigation of the structure of SO_2 and SO_3 on Cu(111) and Ni(111)" by M. J. Harrison, D. P. Woodruff, and J. Robinson, *Surface Science*, **600**, 1827, (2006)

Modeling inhibitor adsorption onto a Pigment Red crystal face

Purpose: Illustrates how to calculate binding energies in order to evaluate the potential of an additive using Adsorption Locator.

Modules: Materials Visualizer, Adsorption Locator, Forcite, COMPASS

Time: 🕒 🕒

Prerequisites: Using the Crystal Builder Visualizer Tutorial

Background

The bulk shape of crystals is critically important to many industrial processes. There are numerous examples of processes in the chemical and pharmaceutical industries where crystal shape is an important factor, including:

- Dissolution rate of chemicals and biological availability of drugs
- Handling, packaging, and storage of crystalline products
- Slurry handling, caking, and filtration during processing
- Milling, grinding, fragmentation, and dusting
- Density and texture optimization
- Wax and scale formation in petrochemicals

The relationship between the crystal morphology and the internal arrangement of atoms in the crystal is therefore of great interest to chemists, chemical engineers, and process engineers. Rationalization of this relationship allows the prediction of crystal shape, the development of tailor-made additives, and the control of solvent and impurity effects. The effect of additives on crystal growth and the resultant morphology is therefore of great interest. Adsorption Locator can model the adsorption of an additive onto a crystal face and thus provide access to the energetics of the adsorption and its effects on crystal growth.

Introduction

Pigment Red (a diphenyl derivative of 1,4-diketopyrrolo(3,4-c)pyrrole, DPP) is a high quality heterocyclic pigment, offering good heat stability, high coloring strength and hiding power, and excellent light and weather fastness. It can be produced as transparent or opaque color by controlling the particle size during manufacture.

In this tutorial, you will study the distances between functional groups on surfaces, the results suggest that an amino acid derivative that could act as a growth inhibitor, slowing down the growth rate of the fast growing faces. The binding of this additive to one fast growing face will be modeled using the Adsorption Locator module and the COMPASS forcefield.

This tutorial covers:

- [Getting started](#)
- [To prepare a crystal surface](#)
- [To create an additive](#)
- [To study interactions between the surface and the additive](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Pigment Red Additive** as the project name, click the **OK** button.

The new project is created with *Pigment Red Additive* listed in the Project Explorer. Now you will import the input file you will be studying.

In the Project Explorer, right-click on the project root and select **Import...** to open the Import Document dialog. Navigate to **Examples/Documents/3D Model**, select **pigment_red_010.xsd** click the **Open** button.

2. To prepare a crystal surface


In this section, you will build a slab (a surface with a region of vacuum) from the (0 1 0) Pigment Red surface. The crystal is constructed by repeating the surface in a given direction using a repeat distance that is greater than the surface thickness. This introduces a region of vacuum between the surface blocks.

The surface needs to be big enough to accommodate the particular inhibitor that is being studied.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase the **Supercell range** to **4** for **U** and **6** for **V**. Click the **Create Supercell** button and **close** the dialog.

This displays an enlarged surface. You can now construct a 3D slab from the 2D surface model.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. On the **Vacuum Slab** tab, change the **Vacuum thickness** to **50 Å** and click the **Build** button.

Click the **Display Style** button  on the **3D Viewer** toolbar to open the Display Style dialog. On the **Lattice** tab, set the **Max** value for **C** to **2.00**.

The vacuum is oriented along the c-axis.


Later on in the tutorial, you will add an additive to the surface. The additive could potentially interact with both the surfaces due to the periodic boundary conditions. Therefore, you have added a large region of vacuum above the surface so that the additive can only interact with one of the surfaces. In this case, the thickness of the (0 1 0) surface is about 20 Å, so a vacuum region thickness of 50 Å should be sufficient.


Set the **Max** value for **C** back to **1.00** and **close** the Display Style dialog.

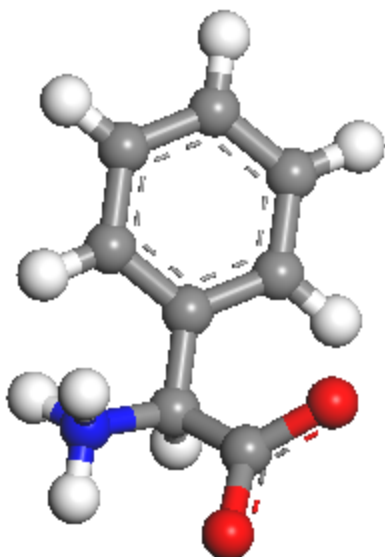
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To create an additive

The inhibitor used in this tutorial, 2-phenylglycine, is an amino acid derivative that exists as a zwitterion.

Click the **New** arrow  and select **3D Atomistic Document** from the dropdown list. In the Project Explorer, right-click on **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Change the name of the document to **inhibitor.xsd**.

Use the tools on the **Sketch** toolbar to construct the 2-phenylglycine molecule (shown below) and then tidy up the structure using the **Clean** tool .



Molecular structure of the inhibitor, 2-phenylglycine

Now you will optimize the molecular structure of the inhibitor using Forcite and the COMPASS forcefield.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog.

Select **Geometry Optimization** from the **Task** dropdown list. On the **Energy** tab, set the **Forcefield** to **COMPASS**. Set both the **Summation methods** to **Atom Based**.

On the **Job Control** tab, select **My Computer** as the **Gateway location** and click the **Run** button.

A new folder called `inhibitor Forcite GeomOpt` is created in the Project Explorer. The calculation should take less than a minute to complete. When the calculation has finished, the minimized structure is saved as `inhibitor.xsd` in the new folder and is displayed in the Materials Visualizer.

Select **File | Save Project** from the menu bar and close all of the open documents.

4. To study interactions between the surface and the additive

Now that you have constructed a 3D slab of the Pigment Red (0 1 0) surface and optimized the structure of the inhibitor, you will position the inhibitor over the surface.

In the Project Explorer, double-click on `pigment_red_010.xsd`.

You will run an adsorption calculation to explore the likely binding site and the orientation of the inhibitor molecule on the surface, followed by a geometry optimization of the inhibitor molecule on the crystal surface to obtain the global minimum energy orientation.

Select **Modules | Adsorption Locator | Calculation** from the menu bar to display the Adsorption Locator Calculation dialog.

On the **Setup** tab, select **Simulated annealing** from the **Task** dropdown list. Choose the optimized **inhibitor.xsd** as the **Adsorbate** and set the **Quality** to **Coarse**.

On the **Energy** tab, set the **Forcefield** to **COMPASS**. Set both the **Summation methods** to **Atom Based**.

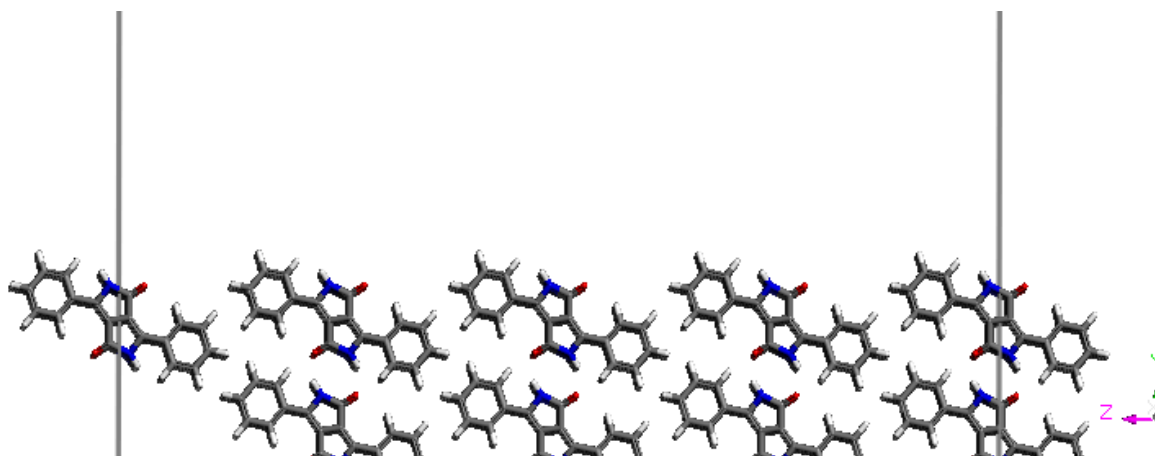
Note: The *Ewald* summation method is more accurate for non-bond energy calculations, but it also requires significant CPU time. For this tutorial you will use the *Atom Based* summation method combined with *Coarse* quality to speed up the calculation.

You can restrict the search space used in the sampling in a number of ways. In this tutorial you will define the search to be within 10 Å of the hydrogen bond donors and acceptors on the surface.

On the **Location** tab, check the **Surface region defined by atom set** checkbox.

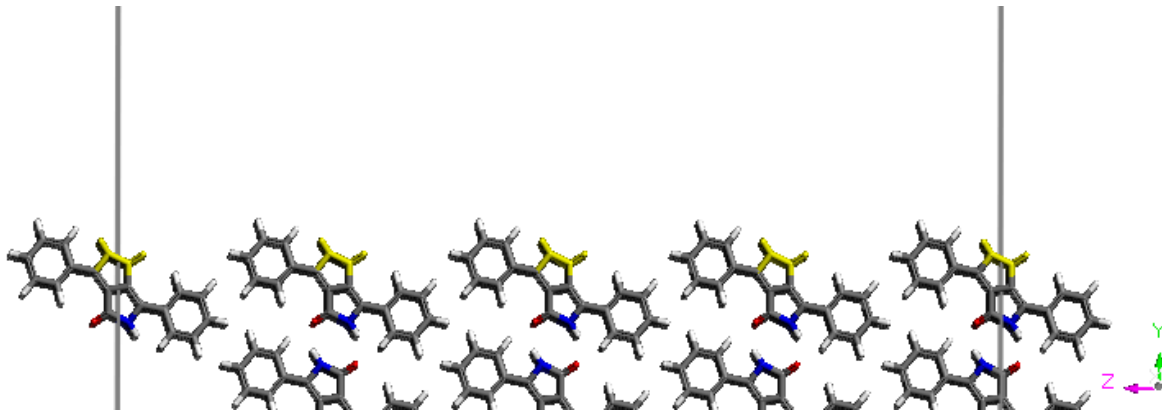
The hydrogen bonding moieties on the surface must be defined as sites where adsorption of the potential inhibitor can occur.

In **pigment_red_010.xsd** rotate and zoom in on the surface of one of the crystal layers.



Pigment Red 010 surface oriented to view the structures side-on

Hold down the **Q + SHIFT** keys and lasso all the **amide** groups in the top layer of molecules.



Pigment Red 010 surface with surface amides selected

On the **Location** tab of the Adsorption Locator Calculation dialog click the **Add selected atoms to TargetAtoms** set button. Check the **Set maximum adsorption distance** checkbox and enter a value of **10.0**.

Click the **Run** button and close the dialog.

A new folder called `pigment_red_010 Adsorption Anneal` is created in the Project Explorer. The calculation could take some time to complete, depending on speed of the processor in your computer.

As the calculation runs, a chart containing various energy contributions is updated. The text document `Status.txt` reports the computation time and the number of steps completed so far. When the calculation is complete, the results are presented in the `pigment_red_010.xsd` document.

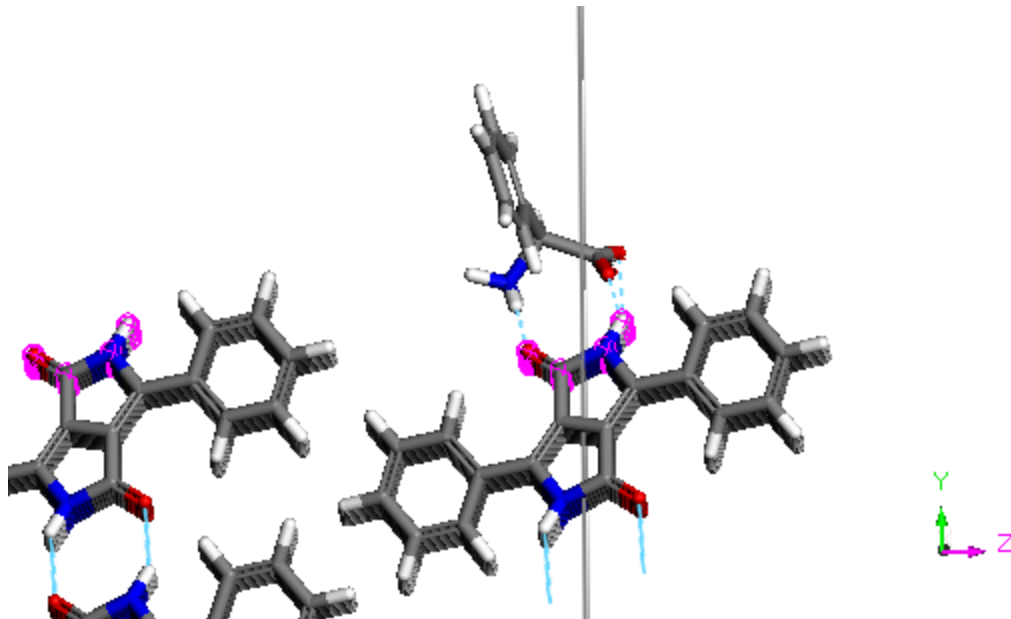
You should wait until the job finishes before proceeding. On completion a study table is returned containing a number of low energy configurations, together with the energetic properties of each configuration.

Open the study table `pigment_red_010.std` and double-click on the structure in the first row.

The interaction between the inhibitor and the surface amide groups can be observed by displaying the hydrogen-bonding patterns.

Click the **Calculate Hydrogen Bonds** button .

Your result may vary slightly from the image below.



Crystal surface with attached inhibitor

The third column *Adsorption energy* contains the most relevant energy parameter for adsorption. It is composed of two parts: the energy of adsorbing the sorbate onto the surface in its input conformation, listed in column *D* and a small deformation energy due to relaxation of the sorbate in the presence of the surface, listed in column *E*. The second column, *Total energy* contains the adsorption energy plus the internal energy of the sorbate. The energy of the framework is not included. The last column *F* is the differential adsorption energy, which is the energy of removing a sorbate of a particular component. Since in this case there is only 1 molecule and 1 component, this is the same as column *C*.

The *attachment energy* for the (0 1 0) face has previously been calculated as around -27 kcal/mol. If you wish to obtain this energy using Materials Studio the procedure in the *Morphology prediction for Pigment Red* tutorial for the Morphology module describes the steps in detail.

You should find that for the (0 1 0) face, the adsorption energy as calculated by Adsorption Locator is more negative than the attachment energy. Therefore, 2-phenylglycine is a good candidate to inhibit the growth of the fast growing (0 1 0) face of Pigment Red crystals, thereby producing a more isometric crystal morphology.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Hartman, P.; Perdok, W. *Acta Crystallogr.*, **8**, 521 (1955).

Bennema, P. J. *Cryst. Growth*, **166**, 17 (1996).

Amorphous Cell tutorials

The following tutorial illustrates how to utilize Amorphous Cell's capabilities.

Amorphous Cell is also used to construct starting structures in several [Forcite Plus](#) tutorials.

Packing molecules into existing structures

Purpose: Demonstrates how to pack molecules into existing structures using Amorphous Cell

Modules: Materials Visualizer, Amorphous Cell

Time: 🕒 🕒

Prerequisites: Sketching organometallic structures, Using the polymer builder, Field segregation and analysis Visualizer Tutorial

Background

The Amorphous Cell module enables the construction of 3D periodic boxes of amorphous polymers and other amorphous materials. However, it can also be used as a fast method to soak a pre-existing structure such as nanocluster with a small molecule or polymer. The Packing task can also be used to build non-orthorhombic amorphous cells by allowing you to pack into an empty cell.

Introduction

In this tutorial you will build a carbon nanotube in a box and then soak the nanotube with water. Using the same nanotube structure, you will use field segregation to pack ferrocenes into the nanotube and polymer around the outside of the nanotube. Such systems have potential commercial applications as nanotube conductors.

This tutorial covers:

- [Getting started](#)
- [To create the nanotube](#)
- [To soak the nanotube with water](#)
- [To set up the structures and isosurfaces](#)
- [To pack into isosurface enclosed volumes](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **packing** as the project name, click the **OK** button.

The new project is created with *packing* listed in the Project Explorer.

2. To create the nanotube

The first step is to build a carbon nanotube using the Nanotube building tools.

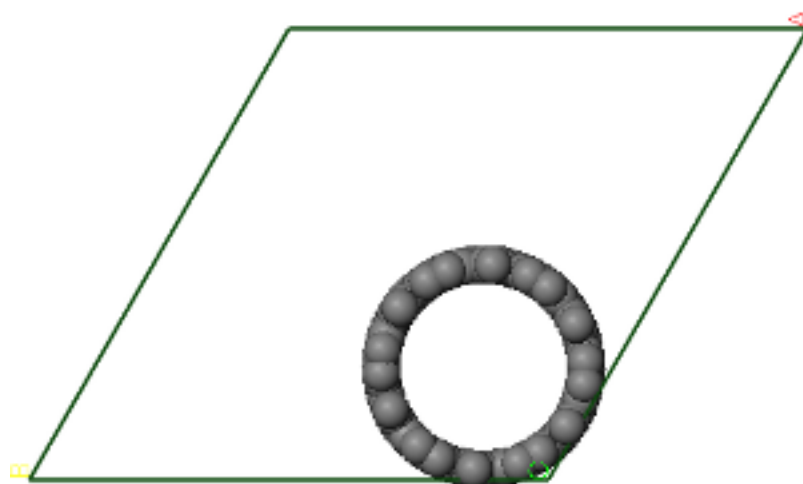
Select **Build | Build Nanostructure | Single-Wall Nanotube** from the menu bar to open the Build Single-Wall Nanotube dialog. Change **N** to **12** and click the **Build** button. Close the dialog.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase **C** to **2** and click the **Create Supercell** button. Close the dialog.

A periodic nanotube is created. You will need some space to pack the polymer so you should increase the size of the lattice, keeping the position of the nanotube constant.

Right-click in the 3D viewer and select **Lattice Parameters** from the shortcut menu to open the Lattice Parameters dialog. On the **Advanced** tab uncheck the **Keep fractional coordinates fixed during changes to the lattice** checkbox. On the **Parameters** tab double the **A** and **B** lengths to **31.55**. Close the dialog.

You should have a structure which looks similar to the one below.



Initial structure containing a single nanotube, displayed in CPK style.

You will use this structure twice so you should make a copy of it.

Select **File | Save As...** to open the Save As dialog. Set the **File name** to **SWNT_water.xsd** and click the **Save** button. Repeat this, naming the second copy **SWNT_polymerFe.xsd**.

You are now ready to pack the first nanotube with water.

3. To soak the nanotube with water

Before soaking the nanotube with water, you need to sketch a molecule of water.

Create a new **3D Atomistic document** and rename the new document **water.xsd**. Use the sketching tools to sketch a molecule of water.

Now you are ready to soak the nanotube with water.

Change focus to **SWNT_water.xsd**. Select **Modules | Amorphous Cell | Calculation** from the menu bar to open the Amorphous Cell Calculation dialog.

The packing task is used to pack molecules into an existing structure.

Change the **Task** to **Packing**.

For the Packing task the components in the system are specified according to their molar ratio. This gives you the option to pack with combinations of molecules. However, in this case, you will pack with water only.

In the **Composition** table, click in the **Molecule** column and select **water.xsd** from the dropdown list.

You can set the density of the packed structure. Note that this is the density of all atoms inside the volume available for packing, which may or may not include the framework atoms. In this tutorial you will explore how to control the packing volume.

The output option allows you to build multiple frames so you can review the building process later. However, in this case, you will just build one frame.

Click the **Options...** button to open the Amorphous Cell Options dialog.

On this dialog, you can control how torsions are defined, the building steps, and whether energies are used in the calculation. For this small molecule, you could switch off energies for the build and just pack with a scaled van der Waals radius penalty. This significantly increases the speed of the packing task. However, you will get a more optimal structure if you build with energies and optimize geometry. In this tutorial you will use the default settings.

Close the **Amorphous Cell Options** dialog. On the **Setup** tab, click the **More...** button to open the Amorphous Cell Packing dialog.

You can choose whether to pack into an isosurface enclosed volume. If you pack into a structure which does not have an isosurface, the density that you specify on the Amorphous Cell Calculation dialog will be the overall density of the cell. If you pack into an isosurface, the density on the Amorphous Cell Calculation dialog is the density of the volume you are packing into. You will perform two packing calculations, one with and one without the isosurface so that you can see the difference. Initially, you will just pack into the structure without an isosurface.

Close the **Amorphous Cell Packing** dialog. Select the **Energy** tab on the Amorphous Cell Calculation dialog.

You can choose which forcefield and energy settings will be used when building the structure. For this tutorial, you can use the default settings.

Click the **Run** button.

A new folder called `SWNT_water AC Packing` is created. This has a subfolder named `Input` which contains a copy of the input documents. When the job completes, the packed structure is called `SWNT_water.xtd`.

Change focus to the results **SWNT_water.xtd**.

You should see that the nanotube is now packed both inside and outside with water.

Change focus to **SWNT_water.txt**. Scroll down to the **Amorphous Cell calculation** section.

Here you can see the components and their loadings. You should see that 426 molecules of water were packed into the box.

Make **SWNT_water.xtd** the active document and, in the **Properties Explorer**, change the **Filter** to **Symmetry System**.

You should see that the density is about 1.0 g cm^{-3} , the value you set in the Amorphous Cell Calculation dialog. Now you will pack into an isosurface and examine the difference. You will pack into a Connolly surface.

Make **SWNT_water.xsd** the active document. Use the **Atom volumes and Surfaces** tool to create a **Connolly surface**.

The isosurface describes the volume where the atoms are located, this is volume that is already occupied. If you try to pack into this isosurface, you will find that the calculation terminates with the error: "The density in the isosurface enclosed volume is greater than the requested density." To enable the packing into a Connolly surface, you need to invert the definition of the isosurface. You can do this using the Display Style dialog.

Select the isosurface and right-click on the selection, choose **Display Style** from the shortcut menu to open the Display Style dialog. On the **Isosurface** tab check the **High values inside** checkbox and close the dialog.

You can now pack into this isosurface.

Tip: If you are using MaterialsScript, you should use `HasFlippedNormals` to control the definition of the isosurface.

On the **Amorphous Cell Calculation** dialog, click the **More...** button for the **Task** to open the Amorphous Cell Packing dialog. Check the **Pack in isosurface enclosed volume** checkbox and close the dialog. Click the **Run** button on the Amorphous Cell Calculation dialog.

When the calculation completes, you can examine the density and the loading.

Open the **SWNT_water.txt** file.

You should see that the loading for water is now 558 molecules.

Make **SWNT_water.xtd** the active document and, in the **Properties Explorer**, change the **Filter** to **Symmetry System**.

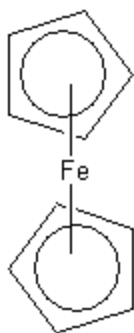
The overall density of the cell should be about 1.2 g cm^{-3} .

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

4. To set up the structures and isosurfaces

Before packing the second nanotube that you created earlier, you need to sketch the ferrocene structure to pack inside the nanotube and build a polymer to pack around the outside.




Open a new **3D Atomistic Document** and rename the document to **ferrocene.xsd**. Use the **Fragment** tools to create a ferrocene structure.



Now you need to build the polymer. In this tutorial, you will just build a 5-mer of polyoxyethylene.

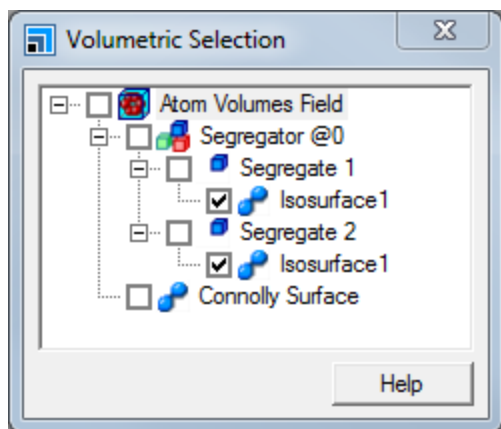
Use the **Homopolymer** building tools to create a 5-mer of **oxyethylene** from the **oxides** library. Rename the structure **peo5.xsd**.

You are going use fields and isosurfaces to indicate what you want to pack. To create the initial fields, you will use Connolly surfaces.

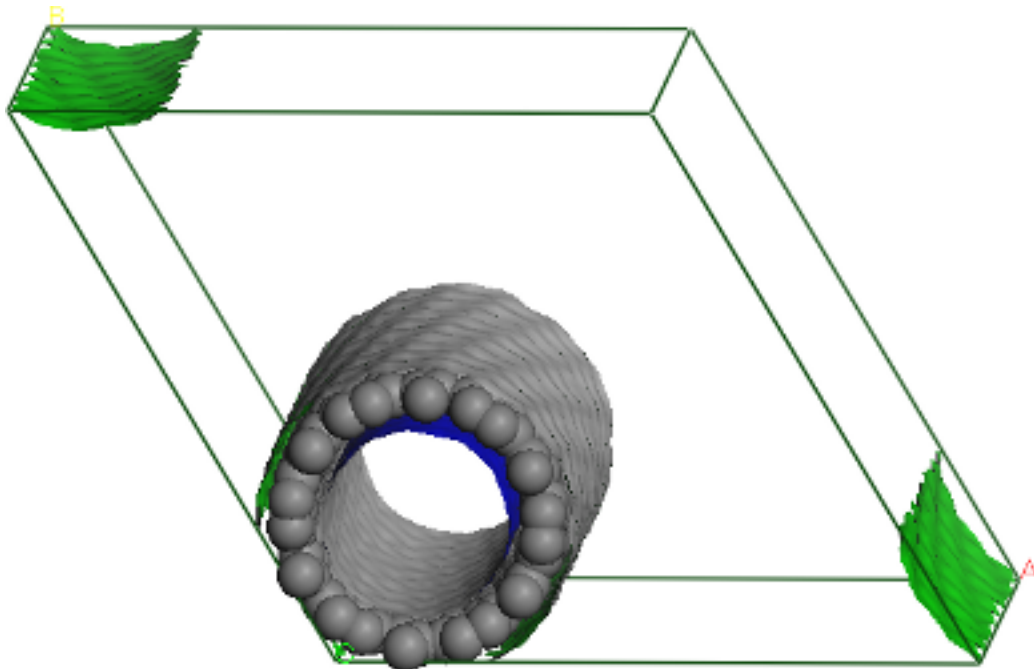
Change focus to **SWNT_polymerFe.xsd** and create a **Connolly surface**. Click the **Create Segregates** button . Click the **Volumetric Selection** button  to open the Volumetric Selection dialog and select both **Segregates**. Click the **Create Isosurfaces** button .

On the Volumetric Selection dialog, **uncheck** the **Connolly Surface**, **Segregate 1**, and **Segregate 2** checkboxes.

You should now have a blue and a green isosurface displayed in SWNT_polymerFe.xsd.



Volumetric selection dialog with the isosurfaces of the segregates displayed



Nanotube with segregated isosurfaces colored green and blue

Note: As the segregated isosurfaces show volumes of free space, you do not have to invert the isosurface as you did for the Connolly surface.

You will pack the ferrocene into the blue isosurface enclosed volume and the polymer into the green isosurface enclosed volume.

5. To pack into isosurface enclosed volumes

The final step is to pack into the two isosurface enclosed volumes using two separate packing calculations. You will pack ferrocene first (the order is not important). However, you can only pack into a single visible isosurface so you need to ensure that the isosurface for Segregate 2 is the only one that is visible.

Ensure that **SWNT_polymerFe.xsd** is in focus. On the Volumetric Selection dialog **uncheck** Segregate 1 -> **Isosurface1**.

Open the **Amorphous Cell Calculation** dialog. Change the **Composition** to **ferrocene**. Set the **Density** to **0.9** and click the **More...** button, check the **Pack in isosurface enclosed volume** checkbox.

You will leave the default values for all other options.

Click the **Run** button.

When the job completes, you should have a 3D atomistic trajectory containing the nanotube with ferrocenes packed in the core of the nanotube. First, make a copy of the output trajectory frame in a new structure document.

Make **SWNT_polymerFe AC Packing/SWNT_polymerFe.xtd** the active document.

On the **Volumetric Selection** dialog, **uncheck** Segregate 2 -> **Isosurface1** and **check** Segregate 1 -> **Isosurface1**.

You should now see the blue isosurface become invisible and the green isosurface is visible again. This time, you will build into the output trajectory from the previous calculation.

Note: If you are doing a multistep packing as in this exercise and you generate multiple frames for the first pack, the second packing will only pack into the current frame in the trajectory not into all the frames.

On the Setup tab of the Amorphous Cell Calculation dialog, change the **Composition** to **peo5** and **Density** to **0.85**. Click the **Run** button.

When the calculation completes, you should have a structure containing a nanotube that is packed with ferrocene and the space between the nanotubes is packed with polymer.

This is the end of the tutorial.

Blends tutorials

The following tutorial illustrates how to utilize Blends' capabilities.

Screening for compatibility in polymer blends

Purpose: Demonstrates the use of Blends for screening molecular interactions.

Modules: Materials Visualizer, Blends, Forcite (optional)

Time: 

Prerequisites: Using the polymer builder Visualizer Tutorial

Background

There are many industrial situations where formulators routinely mix two polymers to produce a blend with improved physical properties. The same is true for surfactants, solvents, and fine chemical intermediates. Generally, the goal is to produce a blended product with optimized physical or chemical properties, at the lowest possible cost. The usual experimental approach involves the screening of a large number of different formulations to find a final formulation that meets all the requirements. Hence, much of the development time is often spent preparing and testing formulations. Formulation stability problems may take weeks or months to become apparent, by which point, a considerable investment in resources and materials may well have been made.

The Blends module in Materials Studio has been developed to provide a desktop IT solution that reduces the need for laboratory experimentation and, more importantly, the risk of product failure.

Introduction

In this tutorial, you will use Blends to predict the miscibility of a polymer with two others. You will import the structures of monomers for poly(oxyethylene), polypropylene, and poly(acrylic acid). You will then set up a Blends calculation to examine the compatibility of poly(oxyethylene) with both polypropylene and poly(acrylic acid).

You will analyze the run to predict properties such as the temperature dependence of the Flory-Huggins chi parameter and the phase diagrams for the two blends. Finally, you will use a study table to examine the 50 lowest energy pairs from each run and overlay these to look at low energy absorption sites.

This tutorial covers:

- [Getting started](#)
- [To prepare the input structures](#)
- [To set up and run the Blends calculation](#)
- [To analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.


1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Polyoxyethylene** as the project name, click the **OK** button.

Materials Studio has an extensive library of pre-defined monomer repeat units and it is these you will use in this tutorial.

In this tutorial, you are going to screen poly(oxyethylene) against polypropylene and poly(acrylic acid).

Select **File | Import...** from the menu bar or click the **Import** button  to open the Import Document dialog. Navigate to and select **Structures/repeat-units/oxides/oxyethylene.msi**, click the **Open** button.

The structure of oxyethylene is imported into the project. Head and tail atoms in the structure are indicated by cyan and magenta cages around the respective atoms.

Repeat the procedure above to import **Structures/repeat-units/olefins/propylene.msi** and **Structures/repeat-units/acrylates/acrylic_acid.msi** into the project.

2. To prepare the input structures

In a Blends calculation, you can screen for polymer-polymer, polymer-solvent, or solvent-solvent interactions. You can define a polymer by specifying head and tail atoms on a monomer repeat unit.

As part of the preparation procedure, you should optimize the geometries of the repeat units before submitting them for the Blends calculation. This requires the Forcite module. If you do not have a license for this module, proceed to [section 3](#).

Make **oxyethylene.xsd** the active document. Choose **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog.

On the **Setup** tab, change the **Task** to **Geometry Optimization**.

On the **Energy** tab, select **Dreiding** from the **Forcefield** dropdown list and change the **Charges** to **Charge using QEq**. Click the **Run** button.

A job is launched and its progress displayed in the Job Explorer. A new folder, oxyethylene Forcite GeomOpt, is created in the Project Explorer. When the calculation is complete, a dialog will appear notifying you of the fact.

The oxyethylene Forcite GeomOpt folder should contain 6 results files:

- **oxyethylene.xsd**: A 3D Atomistic document containing the optimized geometry of the initial structure.
- **oxyethylene - Calculation**: An .xml file containing the settings for the Forcite job. Clicking on this file opens the Forcite Calculation dialog with the settings that you specified for the calculation.
- **oxyethylene Convergence.xcd**: A chart file containing plots of the evolution of the energy change and gradient normal change.
- **oxyethylene Energies.xcd**: A chart file containing a plot of the evolution of the enthalpy.
- **Status.txt**: A text file containing the live update status.
- **oxyethylene.txt**: A file containing the initial job settings and a breakdown of energies for the initial and final structures.

Repeat the geometry optimization calculation for **acrylic_acid.xsd** and **propylene.xsd**. Close the Forcite Calculation dialog.


There will now be a large number of documents open in the workspace area.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

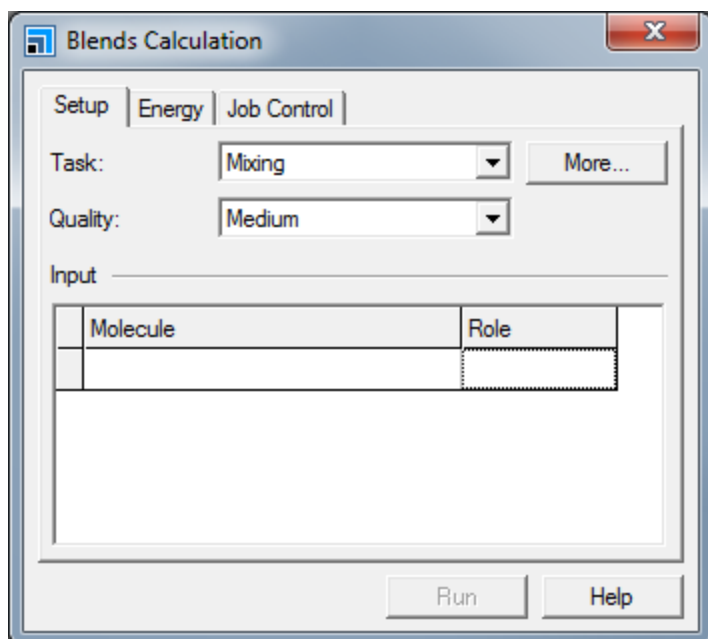
In the Project Explorer, double-click on **oxyethylene.xsd** in the folder **oxyethylene Forcite GeomOpt**, **acrylic_acid.xsd** in the folder **acrylic_acid Forcite GeomOpt**, and **propylene.xsd** in the folder **propylene Forcite GeomOpt**.

3. To set up and run the Blends calculation

A Blends calculation is very simple to set up and consists of defining your molecules, choosing the task, and setting the calculation quality level.

Click the **Blends** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the Blends Calculation dialog.



Blends Calculation dialog, Setup tab

The first step is to define the input molecules.

In the **Input** section of the **Setup** tab, click in the empty **Molecule** cell and select **oxyethylene Forcite GeomOpt/oxyethylene.xsd** from the dropdown list.

The first row of the *Input* grid now contains *oxyethylene.xsd* in the *Molecule* column and this structure has been automatically assigned the *Role* of *Base*. A new empty row has been added below the first one.

Click in the **Molecule** cell in the new empty row and select **acrylic_acid.xsd** in the folder **acrylic_acid Forcite GeomOpt**. Repeat this for **propylene Forcite GeomOpt/propylene.xsd** in the third row of the grid.

Both **propylene.xsd** and **acrylic_acid.xsd** are automatically assigned **Screen** roles. Any molecule with a screen role will be screened against molecules with a base role. In this tutorial, you will obtain interaction energies for oxyethylene-propylene and oxyethylene-acrylic acid mixtures. This is an example of a one-to-many screening calculation.

Click in the **Role** cell for **oxyethylene**.

The role options are **Base+Screen**, **Base**, and **Screen**. If you wanted to calculate interaction energies for all possible combinations of the polymers, that is, poly(oxyethylene)-poly(oxyethylene), poly(oxyethylene)-polypropylene, poly(oxyethylene)-poly(acrylic acid), polypropylene-polypropylene, polypropylene-poly(acrylic acid), and poly(acrylic acid)-poly(acrylic acid), you would need to assign all three input structures a **Base+Screen** role. Choosing the **Base+Screen** role for all the molecules enables a many-to-many screen.

In this tutorial, you will run a one-to-many screening calculation.

Set the **Role** for **oxyethylene.xsd** to **Base**.

The next step is to choose the task. There are three tasks in Blends.

- **Mixing** - Performs both binding energy and coordination number calculations. Predicts mixing energy, interaction energy, and chi parameter values.
- **Binding energies** - Calculates binding energies only. This gives a fast screen on interaction energy
- **Coordination numbers** - Calculates the coordination numbers for a pair of molecules.

Set the **Task** to **Mixing** and click the **More...** button.

This opens the Blends Mixing Options dialog which allows you to fine tune the mixing energy calculation.

On the **Setup** tab on the Blends Calculation dialog, change the **Quality** to **Fine**.

The **Quality** selected affects the number of pairs that are sampled, the energy bin width, and the cluster samples. As you change the **Quality** setting, the values on the Blends Mixing Options dialog change in response. The **Quality** setting also propagates to the **Energy** tab and affects the non-bond cutoff settings on the Blends Non-Bond Options dialog.

On the **Setup** tab on the Blends Calculation dialog, change the **Quality** back to **Medium**.

The Mixing Task Options dialog gives you the option to set head and tail atoms in repeat units as non-contact. This means that any atoms in the input structures that are marked as head or tail atoms will not be allowed to come into close contact with any other atoms in the system. This allows you to use a monomer to mimic a polymer, as the non-contact atoms represent the rest of the polymer.

Make sure that the **Head and tail atoms are non-contact** checkbox is checked.

Note: If you wish to define more than two atoms as non-contact, you should select the atoms and define them as a set with the name NONCONTACT.

You can also request that Blends saves the lowest energy configurations for each base and screen combination in a 3D Atomistic Trajectory document. For each such combination, Blends will return three

trajectory documents containing the configurations of the base-base, base-screen, and screen-screen pair. These configurations can then be analyzed further or optimized.

Check the **Return lowest energy frames** checkbox and change the **Number of frames** to **50**. **Close** the Blends Mixing Options dialog.

Before running the Blends calculation, you should change the energy options to reflect the options you used to minimize the input molecules.

On the Blends Calculation dialog, select the **Energy** tab. Set the **Forcefield** to **Dreiding** and the **Charges** to **Charge using QEq**.

Finally, set the job control options and change the live update frequency.

On the **Job Control** tab select **My Computer** as the **Gateway location**. Click the **More...** button to open the Blends Job Control Options dialog. Check the **Update structure** checkbox and change **Update every** to **2** seconds. **Close** the Blends Job Control Options dialog.

You are now ready to run the calculation.

In the Project Explorer, click on the project root. On the Blends Calculation dialog, click the **Run** button and close the dialog.







A new folder, `oxyethylene Blends Mixing` is created in the Project Explorer. When the calculation is complete, this folder will contain the following documents:

- **Input**: A folder containing the input structures.
- **Lowest energies**: A folder containing 3D Atomistic Trajectory documents comprising the lowest energy configurations for each base and screen combination. For each such combination, Blends returns three trajectory documents containing the configurations of the base-base, base-screen, and screen-screen pair. Any pair that is a duplicate of an existing pair will be omitted.
- **oxyethylene - Calculation**: An xml file containing the settings for the Blends job. Clicking on this file opens the Blends Calculation dialog with the settings that you specified for the calculation.
- **oxyethylene.txt**: A text document containing information about the job run and any warnings.
- **Configurations.xsd**: A 3D Atomistic document containing the structures currently being sampled. This file receives live updates as the job progresses.
- **Energies.xcd**: A chart document containing plots of the energies currently being sampled. This file receives live updates as the job progresses.
- **Status.txt**: A text document containing the status of the run. This file receives live updates as the job progresses.
- **oxyethylene.std**: A study table containing the results of the Blends run.

4. To analyze the results

The study table document, `oxyethylene.std`, contains a summary of the screening results, with each row representing a single pair calculation.

Note: Due to the nature of Blends calculations, some variation in results is expected. Therefore, it is entirely possible that your results will not precisely match those shown below.

	A	B	C	D	E	F	G	H	I
	Base	Screen	Energies	Chi (298 K)	Emix (298 K)	Ebb avg (298 K)	Ebs avg (298 K)	Ess avg (298 K)	Ebb min
1	 oxyethylene	 acrylic_acid	 oxyethylene_acrylic_acid	0.01896795	0.01123258	-0.82694223	-0.86988907	-0.92683774	-2.13848154
2	 oxyethylene	 propylene	 oxyethylene_propylene	1.01904836	0.60346774	-0.82694223	-0.49782388	-0.47122175	-2.13848154

Blends study table output

Columns *A* and *B* contain the structures of the base and screen molecules used in the screening calculation. Column *C* contains a chart document comprising plots of the interaction energies for the base-base, base-screen, and screen-screen combinations. Columns *D* and *E* contain predicted values for the chi parameter and the energy of mixing. Columns *F-Q* contain a breakdown of the interactions energies giving average, minimum, and maximum values. Columns *R-U* contain coordination numbers for each base and screen combination.

Double-click on cell **B2** to open the Study Table Detail View of the propylene monomer.

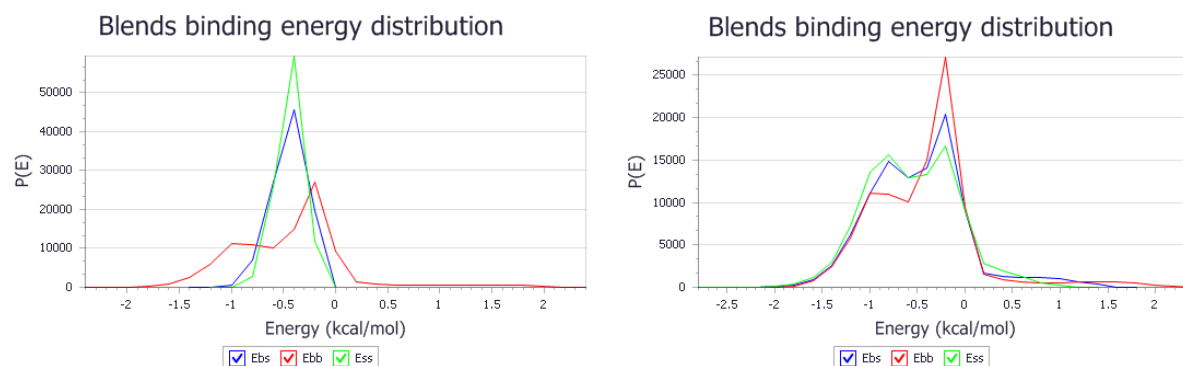
The head and tail atoms are labeled as a non-contact group called NONCONTACT.

Close the detail view.

The energy charts in the study table contain the binding energy distributions for the base and screen pairs.

Double-click on the charts in cells **C1** and **C2**.

If the binding energies for the base-base (E_{bb}), base-screen (E_{bs}), and screen-screen (E_{ss}) combinations have very similar distributions, this is a good indicator that the structures will be compatible. The charts, shown below, indicate that poly(oxyethylene) should be miscible with poly(acrylic acid), but not with polypropylene.



Binding energy distributions for the two base-screen pairs

Close the two detail views.

The next indicators as to miscibility are the χ and E_{mix} values.

Examine the values in columns **D** and **E**.

A χ (chi) value close to zero indicates miscibility, as does an E_{mix} value that is close to zero. The more the χ and E_{mix} values increase, the less miscible the pair is. These values reinforce the conclusions from the energy distributions that poly(oxyethylene) will be miscible with poly(acrylic acid), but not with polypropylene.

Besides reporting these initial results, Blends also provides tools for further analysis. You can perform analyses by selecting the row in the study table containing the polymer pair of interest and choosing an analysis task from the Blends Analysis dialog.

In the study table, select row **1**. Select **Modules | Blends | Analysis** from the menu bar to open the Blends Analysis dialog. With the default analysis mode selected, **Chi parameter**, click the **Analyze** button.

A chart document, **Chi parameter.xcd**, is displayed showing the temperature dependence of χ for poly(oxyethylene) mixed with poly(acrylic acid). You can also perform analysis on more than one study table row at a time, where appropriate.

Close **Chi parameter.xcd** and click the **No** button when prompted to save the file as part of the project.

Hold down the **SHIFT** key, click on row **2** in the study table. Both rows in the study table should now be selected. On the Blends Analysis dialog, click the **Analyze** button.

This time, the chart shows the temperature dependence of χ for both base-screen pairs. You can also plot the energy of mixing for both systems


On the Blends Analysis dialog, select **Mixing energy** and click the **Analyze** button.

A chart document is displayed showing the temperature dependence of the mixing energy for both base-screen pairs. You can also use Blends to predict approximate phase diagrams for systems.


Select **Phase diagram** on the Blends Analysis dialog and change the **Degree of polymerization** to **25** for both **Base** and **Screen**. Click the **Analyze** button.

A chart containing two phase diagrams is displayed. Again, these show that poly(oxyethylene) will be miscible with poly(acrylic acid), but not with polypropylene, except at very high temperatures.

In the final part of this tutorial, you will examine the lowest energy conformations trajectories. You can simply play the trajectories.


Double-click on **oxyethylene acrylic_acid.xtd** in the **Lowest energies** folder. Choose **View | Toolbars | Animation** from the menu bar. Click the **Play** button  on the **Animation** toolbar.

The frames will play very quickly. An alternative approach is to use the Forcite Analysis dialog to analyze the trajectory. You do not need a Forcite license to use Forcite Analysis in this way.

On the **Modules** toolbar, click the **Forcite** button  and select **Analysis** from the dropdown list to open the Forcite Analysis dialog. Select **View in a study table** and check the **Include structures** checkbox. Click the **View** button.

The trajectory, along with related time and energy data, is displayed in a study table document. The *Time* and *Frame step* values are all zero as these were generated from a Monte-Carlo procedure. Most

of the energy values are also zero as bonds, angles, and so on, were not included in the energy equation. You can use the study table tools to sort by energies other than the total energy.

Select column **E, van der Waals energy**. Click the **Sort Ascending** button  on the **Study Table** toolbar.

The rows are ordered with the lowest van der Waals energy conformation at the top of the study table. You can also extract structures from the study table and overlay them in a 3D Atomistic Collection document.

Select column **A**, right-click in one of the selected cells and choose **Extract To Collection** from the shortcut menu. A warning dialog will appear, informing you that this action may take some time. Click the **OK** button.

A new 3D Atomistic Collection document, *Extracted From oxyethylene acrylic_acid.xod*, is displayed. You can easily remove the NONCONTACT labels.

Right-click in the collection document and select **Label** from the shortcut menu to open the Label dialog. Click the **Remove All** button and close the Label dialog.

In the collection document, you should be able to make out three areas along one half of the molecule where binding is concentrated.

Repeat the above steps to view **oxyethylene propylene.xtd** as a collection document.

In this case, there are two main interaction sites and they are not as spread out around the molecule as they were for the poly(oxyethylene)-poly(acrylic acid) pairs.

This is the end of the tutorial.

CASTEP tutorials

The following tutorials illustrate how to utilize CASTEP's capabilities.

- [Predicting the lattice parameters of AIAs from first principles](#)
- [Adsorption of CO onto a Pd\(110\) Surface](#)
- [Calculating elastic constants for BN](#)
- [Predicting the thermodynamic properties of germanium](#)
- [Calculating phonon spectra for ferromagnetic Fe](#)
- [Assigning the ¹⁷O NMR spectrum of L-alanine](#)
- [Charge density difference of CO on Pd\(110\)](#)
- [Simulating the STM profile of CO on Pd\(110\)](#)
- [Predicting the core level spectra of BN from first principles](#)

Predicting the lattice parameters of AIAs from first principles

Purpose: Introduces geometry optimization in CASTEP and the use of the volume visualization tools to display isosurfaces.

Modules: Materials Visualizer, CASTEP

Time: 🕒

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Recent developments in density functional theory (DFT) methods applicable to studies of large periodic systems have become essential in addressing problems in materials design and processing. The DFT tools can be used to guide and lead the design of new materials, allowing researchers to understand the underlying chemistry and physics of processes.

Introduction

This tutorial illustrates how CASTEP can be used to determine the lattice parameters and electronic structure of aluminum arsenide using quantum mechanical methods in Materials Studio. You will learn how to build a crystal structure and set up a CASTEP geometry optimization run, and then analyze the results.

This tutorial covers:

- [Getting started](#)
- [To build an AIAs crystal structure](#)
- [To set up and run the CASTEP calculation](#)
- [To analyze the results](#)
- [To compare the structure with experimental data](#)
 - Visualizing the charge density
 - Density of states and band structure

Note: Completion of this tutorial entails running a CASTEP geometry optimization. Depending on the configuration of your computer server, this calculation could take a considerable amount of time.

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **AIAs_lattice** as the project name, click the **OK** button.

The new project is created with *AIAs_lattice* listed in the Project Explorer. The next step is to create a document in which to generate the AIAs lattice.

In the Project Explorer, right-click on the root and select **New | 3D Atomistic Document** from the shortcut menu. Rename the new document **AIAs.xsd**.

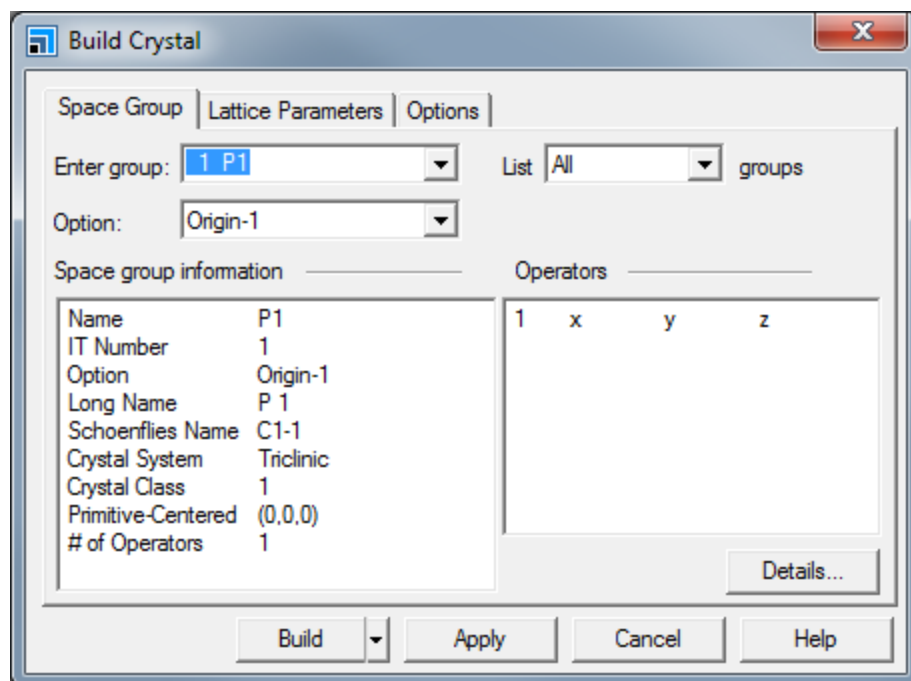
2. To build an AIAs crystal structure

To build a crystal structure, you need to know the space group, lattice parameters, and internal coordinates for the crystal you wish to construct. In the case of AIAs, the space group is F-43m, number 216. There are two atoms in the basis, Al and As with fractional coordinates of (0, 0, 0) and (0.25, 0.25, 0.25), respectively. The lattice parameter is 5.6622 Å.

The first step is to build the lattice.

Choose **Build | Crystals | Build Crystal...** from the menu bar.

This opens the Build Crystal dialog.



Build Crystal dialog, Space Group tab

Click in the **Enter group** box and type **216**, press the **TAB** key.

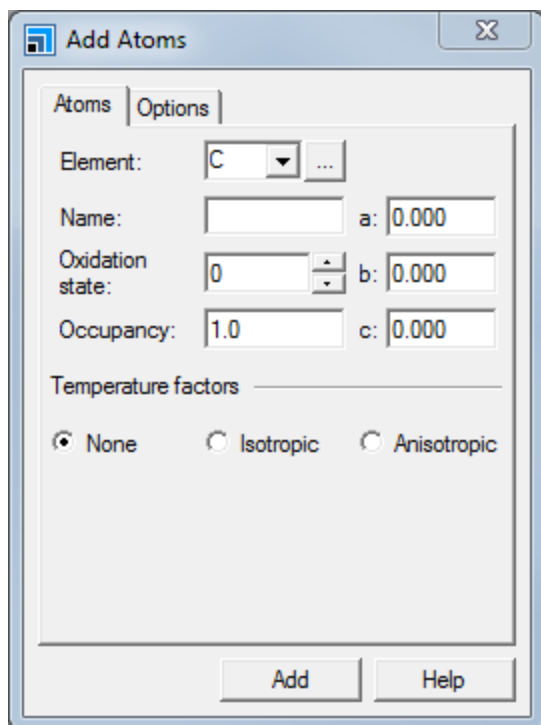
The *Space group information* box updates with the information for the F-43m space group.

Select the **Lattice Parameters** tab. Change the value of **a** from 10.00 to **5.6622**. Press the **TAB** key and click the **Build** button.

An empty 3D lattice is displayed in the 3D Viewer, now you can add the atoms.

Select **Build | Add Atoms** from the menu bar.

This opens the Add Atoms dialog.



Add Atoms dialog, Atoms tab

Using this dialog, you can add atoms at specific positions.

On the Add Atoms dialog, select the **Options** tab and ensure that the **Coordinate system** is set to **Fractional**. Select the **Atoms** tab, in the **Element** text box type **Al**. Click the **Add** button.

The aluminum atoms are added to the structure.

In the **Element** text box, type **As**. Enter **0.25** into the **a**, **b**, and **c** text boxes. Click the **Add** button and close the dialog.

The atoms are added and the symmetry operators are used to build the remaining atoms in the crystal structure. The atoms are also displayed in neighboring unit cells to illustrate the bond topology of the AIAs structure. You can remove these by rebuilding the crystal.

Choose **Build | Crystals | Rebuild Crystal...** from the menu bar to open the Rebuild Crystal dialog. Click the **Rebuild** button.

The extraneous atoms are removed and the crystal structure is displayed. You can change the display style to ball and stick.

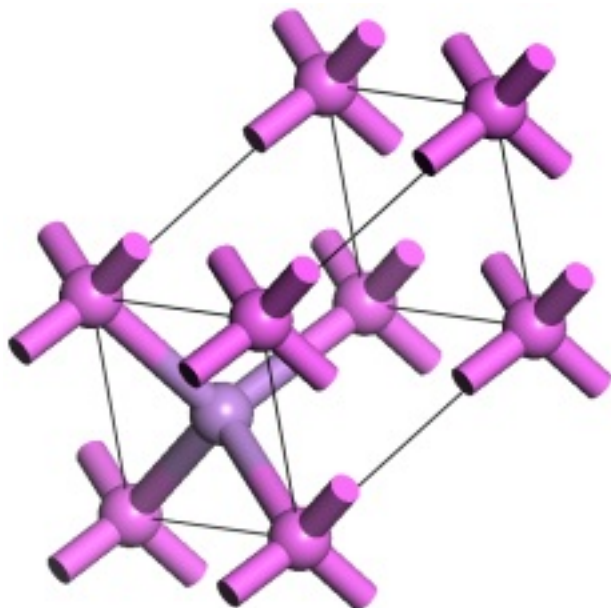
Right-click in the structure document and select **Display Style** from the shortcut menu. On the **Atom** tab, select the **Ball and stick** option and close the dialog.

The crystal structure in the 3D Viewer is the conventional unit cell, which shows the cubic symmetry of the lattice. CASTEP uses the full symmetry of the lattice if any exists. So the primitive lattice, containing 2 atoms per unit cell, can be used, as opposed to the conventional cell, which contains 8 atoms. The charge density, bond distances, and total energy per atom will all be the same no matter how the unit cell is defined, so by using fewer atoms in the unit cell the computation time will be decreased.

Note: When a spin-polarized calculation is performed on a magnetic system care should be taken if the charge density spin wave has a period which is a multiple of the primitive unit cell.


Choose **Build | Symmetry | Primitive Cell** from the menu bar.

The 3D Viewer displays the primitive cell.

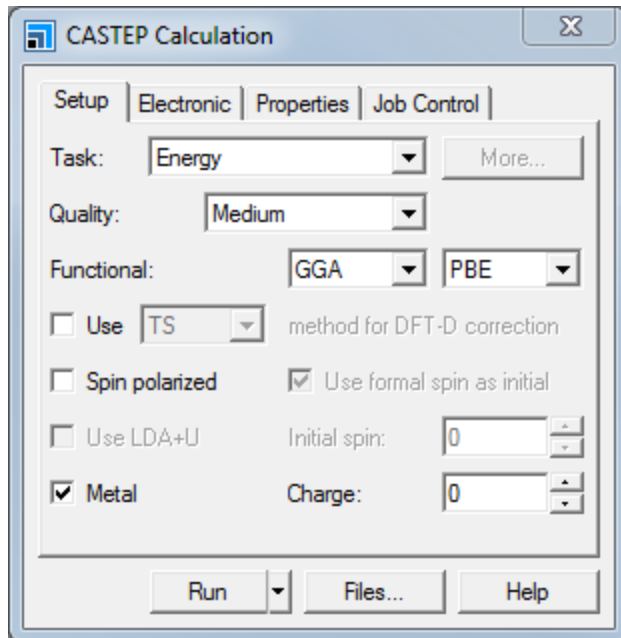


The primitive cell of AlAs

3. To set up and run the CASTEP calculation

Click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** or choose **Modules | CASTEP | Calculation** from the menu bar

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

You are going to optimize the geometry of the structure.

Change the **Task** to **Geometry Optimization** and the **Quality** to **Fine**.

The default setting for optimization is to optimize only the atomic coordinates. However, in this case, you want to optimize the lattice since the atomic coordinates in AlAs structure are fixed by symmetry.

Click the **More...** button for the **Task** to open the CASTEP Geometry Optimization dialog. Check the **Optimize cell** checkbox and close the dialog.

When you change the quality, the other parameters change to reflect this.

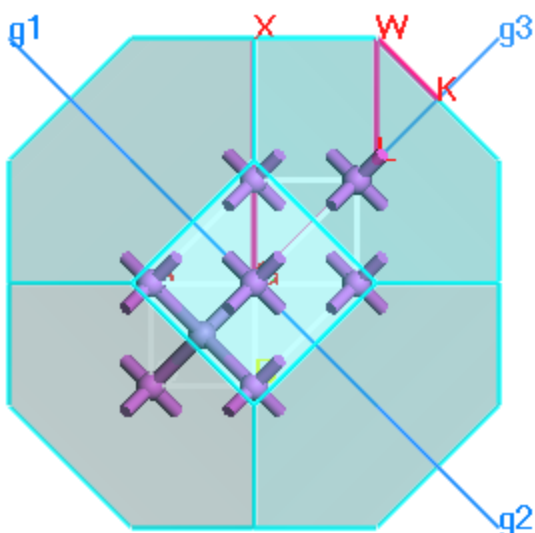
Select the **Properties** tab.

You can specify which properties you want to calculate from the *Properties* tab.

Check the **Band structure** and **Density of states** checkboxes.

With the **Band structure** option selected, click the **More...** button to open the CASTEP Band Structure Options dialog. Click the **Path...** button to open the Brillouin Zone Path dialog. Click the **Create** button and close both dialogs.

The reciprocal lattice and Brillouin zone paths and axes are displayed in the 3D viewer.



AlAs reciprocal lattice and Brillouin zone paths

You can also specify job control options such as live updates.

Select the **Job Control** tab. Click the **More...** button to open the CASTEP Job Control Options dialog. Change the **Update** interval to **5.0** s and close the dialog.

If you are running the calculation on a remote server, you can specify this from the *Job Control* tab.

Click the **Run** button and close the CASTEP Calculation dialog.

After a few seconds, a new folder is displayed in the Project Explorer and this will contain all the results from the calculation. The Job Explorer is displayed, which contains information about the status of the job.

The Job Explorer displays the status of any currently active jobs that are associated with this project. It shows useful information such as the server and job identification number. You can also use this explorer to stop the job if you need to.

As the job progresses, four documents open which relay information on the job status. These documents include the crystal structure, showing updates of the model during optimization, a status document to relay information about the job setup parameters and run information, and charts of the total energy, and convergence in energy, forces, stress, and displacement as a function of the iteration number.

When the job finishes, the files are transferred back to the client and this can take some time due to the size of certain files.

4. To analyze the results

When the results documents are transferred, you should have several documents, among them:

- AlAs .xsd - the final optimized structure
- AlAs .xtd - a trajectory file containing the structure after each optimization step
- AlAs .castep - an output text document containing the optimization information
- AlAs .param - input information for the simulation

For each of the properties calculated, there are also .param and .castep documents.

In the AIAs structure, the forces are zero by symmetry, but the stresses depend on the lattice parameters. CASTEP thus attempts to minimize the total energy by finding the structure that corresponds to the zero stress. Therefore, to ensure that the calculation has completed properly, it is important to check that the stresses have converged.

Make **AIAs.castep** the active document and select **Edit | Find...** from the menu bar to open the Find dialog. Enter **completed successfully** in the text box and click the **Find Next** button. Scroll a few lines up.

You will see a table containing two rows, and the last column in each row should say *Yes*. This indicates that the calculation has succeeded.

5. To compare the structure with experimental data

You know that the lattice length should be 5.6622 Å from when you initially created the cell. You can compare your minimized lattice length with that of the initial experimental length. The experimental lattice length is based on a conventional cell and not a primitive one, so you should convert your cell.

Make the optimized **AIAs.xsd** the active document and select **Build | Symmetry | Conventional Cell** from the menu bar.

The conventional cell is displayed. There are several ways to view the lattice lengths, but the easiest is to open the Lattice Parameters dialog.

Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu.

The lattice vector should be approximately 5.731 Å, giving an error of about 1%. This is within the 1-2% typical error that is expected for pseudopotential plane-wave methods in comparison with experimental results. An over-estimation of the lattice parameters is typical of the GGA functional, use of LDA functionals may result in under-estimation.


Notes:

- More advanced exchange-correlation functionals such as PBESOL or WC are designed to produce more accurate crystal structures
- Convergence testing is always required to establish that the settings are sufficiently accurate. In this case you can repeat the calculations with a higher energy cutoff and with more accurate k-point sampling.

Before continuing, you should save the project and close all the windows.

Choose **File | Save Project** on the menu bar, then **Window | Close All**.

The charge density can be visualized using the CASTEP Analysis tool.

Click the **CASTEP** button  on the **Modules** toolbar and select **Analysis** or choose **Modules | CASTEP | Analysis** from the menu bar to display the CASTEP Analysis dialog.

Choose the **Electron density** option.

A message is displayed reporting that no results file is available, so you need to specify a results file.

In the Project Explorer, double-click on **AIAs.castep**.

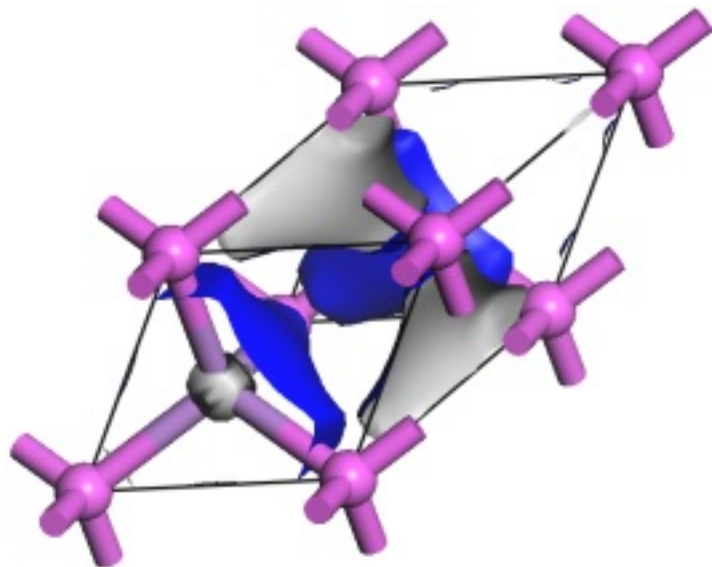
This will associate the results document with the analysis dialog but you also need to designate a 3D Atomistic document in which to display the isosurface.

In the Project Explorer, double-click on the optimized **AIAs.xsd**. Choose **Build | Symmetry | Primitive Cell** from the menu bar.

The *Import* button on the CASTEP Analysis dialog is now active.

Click the **Import** button.

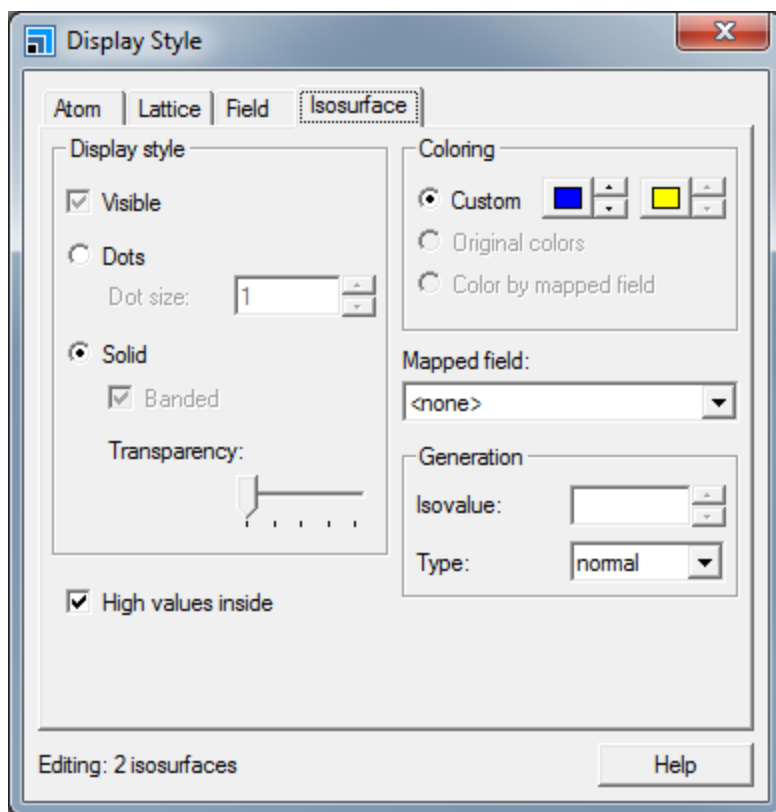
The isosurface is overlaid onto the structure.



Electron density isosurface of AIAs

You can change the isosurface settings using the Display Style dialog.

Open the **Display Style** dialog and select the **Isosurface** tab.



Display Style dialog, Isosurface tab

You can change various settings here.

In the **Isovalue** text box, type **0.1** and press the **TAB** key.

Note how the isosurface changes.

Move the **Transparency** slider bar to the right.

As you move the *Transparency* slider bar, the surface becomes more transparent.

Hold down the right mouse button and move the mouse to rotate the model.

As the model rotates, the isosurface reverts to a dot display to increase the speed of rotation. If you have a fast machine, you can disable this feature by unchecking the *Fast render on move* checkbox on the *Graphics* tab of the Display Options dialog.

You can toggle display of the isosurface at any time by checking or unchecking the *Visible* checkbox on the *Isosurface* tab of the Display Style dialog.

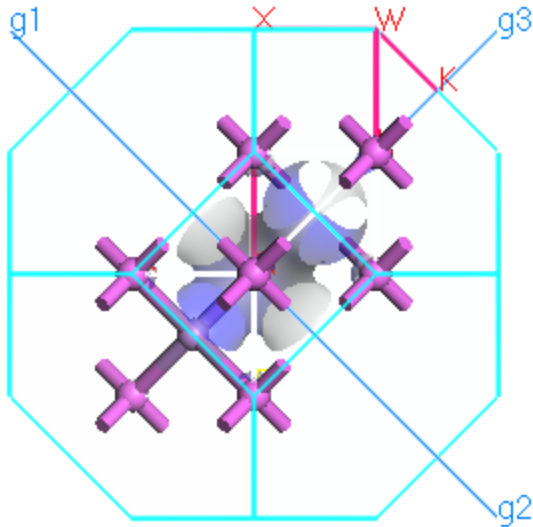
You can display the Brillouin zone path for the reciprocal lattice, see the Brillouin zone theory topic for further information.

Select **Tools | Brillouin Zone Path** from the menu bar to open the Brillouin Zone Path dialog. Click the **Create** button and close the dialog.

The Brillouin zone and k-paths display can be manipulated using the Display Style dialog.

Select the **Reciprocal** tab and move the **Transparency** slider all the way to the right. Set the **Scale** to **33** and change the **Path Line width** to **5.00**. Close the dialog.

Rotate the structure to view the high-symmetry points and the standard Brillouin zone path for this lattice type.



Brillouin zone paths and isosurface of AIs

The CASTEP Analysis tool can be used to display density of states, DOS, and band structure information. Band structure charts show the dependence of electronic energies on k-vector along high symmetry directions in the Brillouin zone. These charts provide a useful tool for qualitative analysis of the electronic structure of the material - for example, it is easy to identify narrow bands of d and f states as opposed to nearly free electron-like bands that correspond to s and p electrons.

DOS and PDOS charts give a quick qualitative picture of the electronic structure of the material, and sometimes they can be directly related to experimental spectroscopic results.

The main CASTEP output file, `AIs.castep`, contains limited band structure and DOS information, but more detailed information is contained in the `AIs_BandStr.castep` and `AIs_DOS.castep` documents, respectively.

On the CASTEP Analysis dialog select the **Band structure** option.

From this dialog, you can choose to display both the band structure and density of states information on the same chart document and control the DOS chart quality.

Note: You can also display them in separate chart documents by analyzing the band structure and density of states separately.

Check the **Show DOS** checkbox and click the **More...** button to open the CASTEP DOS Analysis Options dialog. Set the **Integration method** to **Interpolation** and the **Accuracy level** to **Fine**. Click the **OK** button.

On the CASTEP Analysis dialog, click the **View** button.

A chart document is generated containing the band structure and density of states charts.

Note: You can export any chart document as a comma-separated variable file which can then be read in any spreadsheet package, for example, Excel.

You can also use CASTEP to calculate many other properties, such as reflectivity and dielectric functions. This is the end of the tutorial.

Adsorption of CO onto a Pd(110) surface

Purpose: Introduces the use of CASTEP for calculating the adsorption energy of a gas onto a metal surface.

Modules: Materials Visualizer, CASTEP

Time: 🕒🕒🕒

Prerequisites: Using the crystal builder Visualizer Tutorial

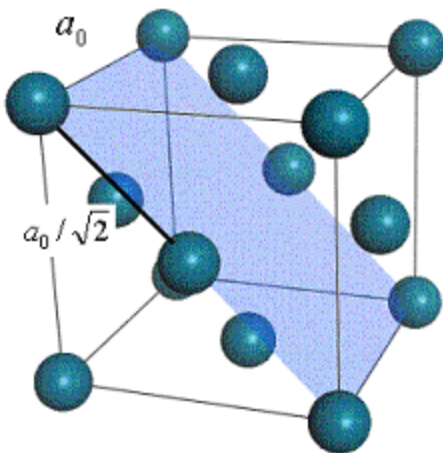
Background

In this tutorial you will examine the adsorption of CO on Pd(110). The Pd surface plays a crucial role in a variety of catalytic reactions. Understanding how molecules interact with such surfaces is one of the first steps to understanding catalytic reactions. In this context, DFT simulations can contribute to this understanding by addressing the following questions:

- Where does the molecule want to adsorb?
- How many molecules will stick to the surface?
- What is the adsorption energy?
- What does the structure look like?
- What are the mechanisms of adsorption?

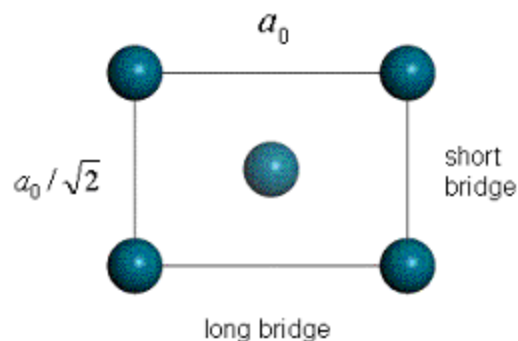
You will focus on one adsorption site, the short bridge site, as it is known to be energetically preferred at fixed coverage. At 1 ML coverage the CO molecules repel each other preventing them from aligning exactly perpendicular to the surface. You will calculate the energy contribution of this tilting to the chemisorption energy by considering a (1×1) and (2×1) surface unit cell.

Pd bulk



Pd(110) surface

Top view



Pd bulk and a top view on the Pd(110) surface. The (110) cleave plane is highlighted in blue. a_0 is the bulk lattice constant, also known as the lattice parameter.

Introduction

In this tutorial, you will use CASTEP to optimize and calculate the total energies of several different systems. Once you have determined these energies, you will be able to calculate the chemisorption energy for CO on Pd(110).

This tutorial covers:

- [Getting started](#)
- [To optimize bulk Pd](#)
- [To build and optimize CO](#)
- [To build the Pd\(110\) surface](#)
- [To relax the Pd\(110\) surface](#)
- [To add CO to the 1 × 1 Pd\(110\) surface and optimize the structure](#)
- [To set up and optimize the 2 × 1 Pd\(110\) surface](#)
- [To analyze the energies](#)
- [To analyze the density of states \(DOS\)](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CO_on_Pd** as the project name, click the **OK** button.

The new project is created with *CO_on_Pd* listed in the Project Explorer.

This tutorial consists of five distinct calculations. To make it easier to manage your project, you should begin by preparing five subfolders in your project.

Right-click on the root icon in the Project Explorer and select **New | Folder**, repeat this four more times. Rename the folders **Pd bulk**, **Pd(110)**, **CO molecule**, **(1x1) CO on Pd(110)** and **(2x1) CO on Pd(110)**.

2. To optimize bulk Pd


The crystal structure of Pd is included in the structure library provided with Materials Studio.

In the Project Explorer, right-click on the **Pd bulk** folder and select **Import...** to open the Import Document dialog. Navigate to **Structures/metals/pure-metals** and import **Pd.msi**.

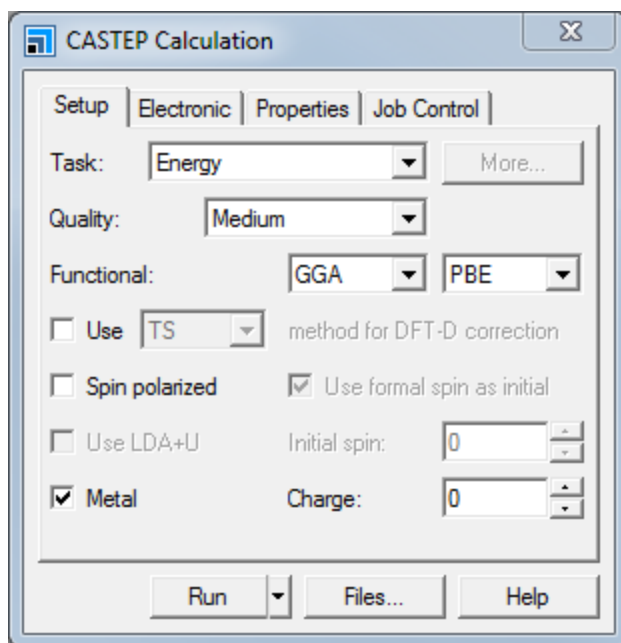
The bulk Pd structure is displayed. You can change the display style to ball and stick.

Right-click in the **Pd.xsd** 3D Viewer and select **Display Style** to open the Display Style dialog. On the **Atom** tab, select **Ball and stick** and close the dialog.

Now optimize the geometry of the bulk Pd using CASTEP.

Click the **CASTEP** button  on the **Modules** toolbar then select **Calculation** or select **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

Cell optimization of crystals requires more accurate calculations than those performed with default settings.

Change the **Quality** from Medium to **Fine**.

To maintain consistency across the calculations that you are going to perform, you should make some changes on the Electronic tab.

Select the **Electronic** tab and click the **More...** button to open the CASTEP Electronic Options dialog. On the **Basis** tab check the **Use custom energy cutoff** checkbox and make sure that the field value is **570.0 eV**. This ensures that all calculations in the tutorial use the same energy cut-off.

The default values for geometry optimization do not include optimization of the cell.

Change the **Task** from Energy to **Geometry Optimization**. Click the **More...** button to open the CASTEP Geometry Optimization dialog. Check the **Optimize cell** checkbox and close the dialog.

Click the **Run** button. A message dialog about conversion to the primitive cell is displayed. Click the **Yes** button.

The job is submitted and starts to run. You should proceed to the [next section](#) and build the CO molecule but return here when the calculation is complete to display the Lattice Parameters.

When the job has finished, you must convert the primitive cell result back to a conventional cell representation in order to proceed with building the Pd(110) surface in step 4.

In the Project Explorer, open **Pd.xsd** located in the **Pd CASTEP GeomOpt** folder. Select **Build | Symmetry | Conventional Cell** from the menu bar.

You should now save your project files.

Select **File | Save Project**, then **Window | Close All** from the menu bar. In the Project Explorer, re-open the optimized **Pd.xsd**.

Right-click in the 3D Viewer and select **Lattice Parameters**.

This opens the Lattice Parameters dialog. The value of a should be approximately 3.962 Å, compared with the experimental value of 3.89 Å.

Close the **Lattice Parameters** dialog and **Pd.xsd**.

3. To build and optimize CO

CASTEP will only work with periodic systems. To optimize the geometry of the CO molecule, you must put it into a crystal lattice.

In the Project Explorer, right-click on the **CO molecule** folder and select **New | 3D Atomistic Document**. Rename the new document **CO.xsd**.

An empty 3D Viewer is displayed. You will use the Build Crystal tool to create an empty cell and then add the CO molecules to it.

Select **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog. Choose the **Lattice Parameters** tab and change each cell **Length a, b, and c** to **8.00**. Click the **Build** button.

An empty cell is displayed in the 3D Viewer.

Select **Build | Add Atoms** from the menu bar to open the Add Atoms dialog.

The C-O bond length in the CO molecule has been determined experimentally as 1.1283 Å. By adding the atoms using Cartesian coordinates you can create your CO molecule with exactly this bond length.

Select the **Options** tab and ensure that the **Coordinate system** is set to **Cartesian**. On the **Atoms** tab click the **Add** button.

A carbon atom is added at the origin of the cell.

Change the **Element** to **O**, leave the **x** and **y** values as **0.000**. Change the **z** value to **1.1283**. Click the **Add** button and close the dialog.

You are now ready to optimize your CO molecule.

Open the **CASTEP Calculation** dialog.

The settings from the previous calculation have been retained. However, you do not need to optimize the cell for this calculation.

Open the **CASTEP Geometry Optimization** dialog. Uncheck the **Optimize cell** checkbox and close the dialog.

On the **Properties** tab of the CASTEP Calculation dialog check the **Density of states** checkbox. Change the **k-point set** to **Gamma** and check the **Calculate PDOS** checkbox. Click the **Run** button.

When asked about converting to higher symmetry, click the **No** button to proceed with the current symmetry.

The calculation starts. You can move onto [building the Pd\(110\) surface](#) as you will analyze the energy at the end of the tutorial.

4. To build the Pd(110) surface

This section of the tutorial uses the optimized Pd structure from the [Pd bulk](#) part of the tutorial.

Select **File | Save Project**, then **Window | Close All** from the menu bar. Open **Pd.xsd** in the **Pd bulk/Pd CASTEP GeomOpt** folder.

Creating the surface is a two step process. The first step is to cleave the surface and the second is to create a slab containing the surface and a region of vacuum.

Select **Build | Surfaces | Cleave Surface** from the menu bar to open the Cleave Surface dialog. Change the **Cleave plane (h k l)** from -1 0 0 to **1 1 0** and press the **TAB** key. Increase the **Fractional Thickness** to **1.5**. Click the **Cleave** button and close the dialog.

A new 3D Viewer is opened containing the 2D periodic surface. However, CASTEP requires a 3D periodic system as input, this is obtained using the Vacuum Slab tool.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. Change the **Vacuum thickness** from 10.00 to **8.00** and click the **Build** button.

The structure changes from 2D to 3D periodic and a vacuum is added above the atoms. Before continuing, you must reorient the lattice.

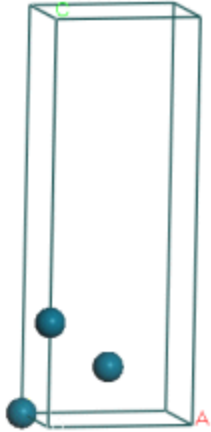
Open the **Lattice Parameters** dialog and select the **Advanced** tab, click the **Re-orient to standard** button. Close the dialog.

You should also change the lattice display style and rotate the structure so that the z-axis is vertical on the screen.

Open the **Display Style** dialog and select the **Lattice** tab. In the **Display style** section, change the **Style** from Default to **Original**. Close the dialog.

Press the **UP** arrow key twice.

The 3D view shown below is displayed:



The Pd atom with the largest z-coordinate will be called "the uppermost Pd layer".

Later in this tutorial, you will need to know the bulk interlayer spacing d_0 . You can calculate this using the atom coordinates.

Select **View | Explorers | Properties Explorer** from the menu bar. Select the Pd atom with **FractionalXYZ x = 0.5** and **y = 0.5**. Note the z value of this atom from the **XYZ** property.

The z value should be 1.401 Å and this is the interlayer spacing. This z value refers to the Z coordinate from the (Cartesian) XYZ property and not FractionalXYZ.

Note: For an fcc(110) system, d_0 can be calculated as

$$d_0 = \frac{a_0}{\sqrt{8}}$$

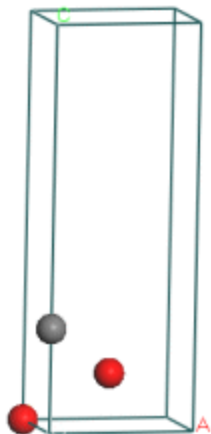
Before you relax the surface, you must constrain the Pd atoms in the bulk as you only need to relax the surface.

Hold down the **SHIFT** key and select all the Pd atoms except the uppermost Pd layer. Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. Check the **Fix fractional position** checkbox and close the dialog.

The bulk atoms have been constrained. You can see the constrained atoms by changing their display color.

In the 3D Viewer, click anywhere to deselect the atoms. Open the **Display Style** dialog and select the **Atom** tab. Change the **Color by** option to **Constraint**.

This 3D view is now displayed:



Change the **Color by** option back to **Element** and close the dialog.

This structure is needed for the Pd(110) surface relaxation and also as a starting model for (1x1) CO on Pd (110) optimization.

Select **File | Save As...** from the menu bar. Navigate to the **Pd(110)** folder and click the **Save** button.

Hold down the **CTRL** key and drag the document into the **(1x1) CO on Pd(110)** folder. Rename the document **(1x1) CO on Pd(110)**.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

5. To relax the Pd(110) surface

Now you are ready to optimize the Pd (110) surface.

From the Project Explorer, open **Pd(110).xsd** in the **Pd(110)** folder. Open the **CASTEP Calculation** dialog and then the **CASTEP Geometry Optimization** dialog. Ensure that the **Optimize cell** checkbox is unchecked and close the dialog.

You should also calculate the density of states for the system.

Select the **Properties** tab on the CASTEP Calculation dialog. Check the **Density of states** and **Calculate PDOS** checkboxes and change the **k-point set** to **Fine**.

You are ready to run the calculation.

Click the **Run** button and close the CASTEP Calculation dialog.

When asked about converting to higher symmetry, click the **No** button to proceed with the current symmetry.

The calculation will take some time to run and so you will perform the analysis at the end. You should move on and construct the next set of surfaces.

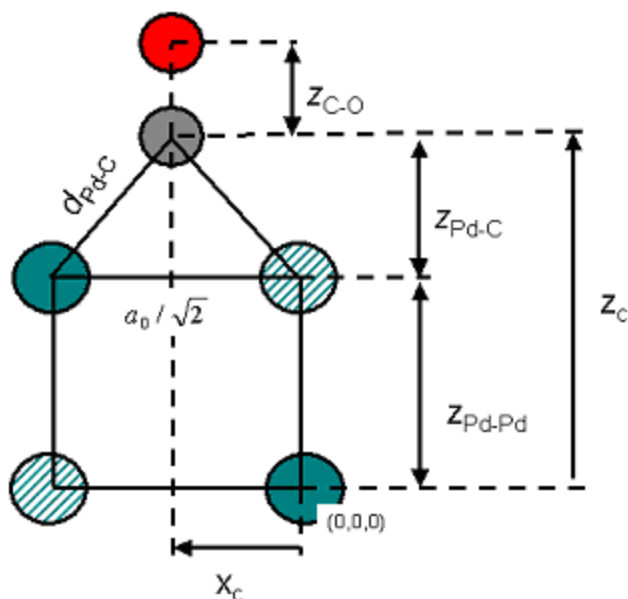
Select **File | Save Project** then **Window | Close All** from the menu bar.

6. To add CO to the 1 × 1 Pd(110) surface and optimize the structure

Now you are going to work with the structure in the (1x1) Co on Pd(110) folder.

In the Project Explorer, open **(1x1) CO on Pd(110).xsd** in the **(1x1) CO on Pd(110)** folder.

Now add the CO molecule above the short bridge position. You will make use of the fact that for CO on Pd(110), bond lengths have been experimentally determined.



Geometry of CO on Pd(110) in the yz-plane. Hatched atoms are not displayed in Lattice: Original display mode.

The first step is to add the carbon atom. The Pd-C bond length (denoted above as $d_{\text{Pd-C}}$) should be 1.93 Å. When you use the Add Atom tool you can enter either Cartesian or fractional coordinates but in this case you will use fractional coordinates, x_c , y_c , and z_c . x_c and y_c are simple as $y_c = 0.5$ and $x_c = 0$. However, determination of z_c is slightly more difficult. You will construct it from the two distances $z_{\text{Pd-C}}$ and $z_{\text{Pd-Pd}}$.

$z_{\text{Pd-Pd}}$ is simply the lattice parameter a_0 divided by $\sqrt{2}$ (it should be 2.80 Å).

$z_{\text{Pd-C}}$ is obtained from the formula

$$z_{\text{Pd-C}} = \sqrt{d_{\text{Pd-C}}^2 - \frac{1}{8}a_0^2} \quad (\text{it should be } 1.33 \text{ \AA}).$$


Add $z_{\text{Pd-C}}$ and $z_{\text{Pd-Pd}}$ to obtain z_c (it should be 4.13 Å). Now convert this distance into a fractional length. You do this using the Lattice parameters.

Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu. Note the value of **c**.

To calculate the fractional z coordinate, you divide z_c by the c lattice parameter (you should obtain 0.382).

Open the **Add Atoms** dialog and choose the **Options** tab. Check that the **Coordinate system** is **Fractional**. On the **Atoms** tab change the **Element** to **C**, change **a** to **0.0**, **b** to **0.5**, and **c** to **0.382**. Click the **Add** button.

If you want to confirm that you have set up the model correctly, use the Measure/Change tool.

Click the **Measure/Change** arrow  on the toolbar and select **Distance** from the dropdown list. Click on the Pd-C bond.


The next step is to add the oxygen atom.

On the **Add Atoms** dialog, change the **Element** to **O**.

Experimentally, the C-O bond length has been determined as 1.15 Å. In fractional coordinates this is 0.107, adding this value to the fractional z-coordinate of carbon (0.382), the z-coordinate of oxygen is 0.489.

Change the value of **c** to **0.489** and click the **Add** button. Close the dialog.

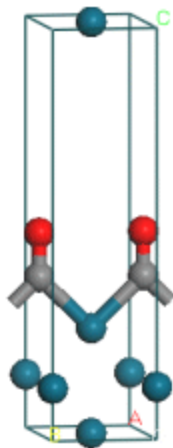
The calculations for the Pd surface model were carried out using P1 symmetry. However, the system has a higher symmetry, even after the addition of the CO molecule. You can find and impose symmetry, using the Find Symmetry tool, to speed up further calculations.

Click the **Find Symmetry** button  on the **Symmetry** toolbar to open the Find Symmetry dialog. Click the **Find Symmetry** button then the **Impose Symmetry** button.

The symmetry is PMM2.

Open the **Display Style** dialog and select the **Lattice** tab. Change the **Style** to **Default**. On the **Atom** tab, select the **Ball and stick** display style and close the dialog.

The structure should look similar to this:



Before you optimize the geometry of the structure, you should save it in the (2x1) CO on Pd(110) folder.

Select **File | Save** from the menu bar to save the 1x1 system. Then also select **File | Save As...** from the menu bar, navigate to the **(2x1) CO on Pd(110)** folder and save the document as **(2x1) CO on Pd (110).xsd**.

You are now ready to optimize the structure.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

In the Project Explorer, open **(1x1)CO on Pd(110).xsd** in the **(1x1)CO on Pd(110)** folder.

Open the **CASTEP Calculation** dialog.

The parameters from the previous calculation should have been retained.

Click the **Run** button and close the dialog.

Once again, you can move onto building the final structure while the calculation progresses.

7. Setting up and optimizing the 2×1 Pd(110) surface

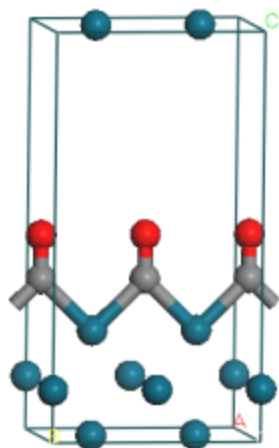
The first step is to open the 3D Atomistic document in the (2×1) CO on Pd(110) folder.

In the Project Explorer, open **(2x1) CO on Pd(110).xsd** in the **(2x1) CO on Pd(110)** folder.

This is currently a 1×1 cell so you need to use the Supercell tool to change it to a 2×1 cell.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase **B** to **2** and click the **Create Supercell** button and close the dialog.

The structure should look like this:



(2×1) Cell of CO on Pd(110)

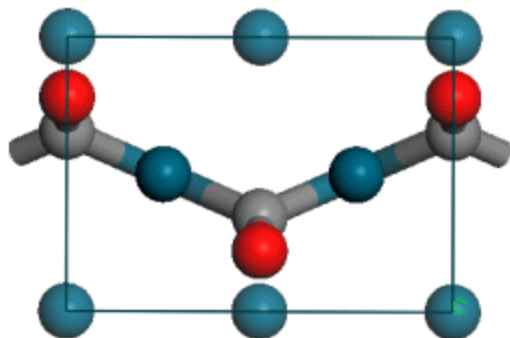
Now tilt the CO molecules with respect to each other. To simplify this operation, identify the CO molecule at $y = 0.5$ as molecule A and the one at $y = 0.0$ as molecule B.

Select the **carbon** atom of molecule B. In the Properties Explorer, open the **XYZ** property and subtract **0.6** from the **X** field. Repeat this for the **oxygen** atom of molecule B but subtract **1.2** from the **X** field.

Now repeat this for molecule A.

Select the **carbon** atom of molecule A. In the Properties Explorer, open the **XYZ** property and add **0.6** to the **X** field. Repeat this for the **oxygen** atom of molecule A but add **1.2** to the **X** field.


The view down the z-axis of the molecule should look like this:




However, you will notice that the Pd-C and C-O bond lengths have changed from their original values.

Select the **carbon** atom in molecule A and use the Properties Explorer to change the **Z** field of the **FractionalXYZ** property to **0.369**. Repeat this for molecule B.

This corrects the Pd-C bond length. You can use the Measure/Change tool to correct the C-O bond length.

Click the **Measure/Change** button  on the **Sketch** toolbar and select **Distance** from the dropdown list. Click on the **C-O** bond for molecule A.

Choose the 3D Viewer **Selection Mode** tool  on the **3D Viewer** toolbar and select the monitor. In the Properties Explorer, change the **Filter** to **Distance**.

Change the **Distance** property to **1.15 Å**. Repeat this for molecule B.

Now recalculate the symmetry of the system.

Open the **Find Symmetry** dialog and click the **Find Symmetry** button then the **Impose Symmetry** button.

The symmetry is PMA2. The view of the unit cell changes from 3 CO molecules on the Pd surface to only 2. You are now ready to optimize the geometry of your system.

Open the **CASTEP Calculation** dialog and click **Run**.

The calculation starts. When the calculation finishes, you will need to extract the total energy of the system as detailed in the next section. You can move onto the next section to extract the energies from the previous calculations.

8. To analyze the energies

In this section you are going to calculate the chemisorption energy ΔE_{chem} . This is defined as:

$$\Delta E_{\text{chem}} = 0.5 * E_{(2 \times 1) \text{ CO on Pd}(110)} - E_{\text{Pd}(110)} - E_{\text{CO molecule}}$$

Allowing the CO atoms to tilt against each other, hence reducing the self repulsion of the CO molecules, should result in a gain in energy. The repulsion energy can be calculated from:

$$\Delta E_{\text{rep}} = 0.5 * E_{(2 \times 1) \text{ CO on Pd}(110)} - E_{(1 \times 1) \text{ CO on Pd}(110)}$$

To calculate these properties, you need to extract the total energies from CASTEP text output documents for each simulation.

In the Project Explorer, open **CO.castep** in the **CO molecule/CO CASTEP GeomOpt** folder. Press **CTRL + F** and search for **Final Enthalpy**. Note down the value that appears in that line. Repeat the procedure to find the total energies of the other systems and so complete the table.


Simulation	Total Energy (eV)
CO molecule	
Pd(110)	
(1×1)CO on Pd(110)	
(2×1)CO on Pd(110)	

Once you have the energies, simply use the above equations to calculate ΔE_{chem} and ΔE_{rep} . These should have values of approximately -1.79 eV and -0.06 eV, respectively.

9. To analyze the density of states (DOS)

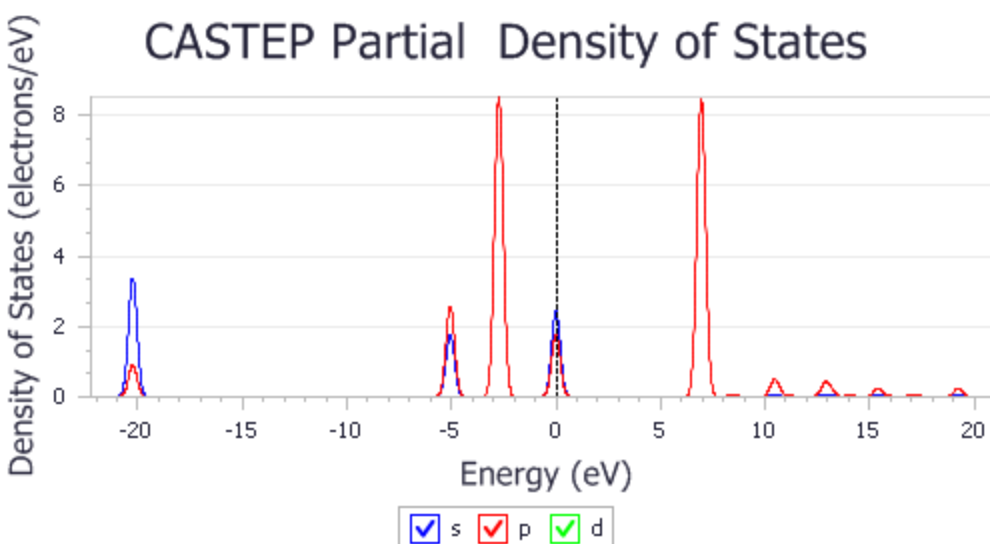
Next, you will examine the changes in the density of states (DOS). This will allow you to obtain an insight into the bonding mechanism of CO on Pd(110). To do this, you need to display the density of states of the isolated CO molecule and of (2×1) CO on Pd(110).

In the Project Explorer, open **CO.xsd** in the **CO molecule/CO CASTEP GeomOpt** folder.

Click the **CASTEP** button  on the **Modules** toolbar, then select **Analysis** to open the CASTEP Analysis dialog.

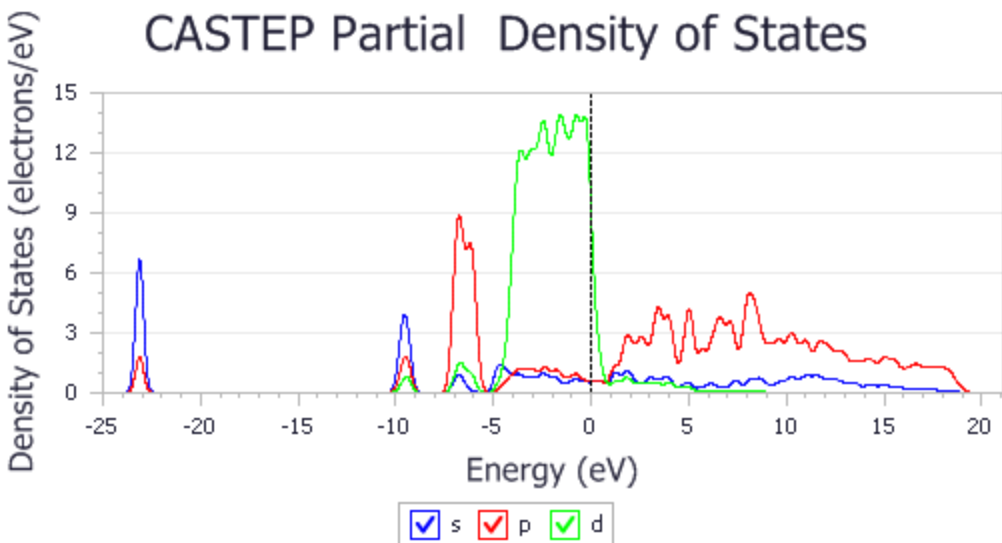
Select the **Density of states**. Click the **Partial** radio button and uncheck the **f** and **sum** checkboxes. Click the **View** button.

A chart document is displayed showing the PDOS for the CO molecule.



PDOS of CO molecule

Repeat the above for **(2x1) CO on Pd(110).xsd**.



PDOS of (2x1) CO on Pd(110)

It is clear that the electronic states of the isolated CO molecule at approximately -20, -5, and -2.5 eV are considerably lowered in energy as the CO binds to the surface.

Note: The default pseudopotential for Pd, Pd_80.otfg, treats 4s and 4p semicore states as valence. This results in sharp peaks in the calculated DOS at about -84 and -49 eV. The chart above excludes those states; this can be achieved by using Properties Explorer to change the maximum and minimum values along X and Y axes.

As an independent exercise you can analyze PDOS further by investigating contributions to the PDOS of the adsorbate complex that arise from the C and O atoms.

Hold down the **SHIFT** key and select all C and O atoms in the **(2x1) CO on Pd(110).xsd** document. Generate **PDOS** - it shows the effect of hybridization with Pd states which manifests itself as broadening of the energy levels and their general shift towards lower energies.

This is the end of the tutorial.

Calculating elastic constants for BN

Purpose: Illustrates the use of CASTEP to calculate elastic constants.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: [Predicting the lattice parameters of AIAs from first principles](#)

Background

Recent developments in density functional theory (DFT) methods applicable to studies of large periodic systems have become essential in addressing problems in materials design and processing. The DFT tools can be used to guide and lead the design of new materials, allowing researchers to understand the underlying chemistry and physics of processes.

Introduction

In this tutorial, you will learn how to use CASTEP to calculate elastic constants and other mechanical properties. In the first part you will optimize the structure of cubic BN and then you will calculate its elastic constants.

This tutorial covers:

- [Getting started](#)
- [To optimize the structure of cubic BN](#)
- [To calculate the elastic constants of BN](#)
- [Description of the elastic constants file](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

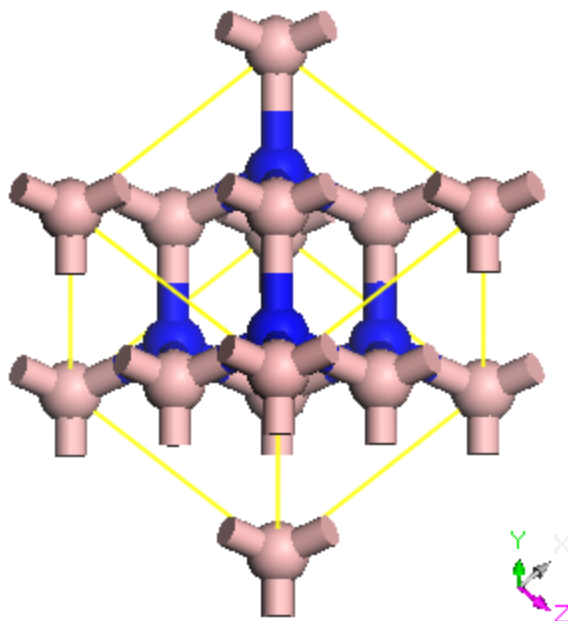
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **BN_elastic** as the project name, click the **OK** button.

The new project is created with *BN_elastic* listed in the Project Explorer. The next step is to import the BN structure.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to the folder **Structures/semiconductors/** and select **BN.msi**. Click the **Open** button.

The crystal structure of BN is displayed.



Structure of BN cubic

This is the conventional representation of the BN structure. In order to reduce the computation time, you should convert to the primitive representation.


Select **Build | Symmetry | Primitive Cell** from the menu bar.

2. To optimize the structure of BN cubic

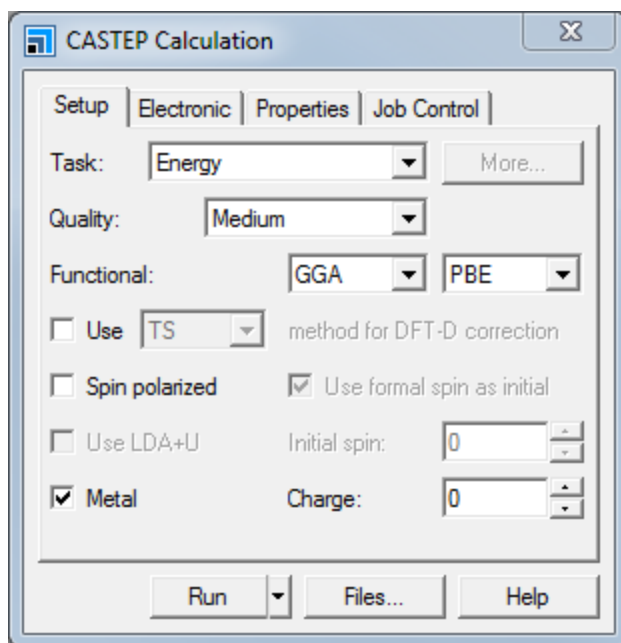
It is not necessary to perform geometry optimization before calculating elastic constants, so you can generate C_{ij} data for experimentally observed structures. However, more consistent results are obtained if you perform full geometry optimization, including cell optimization, and then calculate the elastic constants for the structure corresponding to the theoretical ground state.

The accuracy of the elastic constants, especially of the shear constants, depends strongly on the quality of the SCF calculation and, in particular, on the quality of the Brillouin zone sampling and the degree of convergence of wavefunctions. Therefore, you should use the [Fine](#) setting for SCF tolerance and k-point sampling and a [Fine](#) derived FFT grid.

Now you will set up the geometry optimization.

Click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

On the **Setup** tab, set the **Task** to **Geometry Optimization**, the **Quality** to **Fine**, and the **Functional** to **GGA and PBESOL**.

Click the **More...** button to open the CASTEP Geometry Optimization dialog. Check the **Optimize cell** checkbox and close the dialog.

Choose the **Job Control** tab on the CASTEP Calculation dialog and select the **Gateway** on which you wish to run the CASTEP job.

Click the **Run** button.

After optimization, the structure should have cell parameters of about $a = b = c = 2.553 \text{ \AA}$ which corresponds to 3.610 \AA lattice parameter for the conventional unit cell (experimental value is 3.615 \AA).

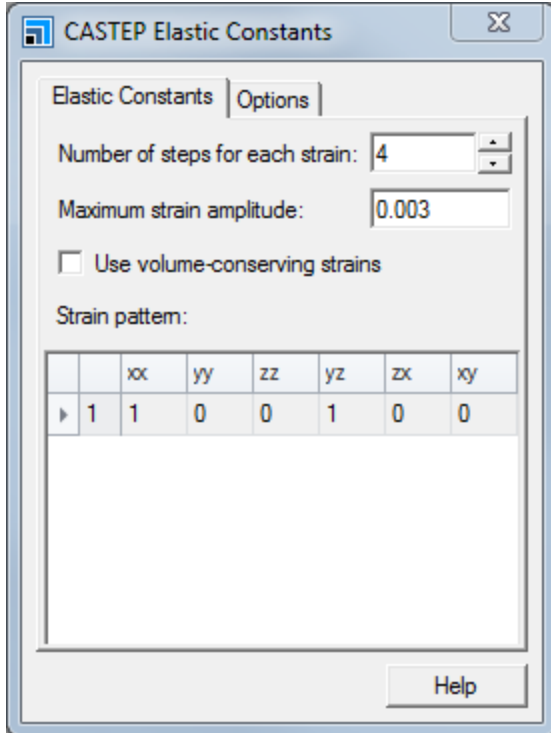
Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu.

The lattice parameters are shown. Now you can go on to calculate the elastic constants of the optimized structure.

3. To calculate the elastic constants of BN

Select the **Setup** tab on the CASTEP Calculation dialog. Select **Elastic Constants** from the **Task** dropdown list and click the **More...** button.

This opens the CASTEP Elastic Constants dialog.



CASTEP Elastic Constants dialog, Elastic Constants tab

Increase the **Number of steps for each strain** from 4 to 6 and close the dialog. Ensure that **BN CASTEP GeomOpt/BN.xsd** is the active document and click the **Run** button on the CASTEP Calculation dialog.


Note: If BN CASTEP GeomOpt/BN.xsd is made active before the CASTEP Elastic Constants dialog is opened, the *Strain pattern* grid on this dialog will contain values.

CASTEP results for the [Elastic Constants](#) task are returned as a set of .castep output files. Each of them represents a geometry optimization run with a fixed cell, for a given strain pattern and strain amplitude. The naming convention for these files is:

seedname_cij__m__n

where m is the current strain pattern and n is the current strain amplitude for the given pattern.

CASTEP can use these results to analyze the calculated stress tensors for each of these runs and generate a file with information about elastic properties.

Click the **CASTEP** button  on the **Modules** toolbar and select **Analysis** from the dropdown list or choose **Modules | CASTEP | Analysis** from the menu bar.

Select the **Elastic constants** option. The results file from the **Elastic Constants** job for BN should be displayed automatically in the **Results file** selector. Click the **Calculate** button.

A new text document, BN Elastic Constants.txt, is created in the results folder.

The information in this document includes a summary of the input strains and calculated stresses, results of linear fitting for each strain pattern (including quality of the fit), the correspondence between

calculated stresses and elastic constants for a given symmetry, a table of elastic constants (C_{ij}) and elastic compliances (S_{ij}). The derived properties, such as bulk modulus and its inverse, compressibility, Young modulus, and Poisson ratios for three directions, and the Lamé constants that are needed for modeling the material as an isotropic medium, are also reported in this document.

3. Description of the elastic constants file

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.

Two strain patterns are required for this lattice type. For each strain pattern, there is a summary of calculated stresses as extracted from the respective .castep files:

```
=====
Elastic constants from Materials Studio: CASTEP
=====
```

```
Summary of the calculated stresses
*****
```

```
Strain pattern:      1
=====
```

```
Current amplitude: 1
```

```
Transformed stress tensor (GPa) :
```

```
  -8.189798    -0.000000    -0.000000
  -0.000000   -10.017367     1.379354
  -0.000000     1.379354   -10.017367
```

```
Current amplitude: 2
```

```
Transformed stress tensor (GPa) :
```

```
  -9.116387    -0.000000    -0.000000
  -0.000000   -10.216365     0.838749
  -0.000000     0.838749   -10.216365
```

```
Current amplitude: 3
```

```
Transformed stress tensor (GPa) :
```

```
 -10.048348    -0.000000    -0.000000
  -0.000000   -10.416477     0.292454
  -0.000000     0.292454   -10.416477
```

```
Current amplitude: 4
```

```
Transformed stress tensor (GPa) :
```

```
 -10.989496    -0.000000    -0.000000
  -0.000000   -10.613140    -0.257999
  -0.000000    -0.257999   -10.613140
```

```
Current amplitude: 5
```

```
Transformed stress tensor (GPa) :
```

```
 -11.916295    -0.000000    -0.000000
  -0.000000   -10.807624    -0.799331
  -0.000000    -0.799331   -10.807624
```

Current amplitude: 6

Transformed stress tensor (GPa) :

-12.834327	-0.000000	-0.000000
-0.000000	-10.998673	-1.335928
-0.000000	-1.335928	-10.998673

Any information about the connection between components of the stress, strain, and elastic constants tensors is provided. At this stage, each elastic constant is represented by a single compact index rather than by a pair of ij indices. The correspondence between the compact notation and the conventional indexing is provided later in the file:

Stress corresponds to elastic coefficients (compact notation):

1 7 7 4 0 0

as induced by the strain components:

1 1 1 4 0 0

A linear fit of the stress-strain relationship for each component of the stress is given in the following format:

Stress index	Cij index	value of stress	value of strain
1	1	-8.189798	-0.003000
1	1	-9.116387	-0.001800
1	1	-10.048348	-0.000600
1	1	-10.989496	0.000600
1	1	-11.916295	0.001800
1	1	-12.834327	0.003000
C (gradient)	:	775.321833	
Error on C	:	1.304724	
Correlation coeff:		0.999994	
Stress intercept :		-10.515775	
2	7	-10.017367	-0.003000
2	7	-10.216365	-0.001800
2	7	-10.416477	-0.000600
2	7	-10.613140	0.000600
2	7	-10.807624	0.001800
2	7	-10.998673	0.003000
C (gradient)	:	163.737381	
Error on C	:	0.695805	
Correlation coeff:		0.999964	
Stress intercept :		-10.511608	
3	7	-10.017367	-0.003000
3	7	-10.216365	-0.001800
3	7	-10.416477	-0.000600
3	7	-10.613140	0.000600
3	7	-10.807624	0.001800
3	7	-10.998673	0.003000
C (gradient)	:	163.737381	

```

Error on C      :      0.695805
Correlation coeff:      0.999964
Stress intercept :     -10.511608

      4      4      1.379354      -0.003000
      4      4      0.838749      -0.001800
      4      4      0.292454      -0.000600
      4      4     -0.257999      0.000600
      4      4     -0.799331      0.001800
      4      4     -1.335928      0.003000
C (gradient)   :      453.359595
Error on C     :      0.836968
Correlation coeff:      0.999993
Stress intercept :      0.019550

```

The gradient provides the value of the elastic constant (or a linear combination of elastic constants); the quality of the fit, indicated by the correlation coefficient, provides the statistical uncertainty of that value. The stress intercept value is not used in further analysis, it is simply an indication of how far the converged ground state was from the initial structure.

The results for all the strain patterns are then summarized:

```

=====
Summary of elastic constants
=====

```

```

id  i  j      Cij (GPa)
1   1  1      775.32183 +/-  1.305
4   4  4      453.35960 +/-  0.837
7   1  2      163.73738 +/-  0.492

```

The errors are only provided when more than two values for the strain amplitude are used, since there is no statistical uncertainty associated with fitting a straight line to only two points.

Elastic constants are then presented in a conventional 6 × 6 tensor form, followed by a similar 6 × 6 representation of the compliances:

```

=====
Elastic Stiffness Constants Cij (GPa)
=====

```

```

775.32183  163.73738  163.73738  0.00000  0.00000  0.00000
163.73738  775.32183  163.73738  0.00000  0.00000  0.00000
163.73738  163.73738  775.32183  0.00000  0.00000  0.00000
0.00000    0.00000    0.00000  453.35960  0.00000  0.00000
0.00000    0.00000    0.00000  0.00000  453.35960  0.00000
0.00000    0.00000    0.00000  0.00000  0.00000  453.35960

```

```

=====
Elastic Compliance Constants Sij (1/GPa)
=====

```

```

0.0013923  -0.0002428  -0.0002428  0.0000000  0.0000000  0.0000000

```

```

-0.0002428  0.0013923  -0.0002428  0.0000000  0.0000000  0.0000000
-0.0002428  -0.0002428  0.0013923  0.0000000  0.0000000  0.0000000
 0.0000000  0.0000000  0.0000000  0.0022058  0.0000000  0.0000000
 0.0000000  0.0000000  0.0000000  0.0000000  0.0022058  0.0000000
 0.0000000  0.0000000  0.0000000  0.0000000  0.0000000  0.0022058

```

The final part of the file contains the derived properties:

Bulk modulus = 367.59887 +/- 0.545 (GPa)

Compressibility = 0.00272 (1/GPa)

Elastic Debye temperature = 1889.26254 K

Averaged sound velocity = 11454.32578 (m/s)

Axis	Young Modulus (GPa)	Poisson Ratios	
X	718.22228	Exy= 0.1744	Exz= 0.1744
Y	718.22228	Eyx= 0.1744	Eyz= 0.1744
Z	718.22228	Ezx= 0.1744	Ezy= 0.1744

```

=====
Elastic constants for polycrystalline material (GPa)
=====

```

		Voigt	Reuss	Hill
Bulk modulus	:	367.59887	367.59887	367.59887
Shear modulus (Lame Mu)	:	394.33265	380.00700	387.16982
Lame lambda	:	104.71043	114.26086	109.48565

Universal anisotropy index: 0.18849

The values reported above are roughly within 10% of experimentally measured values (B=396 GPa, C_{11} =820 GPa, C_{12} =190 GPa, C_{44} =457 GPa) which is typical for DFT calculations.

Calculated elastic properties of crystals are significantly more sensitive to the accuracy of the electronic structure calculation than, for example, calculated lattice parameters and atomic coordinates. It is always necessary to check the convergence of the calculated properties with respect to the following parameters:

- density of k-points (most important)
- energy cutoff
- augmentation density scaling factor - in the case of ultrasoft pseudopotentials, either generated on the fly or tabulated ones

An additional consideration in elastic properties calculations is the choice of exchange-correlation functional. Modern functionals that are designed to reproduce solid state properties more accurately than traditional LDA or PBE functionals are PBESOL and Wu-Cohen; these are recommended for calculating elastic coefficients of solids.

This is the end of the tutorial.

Predicting the thermodynamic properties of germanium

Purpose: Introduces the use of CASTEP for calculating linear response and thermodynamic properties.

Modules: Materials Visualizer, CASTEP

Time: 🕒🕒🕒

Prerequisites: [Predicting the lattice parameters of AIs from first principles](#)

Background

Linear response, or density functional perturbation theory (DFPT), is one of the most popular methods of ab initio calculation of lattice dynamics. However, potential applications of the method extend beyond the study of vibrational properties. Linear response provides an analytical way of computing the second derivative of the total energy with respect to a given perturbation. Depending on the nature of this perturbation, a number of properties can be calculated. A perturbation in ionic positions gives the dynamical matrix and phonons; in magnetic field - NMR response; in unit cell vectors - elastic constants; in an electric field - dielectric response, and so on. The basic theory of phonons, or lattice vibrations, in crystals is well understood and has been described in detail in several textbooks. The importance of the phonon interpretation of lattice dynamics is illustrated by the large number of physical properties that can be understood in terms of phonons: infrared, Raman, and neutron scattering spectra; specific heat, thermal expansion, and heat conduction; electron-phonon interaction and thus resistivity and superconductivity, and so on. Density Functional Theory (DFT) methods can be used to predict such properties and CASTEP provides this functionality.

Note: DFPT phonon calculations using ultrasoft pseudopotentials are not yet supported and nor are DFPT calculations for spin-polarized systems. Nevertheless phonon spectra and related properties can be calculated with those settings in the framework of the finite difference technique.

Introduction

In this tutorial, you will learn how to use CASTEP to perform a linear response calculation in order to calculate phonon dispersion and density of states as well as predict thermodynamic properties such as enthalpy and free energy.

This tutorial covers:

- [Getting started](#)
- [To optimize the structure of the germanium cell](#)
- [To calculate phonon dispersion and density of states \(DOS\)](#)
- [To display phonon dispersion and density of states](#)
- [To display thermodynamic properties](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Ge_phonon** as the project name, click the **OK** button.

The new project is created with *Ge_phonon* listed in the Project Explorer.

Begin by importing the Ge structure, which is included in the structure library provided with Materials Studio.

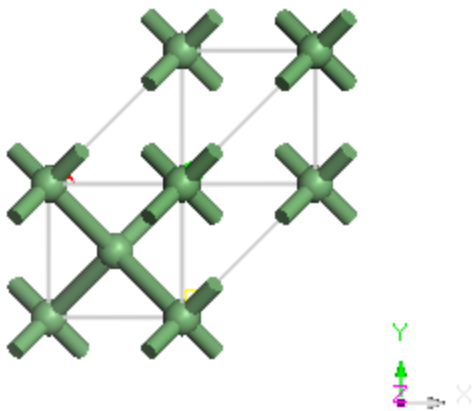
Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Structures/metals/pure-metals** and select **Ge.msi**.

2. To optimize the structure of the germanium cell


It is often possible to get significant speedup by converting the structure to a primitive cell.

Select **Build | Symmetry | Primitive Cell** from the menu bar.

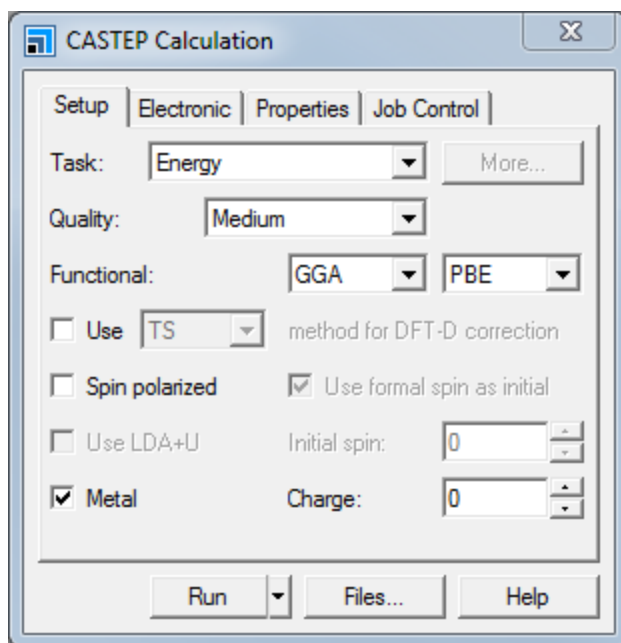
The primitive germanium cell is displayed.



Now optimize the geometry of the Ge structure using CASTEP.

Click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

The default values for geometry optimization do not include optimization of the cell.

On the **Setup** tab change the **Task** from Energy to **Geometry Optimization** and the **Functional** to **LDA**. Uncheck the **Metal** checkbox as Ge is a semiconductor. Change **Quality** to **Ultra-fine**, which is a recommended setting for calculating vibrational properties of materials.

Click the **More...** button to open the CASTEP Geometry Optimization dialog, check the **Optimize cell** checkbox and close the dialog.

Select the **Electronic** tab of the CASTEP Calculation dialog and set **Pseudopotentials** to **Norm conserving** (linear response calculations of phonon properties are available only for norm-conserving potentials).

On the **Job Control** tab select the location for the job to run in the **Gateway location** dropdown list, and set the **Runtime optimization** to **Speed**.

Click the **Run** button to start the job.

The job is submitted and starts to run. It should take a few minutes, depending on the speed of your computer. The results are placed in a new folder called Ge CASTEP GeomOpt.

3. To calculate phonon dispersion and phonon density of states (DOS)

DFPT gives an opportunity to accurately calculate phonon frequencies at any given point in reciprocal space. However, a calculation for each q-point can be expensive. An alternative approach may be used for calculations that require phonon frequencies for large numbers of q-points, for example, for phonon DOS and thermodynamic properties. This alternative scheme takes advantage of the relatively short range of effective ion-ion interactions in crystals. Interpolation can be used to reduce computation time without loss of accuracy. The accurate DFPT calculations are performed only at a small number of q-vectors, and then a cheap interpolation procedure is used to obtain frequencies at other q-points of

interest. One advantage of using an interpolation scheme instead of the exact calculation is that thermodynamic properties at low temperatures depend strongly on the number of points in the phonon DOS grid. Using the interpolation approach, this number can be increased at no computational cost.

In order to calculate the phonon dispersion and phonon density of states you must perform a single point energy calculation, after selecting the appropriate properties from the *Properties* tab on the *CASTEP Calculation* dialog.

Ensure that **Ge.xsd** in the **Ge CASTEP GeomOpt** folder is the active document.

On the **Setup** tab of the CASTEP Calculation dialog set the **Task** to **Energy**.

On the **Properties** tab choose **Phonons** and request Density of states and Dispersion by selecting the **Both** option.

Click the **More...** button, to display the CASTEP Phonon Properties Setup dialog. Ensure the **Method** is **Linear response** and the **Use interpolation** checkbox is checked. Ensure that **q-vector grid spacing for interpolation** is **0.05 1/Å**, and the **Quality** for **Dispersion** and **Density of states** is set to **Fine**. Close the dialog.

Click the **Run** button and close the CASTEP Calculation dialog.

The job is submitted and starts to run. This is a more time-consuming job and could take a few hours on a multi-core computer. A new folder, called **Ge CASTEP Energy**, is created in the **Ge CASTEP GeomOpt** folder. When the energy calculation is finished two new results files are placed in this folder, **Ge_PhonDisp.castep** and **Ge_PhonDOS.castep**.

4. To display phonon dispersion and density of states

Phonon dispersion curves show how phonon energy depends on the q-vector, along high symmetry directions in the Brillouin zone. This information can be obtained experimentally from neutron scattering experiments on single crystals. Such experimental data are available for only a small number of materials, so theoretical dispersion curves are useful for establishing the validity of a modeling approach to demonstrate the predictive power of ab initio calculations. In certain circumstances it is possible to measure the density of states (DOS) rather than the phonon dispersion. Furthermore, the electron-phonon interaction function, which is directly related to the phonon DOS can be measured directly in the tunneling experiments. It is therefore important to be able to calculate phonon DOS from first principles. Materials Studio can produce phonon dispersion and DOS charts from any **.phonon** CASTEP output file. These files are hidden in the Project Explorer but a **.phonon** file is generated with every **.castep** file that has a **PhonDisp** or **PhonDOS** suffix.

Tip: When evaluating phonon DOS, use only the results of phonon calculations on the Monkhorst-Pack grid.

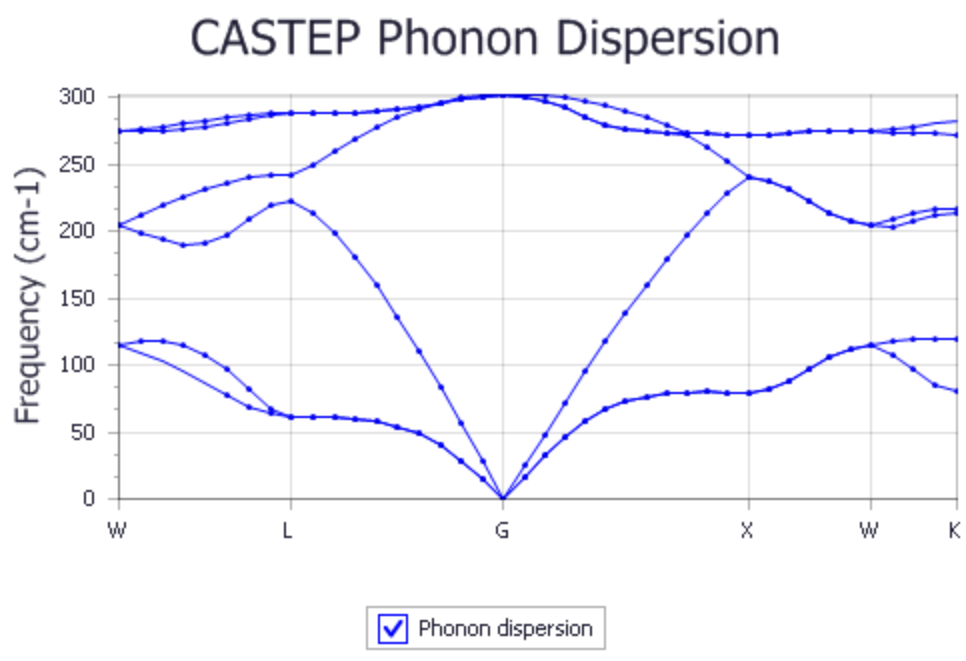
Now use the results of the previous calculation to create a phonon dispersion chart.

Select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog. Choose **Phonon dispersion** from the list of properties. Ensure that the **Results file** selector displays **Ge_PhonDisp.castep**.

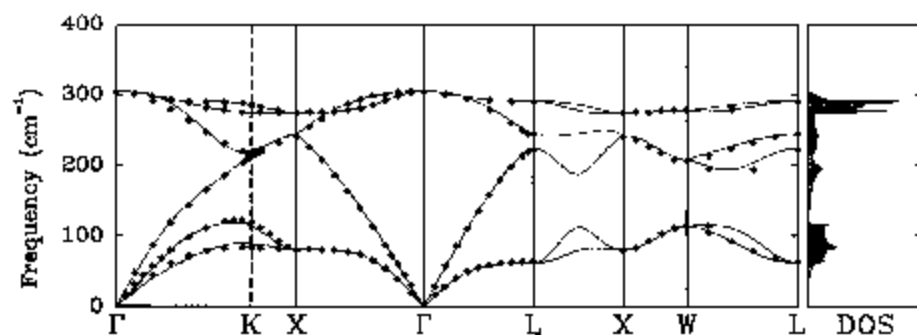
Select **cm-1** from the **Units** dropdown list and **Line** from the **Graph style** dropdown list.

Click the **View** button.

A new chart document, **Ge Phonon Dispersion.xcd**, is created in the results folder. It should look something like the chart shown below:



The experimental phonon dispersion is shown below:



The predicted frequencies are available in the **Ge_PhonDisp.castep** file.

Double-click on **Ge_PhonDisp.castep** in the Project Explorer. Press the **CTRL + F** keys and search for **Vibrational Frequencies**.

The following portion of the results file is displayed:

```

=====
==
+                               Vibrational Frequencies
+                               -----
+
+
+
+
+ Performing frequency calculation at 40 wavevectors (q-pts)
+
+
===== +
+
+
+ -----
- +
+ q-pt= 1 ( 0.500000 0.250000 0.750000) 0.0487804878
+
+ -----
- +
+ Acoustic sum rule correction < 0.002528 cm-1 applied
+
+ N      Frequency irrep.
+
+      (cm-1)
+
+
+
+ 1      114.828225  a
+
+ 2      114.828225  a
+
+ 3      204.776057  b
+
+ 4      204.776057  b
+
+ 5      274.984105  a
+
+ 6      274.984105  a
+
+
+
+ ..... +
+ Character table from group theory analysis of eigenvectors
+
+ Point Group = 32, Oh
+
+
+ ..... +

```

$$\begin{array}{r}
 + \text{ Rep } \text{Mu1} \mid \text{ E } 2 \ 2 \ \text{m } -4 \\
 + \\
 + \mid \text{-----} \\
 + \\
 + \text{ a } \quad 2 \mid \quad 2 \ 0 \ 0 \ 0 \ -1 \\
 + \\
 + \text{ b } \quad 1 \mid \quad 2 \ 0 \ 0 \ 0 \ 1 \\
 + \\
 + \text{-----} \\
 - + \\
 \dots
 \end{array}$$

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.

The frequencies for every q-point and for every branch (Longitudinal Optical or Acoustical (LO/LA), Transverse Optical or Acoustical (TO/TA)) are given in cm^{-1} , as well as the positions of the q-points, in the reciprocal space. The high symmetry points Γ , L and X are at reciprocal space positions (0 0 0), (0.5 0.5 0.5) and (0.5 0 0.5) respectively.

The predicted and experimental frequencies in cm^{-1} are:

	Predicted	Experimental
Γ^{TO}	302	304
Γ^{LO}	302	304
Γ^{TA}	0	0
Γ^{LA}	0	0
L^{TA}	62	63
L^{LA}	223	222
L^{TO}	243	245
L^{LO}	288	290
X^{TA}	80	80
X^{LA}	241	241
X^{TO}	272	276

Overall, the accuracy of the calculation is acceptable. Better agreement with the experimental results may be obtained by running the calculation with a better SCF k-point grid.

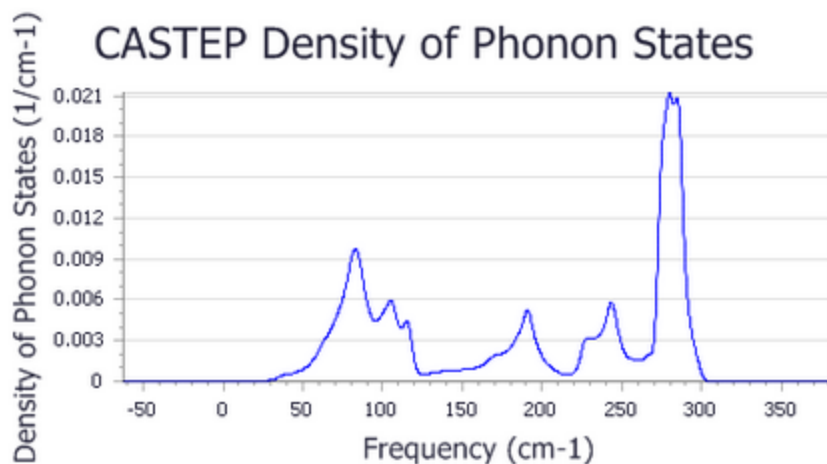
Now create a phonon DOS chart.

On the CASTEP Analysis dialog select **Phonon density of states** from the list of properties. Make **Ge.xsd** the active document and ensure that the **Results file** selector displays **Ge_PhonDOS.castep**.

Set **Display DOS** to **Full**. Click the **More...** button to open the CASTEP Phonon DOS Analysis Options dialog. Select **Interpolation** from the **Integration method** dropdown list and set the **Accuracy level** to **Fine**. Click the **OK** button and on the CASTEP Analysis dialog click the **View** button to create the DOS chart.

Interpolation scheme was chosen to get the best representation of DOS; an alternative setting, smearing, produces DOS with too few fine details.

A new chart document, Ge Phonon DOS .xcd, is created. It should look something like the chart shown below:



5. To display thermodynamic properties

Phonon calculations in CASTEP can be used to evaluate the temperature dependence of the enthalpy, entropy, free energy, and lattice heat capacity of a crystal in a quasi-harmonic approximation. These results can be compared with experimental data (for example heat capacity measurements) or used to predict phase stability of different structural modifications or phase transitions.

All energy-related properties are plotted on one graph, and the calculated value of the zero-point energy is included. The heat capacity is plotted separately on the right.

Note: The entropy is present as a TS product to allow comparison with the enthalpy.

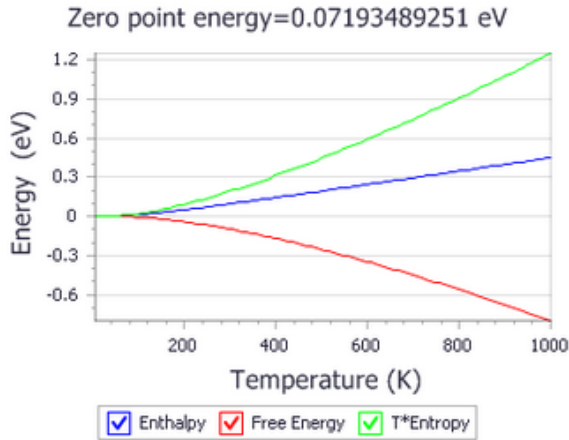
Now use the results of the phonon calculation to create a thermodynamic properties chart.

On the **CASTEP Analysis** dialog choose **Thermodynamic properties** from the list of properties. Make **Ge.xsd** the active document and ensure that the **Results file** selector displays **Ge_PhonDOS.castep**.

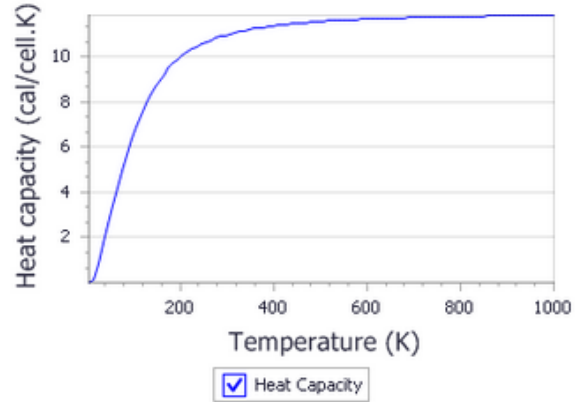
Check the **Plot Debye temperature** checkbox and click the **View** button.

Two new chart documents, Ge Thermodynamic Properties .xcd and Ge Debye Temperature .xcd, are created in the results folder:

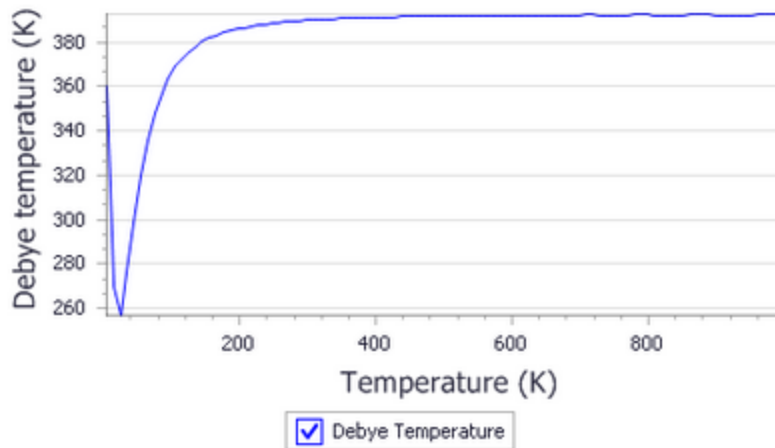
CASTEP Thermodynamic Properties



CASTEP Thermodynamic Properties



CASTEP Thermodynamic Properties



Experimental results without anharmonicity ([Flubacher et al., 1959](#)) show that the Debye temperature at the high temperature limit is 395(3) K. The simulated Debye temperature is 392 K, in excellent agreement with the experimental value.

Overall, the experimental plot is qualitatively very similar to the one generated by CASTEP. There is a dip at about 25 K, with the lowest value of Debye temperature of the order of 255 K, exactly as predicted by CASTEP results. The exact shape of the curve at very low temperatures is not accurate with the calculation settings used in this tutorial. A better sampling of low-frequency acoustic modes is required, and this can be achieved by using a finer Monkhorst-Pack grid in the phonon density of states calculation.

6. To display atomic displacement parameters

Atomic displacement parameters, also known as temperature factors, can be estimated from phonon calculations and displayed in the visualizer as ellipsoids.

On the **CASTEP Analysis** dialog choose **Thermodynamic properties** from the list of properties. Make **Ge.xsd** the active document and ensure that the **Results file** selector displays **Ge_PhonDOS.castep**.

Click **Assign temperature factors to structure** button.

This action adds information about anisotropic temperature factors to each atom. The values can be examined using Properties Explorer. The value of the B factor produced in this tutorial, 0.545 \AA^2 , is in excellent agreement with experimental reports (between 0.52 and 0.55 \AA^2).

In order to visualize temperature factors as ellipsoids, open **Temperature Factors** tab of the **Display Style** dialog and click **Add**. Ellipsoids are added to the display, but they might be obscured by the reciprocal space objects. You can hide reciprocal space objects by clearing the **Display reciprocal lattice** checkbox on the **Reciprocal** tab of the **Display Style** dialog.

This is the end of the tutorial.

References

Flubacher, P.; Leadbetter, A. J.; Morrison, J. A. "The heat capacity of pure silicon and germanium and properties of their vibrational frequency spectra", *Phil. Mag.*, **4**, 273-294 (1959).

Calculating phonon spectra for ferromagnetic iron

Purpose: Introduces the use of CASTEP for calculating phonon spectra using the finite difference formalism.

Modules: Materials Visualizer, CASTEP

Time: 🕒🕒🕒

Prerequisites: [Predicting the lattice parameters of AlAs from first principles](#), [Predicting the thermodynamic properties of germanium](#)

Background

Phonons are an important concept in solid state physics, which provides access to a wide range of important properties such as specific heat, thermal expansion, heat conduction, electron-phonon interactions, resistivity, and superconductivity. Density Functional Theory (DFT) methods are able to predict such properties, and CASTEP provides the necessary functionality. There are two main approaches in lattice dynamics calculations: density functional perturbation theory (DFPT) and the finite displacement method. The first is generally faster and more accurate, but its implementation is problematic and is subject to a set of restrictions. Currently, DFPT in CASTEP can only be used without spin-polarization and only for norm-conserving pseudopotentials. So, for a wide class of materials (including magnetic materials and metals), phonon calculations can only be carried out by using the finite displacement algorithm.

Note: The calculations in this tutorial are demanding in terms of CPU time and memory requirements.

Introduction

In this tutorial, you will learn how to use CASTEP to perform a finite displacement calculation to obtain the phonon dispersion and density of states for a magnetic metal.

This tutorial covers:

- [Getting started](#)
- [To optimize the structure of the iron cell](#)
- [To calculate phonon dispersion and density of states \(DOS\)](#)
- [To display phonon dispersion and density of states](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Fe_phonon** as the project name, click the **OK** button.

The new project is created with *Fe_phonon* listed in the Project Explorer.

Begin by importing the Fe structure, which is included in the structure library provided with Materials Studio.

Select **File | Import...** from the menu bar to open the Import File dialog. Navigate to **Structures/metals/pure-metals** and select **Fe.msi**. Click the **Open** button.


It is often possible to decrease the calculation time by converting the structure to a primitive cell.

Select **Build | Symmetry | Primitive Cell** from the menu bar.

The primitive cell of iron is displayed.

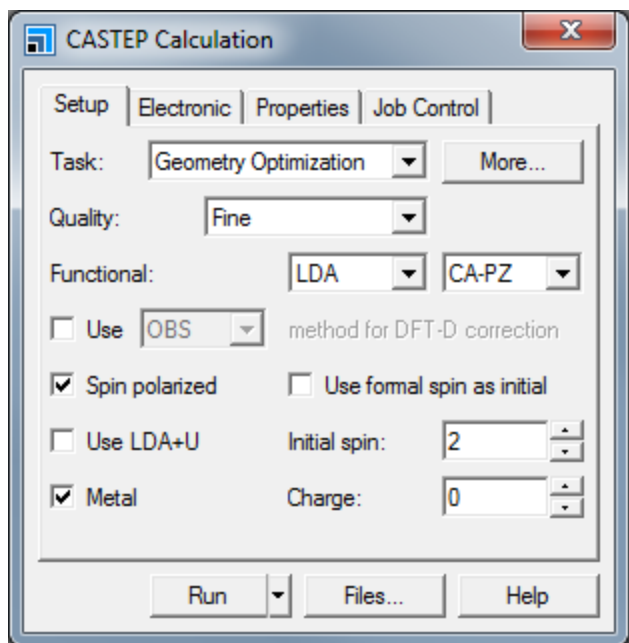
2. Optimizing the structure of iron

Now optimize the geometry of the Fe structure using CASTEP.

Click the **CASTEP** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.

On the **Setup** tab, change the **Task** from Energy to **Geometry Optimization**, set the **Quality** to **Fine**, and the **Functional** to **LDA**. Check the **Spin polarized** checkbox and uncheck the **Use formal spin as initial** checkbox. Set the **Initial spin** value to **2**.



CASTEP Calculation dialog, Setup tab

The default values for geometry optimization do not include optimization of the cell.

Click the **More...** button to open the CASTEP Geometry Optimization dialog, check the **Optimize cell** checkbox and close the dialog.

On the **Electronic** tab select **OTFG ultrasoft** from the **Pseudopotentials** dropdown list.

On the **Job Control** tab, select the **Gateway location** for the job.

Click the **More...** button to open the CASTEP Job Control Options dialog, **uncheck** all of the options in the **Live updates** section, and close the dialog.

Click the **Run** button to start the job.

Note: If you are running this calculation on a cluster with a large amount of RAM (for example more than 10 GB in total) you should use *Speed* for the *Runtime optimization*.

When the job has completed the results are placed in new folder called Fe CASTEP GeomOpt.

3. To calculate phonon dispersion and phonon density of states (DOS)

In order to calculate the phonon dispersion and phonon density of states you have to perform a single point energy calculation, with the appropriate properties selected for calculation.

Ensure that **Fe.xsd** in the **Fe CASTEP GeomOpt** folder is the active document.

On the **Setup** tab on the CASTEP Calculation dialog, set the **Task** to **Energy**.

On the **Properties** tab, check the **Phonons** checkbox and request both density of states and dispersion by selecting the **Both** radio button. Uncheck the **Calculate LO-TO splitting** checkbox and choose **Finite displacement** from the **Method** dropdown list.

The finite displacement scheme has been designed for use with metallic and spin-polarized systems (as well as for calculations that make use of efficient ultrasoft potentials). This is ideal for calculating phonon properties for ferromagnetic iron.

Click the **More...** button to open the CASTEP Phonon Properties Setup dialog. Ensure that the **Method** is **Finite displacement**. Set the **Supercell defined by cutoff radius** to **3.5 Å**. Set the **Quality** for both **Dispersion** and **Density of states** to **Fine** and close the dialog.

Note: The cutoff radius chosen is a crucial parameter for a finite displacement calculation. The accuracy is higher when a larger cutoff radius is used, as longer range interactions are taken into account. The computational time, however, grows very rapidly with the increase of this value. For practical reasons, in this tutorial, a small value is chosen for this parameter. The convergence of the phonon frequencies as a function of the cutoff radius should be investigated when performing meaningful calculations.

On the **Job Control** tab select a **Gateway** for the calculation.

Click the **More...** button to open the CASTEP Job Control Options dialog and check all of the **Live updates** options and close the dialog.

Click the **Run** button and close the CASTEP Calculation dialog.

The job is submitted and starts to run. A new folder, named **Fe CASTEP Energy**, is created in the **Fe CASTEP GeomOpt** folder. When the energy calculation is finished the new results files are placed in this folder, including **Fe_PhonDisp.castep** and **Fe_PhonDOS.castep**.

If you decide not wait for the job to finish, you can access pre-computed version of these files as follows.

Use Windows Explorer to navigate to the **share\Examples\Projects\CASTEP** directory, from the top level of your Materials Studio installation. Double-click on the file **Fe_phonons.stp**.

Tip: For Windows users who are not administrators, you should copy the *Fe_phonons.stp* project and associated *Fe_phonons_Files* folder to a location where you have write permissions. Then open the new copy of the *Fe_phonons.stp* project.

4. To display phonon dispersion and density of states

Phonon dispersion curves show how phonon energy depends on the q-vector, along high symmetry directions in the Brillouin zone. This information can be obtained experimentally from neutron scattering experiments on single crystals. Such experimental data are available for only a small number of materials, so theoretical dispersion curves are useful both for establishing the validity of a modeling approach and to demonstrate the predictive power of ab initio calculations. In certain circumstances it is possible to measure the density of states (DOS) rather than the phonon dispersion. Furthermore, the electron-phonon interaction function, which is directly related to the phonon DOS, can be measured directly in the tunneling experiments. It is therefore important to be able to calculate phonon DOS from first principles.

Materials Studio can produce phonon dispersion and DOS charts from any **.phonon** CASTEP output file. This file is generated with every CASTEP job that includes a calculation of Phonon Dispersion or Phonon DOS. The **.phonon** file is hidden, so you will not see it in the Project Explorer.

Tip: When evaluating phonon DOS, use only the results of phonon calculations on the Monkhorst-Pack grid.

Now use the results of the previous calculation to create a phonon dispersion chart.

Ensure that **Fe.xsd** is the active document.

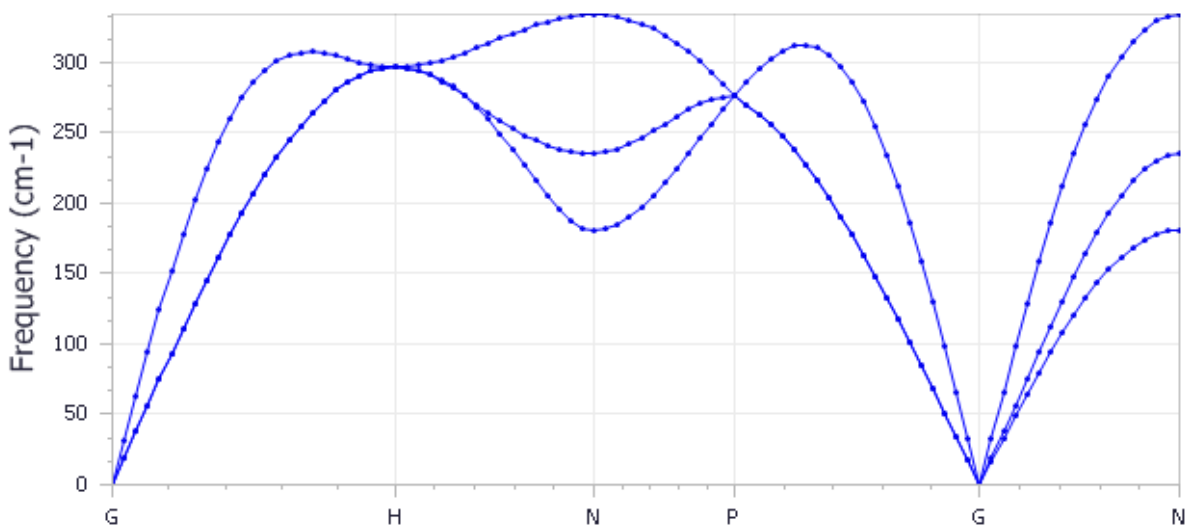
Select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog. Select **Phonon dispersion** from the list of properties. Ensure that the **Results file** is **Fe_PhonDisp.castep**.

Select **cm⁻¹** from the **Units** dropdown list and **Line** from the **Graph style** dropdown list.

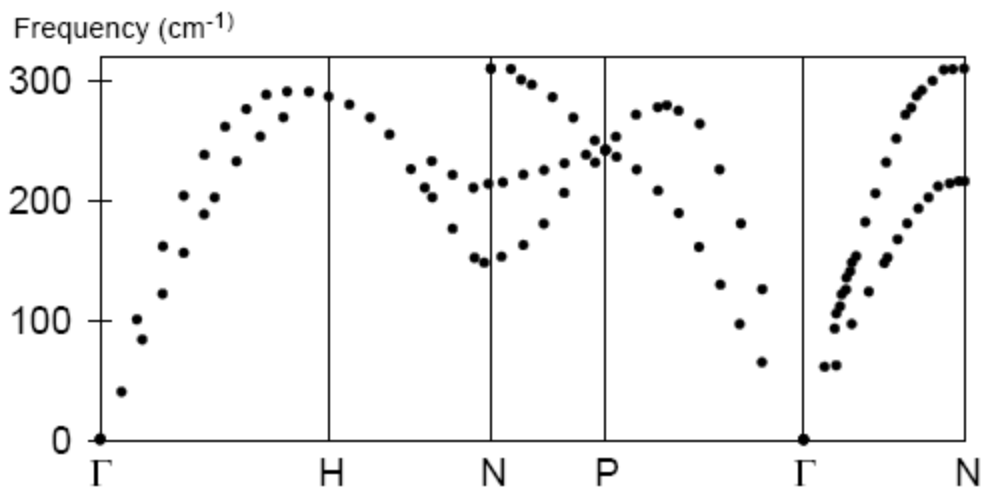
Click the **View** button.

A new chart document, **Fe Phonon Dispersion.xcd**, is created in the results folder. It should be similar to the chart shown below:

CASTEP Phonon Dispersion



The experimental phonon dispersion ([Minkiewicz et al., 1967](#)) is shown below:



Overall, the accuracy of the calculation is qualitatively acceptable, better agreement with the experimental results will be obtained by running the calculation with a larger cutoff radius.

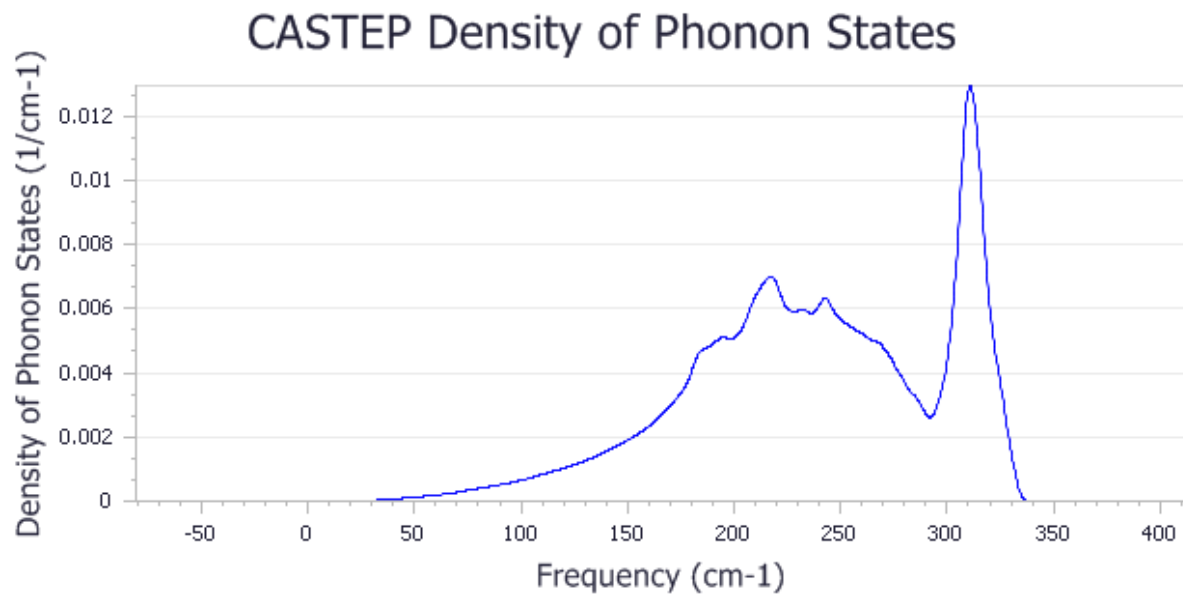
Now create a phonon DOS chart.

Make **Fe.xsd** the active document and select **Phonon density of states** from the list of properties on the CASTEP Analysis dialog. Ensure that the **Results file** is **Fe_PhonDOS.castep**.

Set **Display DOS** to **Full**. Click the **More...** button to open the CASTEP Phonon DOS Analysis Options dialog. Select **Interpolation** as the **Integration method** and **Fine** as the **Accuracy level**. Click the **OK** button.

On the CASTEP Analysis dialog click the **View** button.

A new chart document, Fe Phonon DOS .xcd, is created. It should look similar to the chart shown below:



Phonon calculations in CASTEP can be used to evaluate the temperature dependence of the enthalpy, entropy, free energy, and lattice heat capacity of a crystal in a quasi-harmonic approximation. These results can be compared with experimental data (for example, heat capacity measurements) and used to predict phase stability of different structural modifications or phase transitions.

More details can be found in the [Predicting the thermodynamic properties of germanium](#) tutorial.

This is the end of the tutorial.

References

Minkiewicz, V. J.; Shirane, G.; Nathans, R. "Phonon Dispersion Relation for Iron ", *Phys. Rev.*, **162**, 528-531 (1967).

Assigning the ^{17}O NMR spectrum of L-alanine

Purpose: Introduces the capabilities of NMR CASTEP and the use of the visualization tools for displaying isotropic shielding values.

Modules: Materials Visualizer, CASTEP, NMR CASTEP

Time: 🕒🕒🕒

Prerequisites: [Predicting the lattice parameters of AlAs from first principles](#)

Background

NMR CASTEP predicts the NMR chemical shielding of molecules and solid-state materials from first principles. Based on density functional theory (DFT), NMR CASTEP provides a way to predict key magnetic resonance properties, NMR chemical shielding and electric field gradient (EFG) tensors, with unprecedented accuracy. The method can be applied to compute the NMR shifts of molecules, solids, interfaces, and surfaces for a wide range of materials classes including organic molecules, ceramics and semiconductors. First-principles calculations allow researchers to investigate the nature and origin of the magnetic resonance properties of a system without the need for any empirical parameters.

NMR is often used as an analytical tool to aid in structure prediction. The relative complexity of solid-state structures makes this a challenging task. Often, even though the general features of the crystal structure are understood, a detailed analysis of the geometry proves elusive. Using NMR CASTEP it is possible to simulate the NMR spectrum for a series of related structures until a match is discovered between the computed and experimental results. In this way, theory complements experiment, with both contributing to the determination of the structure.

Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Introduction

In this tutorial, you will use NMR CASTEP to assign the observed ^{17}O chemical shifts to the two unique atoms in crystalline L-alanine. You will learn how to run an NMR CASTEP calculation, display the results in the Materials Visualizer, and to interpret the results.

L-Alanine is one of the smaller amino acids. The unit cell contains 4 molecules for a total of 48 atoms. There are 2 distinct oxygen sites. This tutorial will use the computed NMR chemical isotropic shielding values to tell them apart. Experiment can also distinguish between the two oxygens, but only with a very sophisticated solid-state NMR apparatus.

This tutorial covers:

- [Getting started](#)
- [To run an NMR CASTEP calculation](#)
- [To analyze the results](#)
- [To compare the results with experimental data](#)

Note: Completion of this tutorial entails running an NMR CASTEP calculation. Depending on the configuration of your compute server, this calculation could take a considerable amount of time.

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

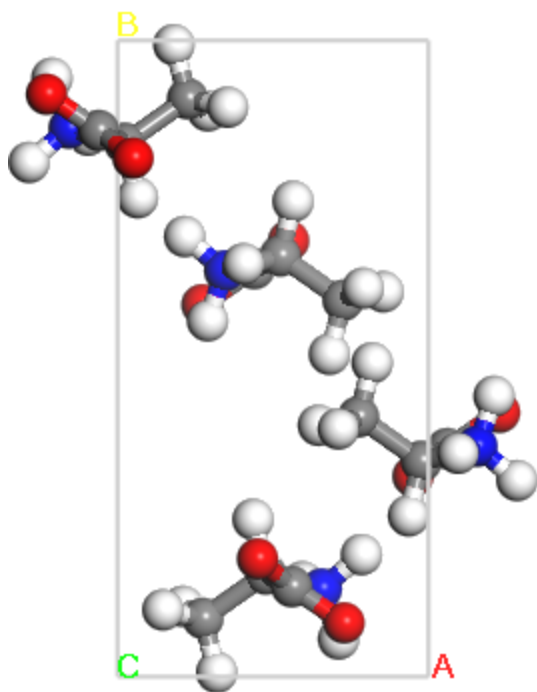
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **NMR_alanine** as the project name, click the **OK** button.

The new project is created with *NMR_alanine* listed in the Project Explorer. The next step is to import the structure.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Examples\Documents\3D Model** and select the **l_alanine.xsd** file, click the **Open** button.


The *l_alanine* document is displayed.



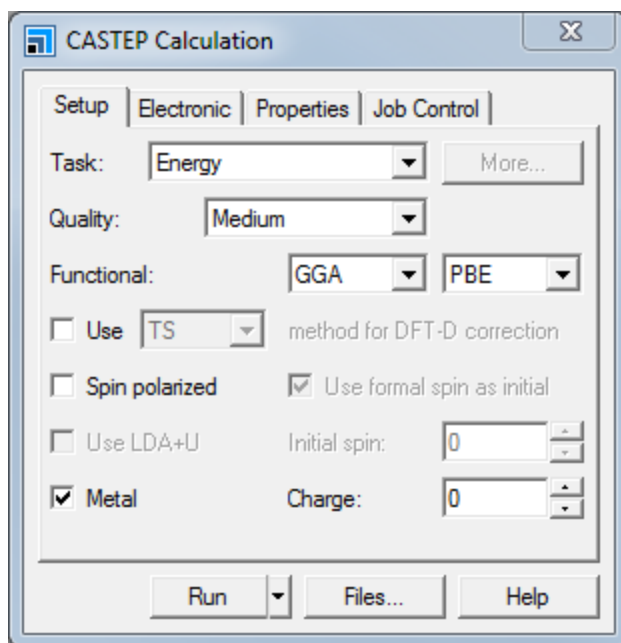
Crystal structure of L-alanine

2. To run an NMR CASTEP calculation

Begin by opening the crystal structure for L-alanine. This is a neutron diffraction crystal structure ([Lehmann et al., 1972](#)). You could also build this crystal structure from scratch and optimize it with CASTEP. Using experimental crystal structures, however, yields results comparable with the DFT-optimized geometry and saves computation time.

Click the **CASTEP** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

You are going to run an energy calculation on the structure and request a calculation of the NMR chemical shielding tensor.

Ensure that the **Task** is set to **Energy** and the **Functional** is **GGA PBE**. Change the **Quality** to **Ultra-fine**. Uncheck the **Metal** checkbox (chemical shielding cannot be calculated for metallic systems).

Note: As a rule, the computed NMR results are sensitive to the *Quality* of the calculation. In order to obtain results that are comparable with experiment, you should use the **Ultra-fine Quality** setting. These calculations will take longer than **Fine** or **Medium** calculations, but the results are considerably more reliable.

On the **Electronic** tab select **OTFG ultrasoft** from the **Pseudopotentials** dropdown list.

On the fly (OTFG) pseudopotentials are required to compute the magnetic shielding properties. If you choose a different type of pseudopotential, the NMR calculation cannot be performed.

Now specify the properties you want to calculate from the *Properties* tab.

On the **Properties** tab check the **NMR** checkbox and ensure that the **Shielding** and **EFG** checkboxes are checked.

This will compute both the NMR chemical shielding and the value of the electric field gradient at the nuclei. If you are running the calculation on a remote server, you can specify the server using the *Job Control* tab.

On the **Job Control** tab choose an appropriate server from the **Gateway** dropdown list.

Click the **Run** button and close the dialog.

Depending on the speed of the computer you are using the NMR calculation will take quite some time to complete. As a point of reference, using the **Ultra-fine** quality settings the NMR shielding calculation on

L-alanine required about 18 hours on a 1.70 GHz laptop computer. You can complete the calculation using the [Medium Quality](#) setting in about 20% of that time. This will give you an understanding of how to run an NMR calculation; however, the results will not be the same as those discussed in the subsequent sections of the tutorial. Alternatively, rather than running the calculation yourself, you can open the pre-computed results in the `Examples` folder as described below.

While the calculation is running several things will happen in the Materials Studio interface. After a few seconds, a new folder is displayed in the Project Explorer and this will contain all the results when the calculation is complete. The Job Explorer is displayed, which contains information about the status of the job. The Job Explorer displays the status of any currently active jobs that are associated with this project. It shows useful information such as the server and job identification number. You can also use this explorer to stop the job if you need to.

As the job progresses, four documents open which relay information on the job status. These documents include the crystal structure, a status document to relay information about the job setup parameters and run information, and charts of the total energy and its convergence as a function of the iteration number.

When the job finishes, the files are transferred back to the client and this can take some time due to the size of certain files.

3. To analyze the results

When the results are transferred, you should have several documents, among them:

- `l_alanine.xsd` - the crystal structure
- `l_alanine.castep` - an output file from the CASTEP energy calculation
- `l_alanine_NMR.castep` - an output file from the NMR CASTEP calculation
- `l_alanine.param` - input information
- `l_alanine.castep_bin` and `l_alanine_NMR.castep_bin` - binary files containing a summary of the results. Although not visible in the Explorer, these hidden files are required for the analysis

If you chose to run the NMR calculation, you should find these files in folder called `l_alanine CASTEP Energy` once the calculation completes.

If you decide not to wait for the job to finish, you can access a pre-computed version of these files as follows.

Use Windows Explorer to navigate to the `\share\Examples\Projects\CASTEP` directory, from the top level of your Materials Studio installation. Double-click on the file `l_alanine.stp`.

Tip: For Windows users who are not administrators, you should copy the `l_alanine.stp` project and associated `l_alanine Files` folder to a location where you have write permissions. Then open the new copy of the `l_alanine.stp` project.

Whether you choose to wait for the long calculation to finish or you decide to open the pre-computed results, the tutorial is the same from this point. If you ran the `l_alanine` calculations using the [Medium Quality](#) setting to save time, the steps are still the same, but your numerical results will differ from the ones discussed here. First, examine the data in the NMR output file.

In the Project Explorer, open `l_alanine CASTEP Energy/l_alanine_NMR.castep` and locate the line that reads **Chemical Shielding and Electric Field Gradient Tensors**.

This is located about 100 lines up from the end of the file. The output data will look something like this (for clarity, the results for H, C, and N have been removed):

Chemical Shielding and Electric Field Gradient Tensors						
Nucleus		Shielding tensor			EFG Tensor	
Species	Ion	Iso(ppm)	Aniso(ppm)	Asym	Cq(MHz)	Eta
0	1	-27.61	419.12	0.49	8.304E+00	0.26
0	2	-9.52	307.31	0.66	6.773E+00	0.65
0	3	-27.61	419.12	0.49	8.304E+00	0.26
0	4	-9.52	307.31	0.66	6.773E+00	0.65
0	5	-27.61	419.12	0.49	8.304E+00	0.26
0	6	-9.52	307.31	0.66	6.773E+00	0.65
0	7	-27.61	419.12	0.49	8.304E+00	0.26
0	8	-9.52	307.31	0.66	6.773E+00	0.65

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.


The magnetic shielding data are displayed for each element that used an OTFG pseudopotential. In the case of L-alanine, this includes the elements, H, C, N, and O. In this tutorial, you will focus on the ^{17}O results.

The first column of the results simply indicates the element symbol. The second column, called *Ion*, is the relative order of a particular atom in the input file. The subsequent columns are defined as follows:

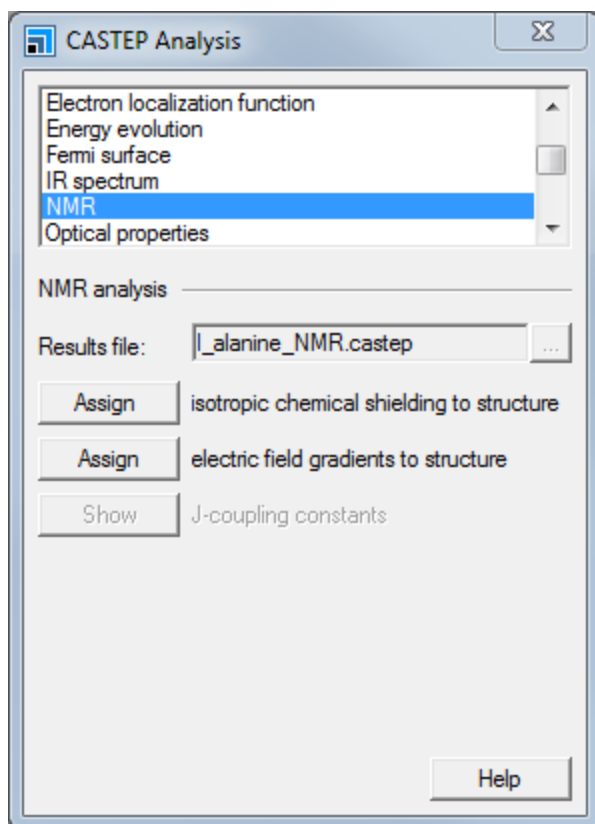
- Iso (ppm) - the isotropic chemical shielding in ppm. This is defined as $\sigma_{\text{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, where σ refers to the chemical shielding tensor in the principal axis frame, that is after diagonalization. This is an *absolute* value of the isotropic chemical shielding, not relative to a standard.
- Aniso (ppm) - the anisotropy defined as $\Delta = \sigma_{zz} - \sigma_{\text{iso}}$.
- Asym - the asymmetry parameter defined as $\eta = (\sigma_{xx} - \sigma_{yy})/\Delta$.
- Cq (MHz) - the quadrupolar coupling constant, $C_Q = eQV_{zz}/h$, where V_{zz} is the largest component of the diagonalized EFG tensor, Q is the nuclear quadrupole moment, and h is Planck's constant.
- Eta - the quadrupolar asymmetry parameter, $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$.

Scroll down to the results for oxygen. Notice that although there are 8 individual oxygen atoms in the unit cell, there are only 2 distinct results. This is because there are only 2 symmetry-unique oxygen atoms in the cell. Now you will use the Materials Visualizer and the experimental data to determine which NMR signal corresponds to which atom.

Open **I_alanine CASTEP Energy/I_alanine.xsd**.

Click the **CASTEP** button  on the **Modules** toolbar, then choose **Analysis** or select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog.

Choose the **NMR** option and click the **Assign isotropic chemical shielding to structure** button.



CASTEP Analysis dialog, NMR selection

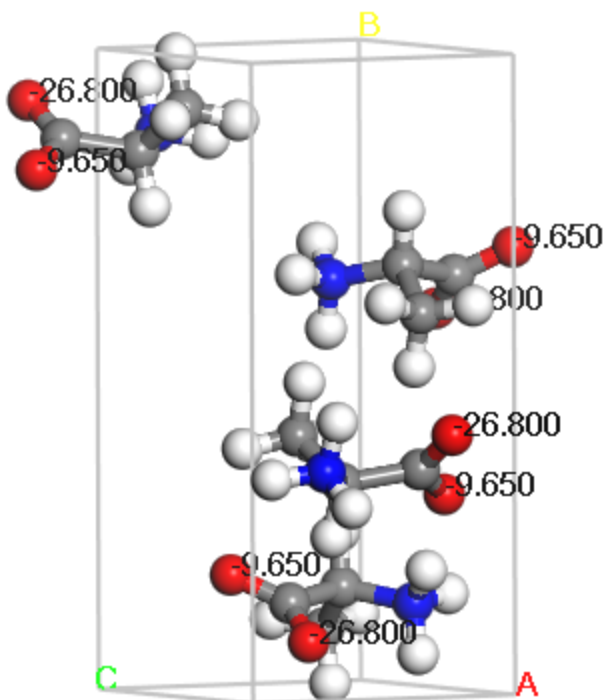
The isotropic chemical shielding values have been loaded into the structure. Now you will display the shielding values for the oxygen atoms.

Hold down the **ALT** key and double-click on any of the oxygen atoms.

This selects all the oxygen atoms in the system.

Right-click in **I_alanine.xsd** and select **Label** from the shortcut menu to open the Label dialog. From the **Properties** select **NMRShielding** and click the **Apply** button.

The NMR isotropic shielding values are displayed for the oxygen atoms.



L-Alanine with ^{17}O isotropic chemical shielding displayed

You can use a similar process to import the electric field gradient data. Atoms can be labeled using either the quadrupolar coupling or the asymmetry parameter.

4. To compare the structure with experimental data

The experimental results for the ^{17}O magnetic resonance data may be found in [Pike et al., \(2004\)](#). In general, the EFG values and asymmetry parameters can be compared directly with experiment. The isotropic chemical shifts require some analysis because the program reports *absolute* chemical shielding whereas most experimentalists are concerned with shifts relative to a known standard. This difference can be dealt with in 2 ways:

1. In most cases, such as in this example, the primary interest is in comparative shifts, which shift is lowest and which is highest, so there is no need to convert the shielding to the same relative standard used by the experiment. The relative positions are all that is needed in order to assign the shifts to atoms unambiguously. This is easy to do because the relative positions of the peaks do not change when shifted with respect to a standard.
2. When dealing with several related systems, it is necessary to determine a value empirically such that you can convert the shielding to a relative shift. Rather than calculate the chemical shielding of the reference compound explicitly, the reference is obtained by comparing it to a system that is experimentally well-characterized and is similar to the systems being investigated. For example, [Yates et al. \(2004\)](#) investigated ^{17}O shifts for glutamic acid polymorphs. The reference that was chosen was the one which provided the best match between computed and observed values for D-glutamic acid-HCl. The same value was applied to *all* of the polymorphs.

So, why not compute the value of the standard? Typical standards are liquids like water and tetramethylsilane (TMS). A simple calculation on an isolated molecule is quite easy to do, but yields a result very different from the experimental value. On the other hand, computing a value for the liquid state is a complex task, involving the creation of an accurate model of the liquid and subsequent evaluation of the NMR chemical shielding averaged over time and molecular orientation. The results

obtained by comparing to one known experimental system provides a more rapid approach, and in addition, provides an immediate sanity check on the results.

The table below summarizes the computed and observed results.

Quantity	Theory	Experiment
$\sigma^{\text{iso}} \text{ O1 (ppm)}$	-27.61	
$\delta^{\text{iso}} \text{ O1 (ppm)}$		284
$\sigma^{\text{iso}} \text{ O2 (ppm)}$	-9.52	
$\delta^{\text{iso}} \text{ O2 (ppm)}$		260.5
$ \delta \text{ O1} - \delta \text{ O2} $	18.09	23.5
$C^{\text{Q}} \text{ O1 (MHz)}$	8.30	7.86
$C^{\text{Q}} \text{ O2 (MHz)}$	6.77	6.53
$\eta^{\text{Q}} \text{ O1}$	0.26	0.28
$\eta^{\text{Q}} \text{ O2}$	0.65	0.70

Notice that the values of C_{O} and η_{O} are in close enough agreement to experiment to provide an unambiguous assignment of the spectrum. Notice also that the spacing between the ^{17}O peaks is comparable: 18.09 ppm versus 23.5 ppm. The *larger* experimentally observed shift corresponds to the *smaller* (more negative) computed value of the shielding. This is because of the way the experimentally observed shifts are computed with respect to the standard:

$$\delta_{\text{iso}} = \sigma_{\text{reference}} - \sigma_{\text{observed}}$$

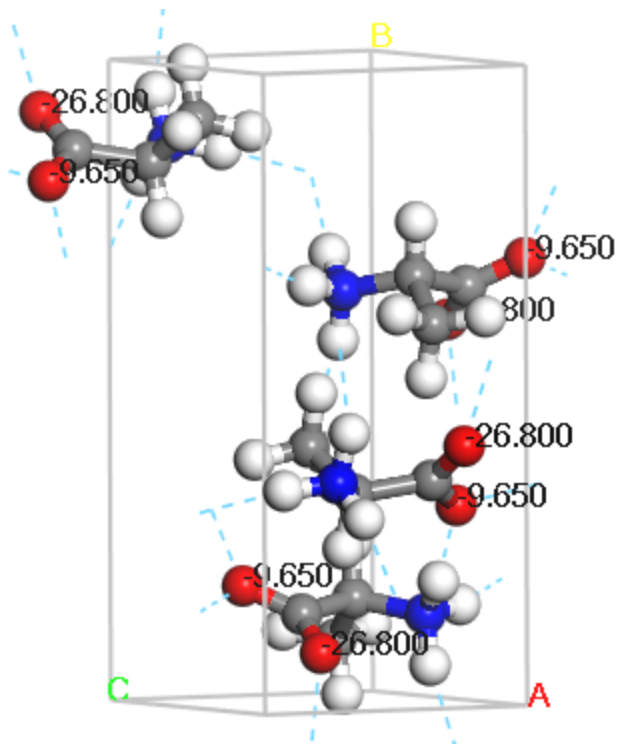
Assume a reference value of 267.3 ppm and convert each computed σ_{iso} into a δ_{iso} . How well do the computed and observed shifts match?

You can see how hydrogen bonding in the crystal affects the chemical shifts.

Label the oxygen atoms by the NMR chemical shifts as you did at the end of [section 3](#).

Select **Build | Hydrogen Bonds** from the menu bar to open the Hydrogen Bond Calculation dialog, click the **Calculate** button.

Hydrogen bonds are displayed as dashed lines.



L-Alanine with hydrogen bonds displayed

Notice that one oxygen is hydrogen bonded to 2 hydrogen atoms associated with the amine group, whereas the other is bonded only to one. The oxygen bonded to 2 hydrogen atoms is nominally the hydroxyl oxygen while the other is the carbonyl oxygen. Based on the computed results and the visualization you can see that the carbonyl oxygen is the one with the observed shift of 284 ppm and the hydroxyl oxygen has the observed shift of 260.5 ppm.

This is the end of the tutorial.

References

Lehmann, M. S.; Koetzle, T. F.; Hamilton, W. C. *J. Am. Chem. Soc.*, **94**, 2657 (1972).

Pike, K. J., et al. *J. Phys. Chem. B*, **108**, 9256 (2004).

Yates, J. R., et al. *J. Phys. Chem A*, **108**, 6032 (2004).

Charge density difference of CO on Pd(110)

Purpose: Demonstrates the use of CASTEP for calculating the charge density difference that occurs when a molecule adsorbs on a surface.

Modules: Materials Visualizer, CASTEP

Time: 🕒

Prerequisites: [Adsorption of CO onto a Pd\(110\) surface](#)

Background

In this tutorial you will investigate how the bonding of the CO molecule affects the electron distribution relative to the isolated CO molecule and the unperturbed Pd(110) surface. The charge density difference can be computed in two different ways. The first option is to compute the charge density with respect to fragments. This is useful for describing the formation of large systems in terms of smaller ones. This method illustrates how the charge density changes during a chemical reaction or on binding of a molecule to a surface. In the case of CO on Pd(110) the electron density difference can be expressed as:

$$\Delta\rho = \rho_{\text{CO@Pd(110)}} - (\rho_{\text{CO}} + \rho_{\text{Pd(110)}})$$

where $\rho_{\text{CO@Pd(110)}}$ is the electron density of the total CO + Pd(110) system, and ρ_{CO} and $\rho_{\text{Pd(110)}}$ are the unperturbed electron densities of the sorbate and substrate, respectively.

The other option is to compute the density difference with respect to atoms:

$$\Delta\rho = \rho_{\text{CO@Pd(110)}} - \sum (\rho_i)$$

where the subscript i runs over all atoms. This option shows the changes in the electron distribution due to the formation of all the bonds. It is useful for illustrating how chemical bonds are formed across the whole system by delocalization of atomic charge density.

The display of the density difference can contribute to an understanding of adsorption processes. Where does the molecule want to adsorb? Why does the molecule adsorb there? What bonding mechanisms contribute to the stabilization of the molecule at this site?

You will focus on one adsorption site: the short bridge site you studied in the tutorial [Adsorption of CO onto a Pd\(110\) surface](#).

Introduction

In this tutorial, you will use CASTEP to compute the charge density difference of CO on Pd(110) in two different ways. You will use the optimized geometry of CO on Pd, as determined [previously](#). Once you have completed the calculations you will use the Materials Visualizer to display the density differences as 3D fields and 2D slices.

This tutorial covers:

- [Getting started](#)
- [To define fragments](#)
- [To run the calculation](#)
- [To display the fragment density difference](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by opening the Materials Studio project that you created for the tutorial [Adsorption of CO onto a Pd\(110\) surface](#). If you have not performed this tutorial or if you did not save the project files, you must do so before proceeding.

Open the file **(1x1) CO on Pd(110).xsd** in the folder **(1x1) CO on Pd(110)\(1x1) CO on Pd (1 1 0) CASTEP GeomOpt**.

2. To define fragments

To compute the fragment density difference you must first define the fragments. You will do this using the *Edit Sets* option. Begin by creating a set containing the carbon and oxygen atoms.

Select **Edit | Edit Sets** from the menu bar to open the Edit Sets dialog.

Click on the **carbon** atom to select it. Hold down the **SHIFT** key and click on the **oxygen** atom.

On the Edit Sets dialog, click the **New...** button to open the **Define New Set** dialog. Enter the name **CO DensityDifference**, click the **OK** button and close the dialog.

Tip: In order for CASTEP to recognize the set as a fragment for charge density difference calculations, the name must contain the text string *DensityDifference*.

Notice that in the model **(1x1) CO on Pd (1 1 0).xsd** the CO molecule is now highlighted and labeled using the name you gave the set. You do not have to define the Pd surface as set since CASTEP automatically assumes that the remaining atoms are to be subtracted when computing the electron density difference.

Atoms belonging to a set are displayed with a mesh around them. You can hide the mesh as follows.

Click on the mesh to select the set. Select **View | Explorers | Properties Explorer** from the menu bar.

In the **Properties Explorer**, set the value of the **Filter** to **Set**.

The list of properties for *Set* includes **IsVisible**.

Edit **IsVisible** property: select **No** to remove display of the set.

The set is no longer highlighted with the mesh.

Tip: In order to remove the label *CO DensityDifference*, select it with the mouse and press the **DELETE** key.

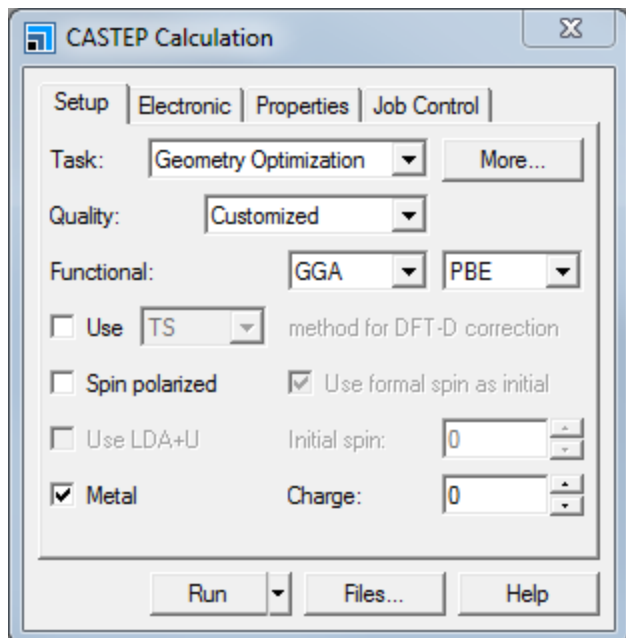
Finally, before you can start the calculation, you must reset the symmetry of the structure to P1.

Select **Build | Symmetry | Make P1** from the menu bar.

3. To run the calculation

Double-click on the **(1x1) CO on Pd(110) Calculation** file in the **(1x1) CO on Pd(110)\(1x1) CO on Pd (1 1 0) CASTEP GeomOpt** folder.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

Since you have already run a geometry optimization on the system, you only need to perform a single point energy calculation in order to obtain the density differences.

Change the **Task** to **Energy**.

On the **Properties** tab select the **Electron density difference** and select the **Both atomic densities and sets of atoms** radio button. Ensure that you uncheck any other properties.

Click the **Run** button.

The job is submitted and begins to run. You should wait for it to complete before proceeding to the [next section](#).

When the job has finished, you should save the project.

Select **File | Save Project** from the menu bar.

4. To display the fragment density difference

When the calculation finishes, you can display the charge density difference. Begin by closing all the open windows.

Select **Window | Close All** from the menu bar.

Now open the output structure for the job you just ran.

Open the document **(1x1) CO on Pd (1 1 0).xsd** in the folder **(1x1) CO on Pd (1 1 0) CASTEP Energy**.

Click the **CASTEP** button  on the **Modules** toolbar and select **Analysis**.

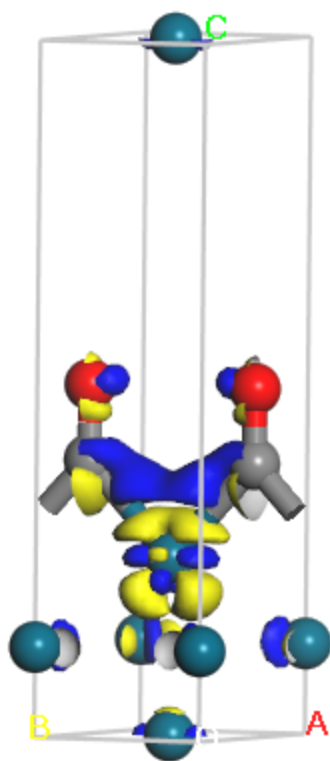
Select the **Electron density difference** option, check the **View isosurface on import** checkbox and uncheck the **Use atomic densities** checkbox. Click the **Import** button.

Tip: When you select *Use atomic densities* the density difference is computed with respect to atoms. When it is unchecked, the difference is computed with respect to fragments.

This displays an isosurface of the difference density at a value of about 0.1 electrons / Å³. Now you should create a more chemically useful isosurface.

Right-click on the document and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Isosurface** tab set the **Isovalue** to **0.05** and select **+/-** from the **Type** dropdown list.

This procedure displays two isosurfaces together. One is at a value of 0.05 and is colored blue, the other is at -0.05 and is colored yellow. The blue areas show where the electron density has been enriched with respect to the fragments. Conversely, the yellow areas show where the density has been depleted.



Charge density difference for CO Pd (110)


You can gain further insight into the changes in bonding by displaying the density difference as a 2D slice. You can do this using the *Volume Visualization* toolbar.

Select one of the isosurfaces and press the **DELETE** key.

Tip: The visibility of isosurfaces and slices can also be controlled, without deleting, using the Volumetric Selection dialog.


Select **View | Toolbars | Volume Visualization** from the menu bar.

Now use the *Create Slices* tool to create a 2D slice from the data.

Click the **Create Slices** arrow  tool and select **Parallel to B & C Axis** from the dropdown list.

Click on the 2D slice to select it, hold down the **SHIFT** and **ALT** keys and the **right mouse** button to move the slice so that it cuts through the CO molecule.

You now have a 2D slice showing the density difference through the CO molecule. Next you will adjust the data range of the slice and change the color scheme to differentiate more easily between regions of electron depletion and electron enrichment.

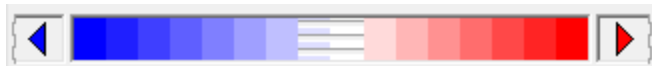
Select the slice. Click the **Color Maps** button  on the **Volume Visualization** toolbar to open the Color Maps dialog.

Change the **Spectrum** to **Blue-White-Red**, set **From** to **-0.2** and **To** to **0.2**, and set the value of **Bands** to **16**.

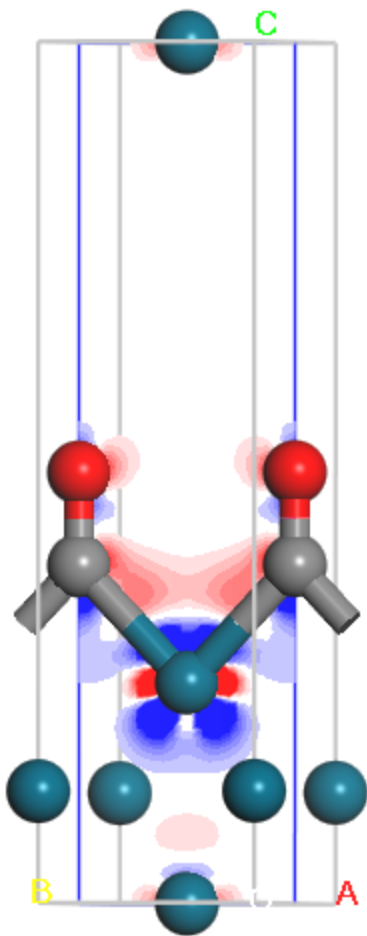
Each of the 16 colors represents a specific range of the charge density. In this plot a loss of electrons is indicated in blue, while electron enrichment is indicated in red. White indicates regions with very little change in the electron density. You can see the red and blue areas more clearly if you hide the white areas.

Click on the two colors in the center of the **selector** on the Color Maps dialog.

The *selector* should now look like this:



The final image should resemble the one shown here:



2D charge density difference for CO Pd (110)

Based on this, which atoms have lost electron density? Can you tell which orbitals lost electrons? Which orbitals on which atoms gained electrons? Does this match your expectations for carbon-metal bonding?

If you are interested you could repeat this section of the tutorial using the atomic density difference rather than the fragment density difference. Simply make sure that you check *Use atomic densities* when you import the density difference.

This is the end of the tutorial.

Simulating the STM profile of CO on Pd(110)

Purpose: Demonstrates the use of CASTEP for simulating the transmission microscope (STM) profile of a system.

Modules: Materials Visualizer, CASTEP

Time: 🕒

Prerequisites: [Adsorption of CO onto a Pd\(110\) surface](#)

Background

The scanning transmission microscope (STM) provides an image of a material, but it can also be used to provide quantitative information at the atomic scale. The ability to simulate the STM image therefore provides a way to compare computed results with experiment.

CASTEP models the STM profile by representing it as an isosurface of the electron density generated only by states at a certain energy away from the Fermi level. The distance from the Fermi level corresponds to the applied bias in STM experiments: positive bias corresponds to empty (conduction) states and negative bias to occupied (valence) states. This approach neglects the actual geometry of the STM tip.

STM profile visualization makes sense only for models that represent surfaces in the slab supercell geometry. In addition, information about charge density at a distance from the surface is likely to be inaccurate as a result of DFT failing to reproduce the asymptotics of the wavefunction decay into a vacuum.

Introduction

In this tutorial, you will use CASTEP to simulate the STM profile of a CO molecule adsorbed onto a Pd (110) surface. The aim of the tutorial is to check whether STM is likely to confirm that the 2x1 structure found in the tutorial "Adsorption of CO onto a Pd(110) surface" is more stable or whether there will be little difference observed between the 1x1 and 2x1 systems. You will make use of results obtained [previously](#) for this system.

This tutorial covers:

- [Getting started](#)
- [To run the calculation](#)
- [To create an STM isosurface](#)
- [To add extra information to the STM isosurface](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by opening the Materials Studio project that you created for the tutorial [Adsorption of CO onto a Pd\(110\) surface](#). If you have not performed this tutorial or if you did not save the project files, you must do so before proceeding.

Select **File | Open Project...** from the menu bar to open the Open Project dialog. Navigate to the **CO_on_Pd.stp** project and click the **Open** button.

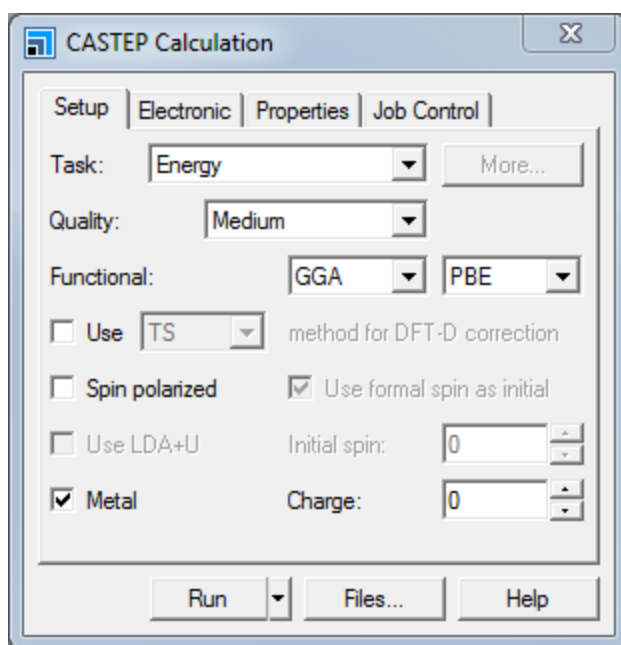
You will use the Pd(1 1 0) surface with CO adsorbed for this calculation.

Open the file **(1x1) CO on Pd(110).xsd** in the **(1x1) CO on Pd(110)\(1x1) CO on Pd (110) CASTEP GeomOpt** folder.

2. To run the calculation

Click the **CASTEP** button  on the **Modules** toolbar then select **Calculation** or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

Since you have already run a geometry optimization on the system, you only need to perform a single point energy calculation in order to obtain the orbitals.

Change the **Task** to **Energy**.

On the **Properties** tab check the **Orbitals** checkbox and ensure that you **uncheck** any other properties.

On the **Electronic** tab click the **More...** button to open the CASTEP Electronic Options dialog. On the **k-points** tab ensure that the **Custom grid parameters** radio button is selected and that the **Grid parameters** fields are set as **a** to **3**, **b** to **4** and **c** to **1**.

Click the **Run** button.

The job is submitted and begins to run.

Repeat the same procedure for the optimized 2x1 structure in **(2x1) CO on Pd(110).xsd** located in the **(2x1) CO on Pd(110)** folder, making sure that the k-points Grid parameters are set as **a** to **2**, **b** to **3** and **c** to **1**.

Click the **Run** button on the CASTEP Calculation dialog and close both dialogs.

When the job has finished, you should save the project.

Select **File | Save Project** from the menu bar.

3. To create an STM isosurface

When the calculation finishes, you can display the charge density difference. Begin by closing all the open windows.

Select **Window | Close All** from the menu bar.

Now open the output structure for the (1x1) and (2x1) calculations side by side.

Open **(1x1) CO on Pd (110).xsd** in the **(1x1) CO on Pd (110) CASTEP Energy** folder. Also open **(2x1) CO on Pd(110).xsd** in the **(2x1) CO on Pd (110) CASTEP Energy** folder. Select **Window | Tile Vertically** from the menu bar.

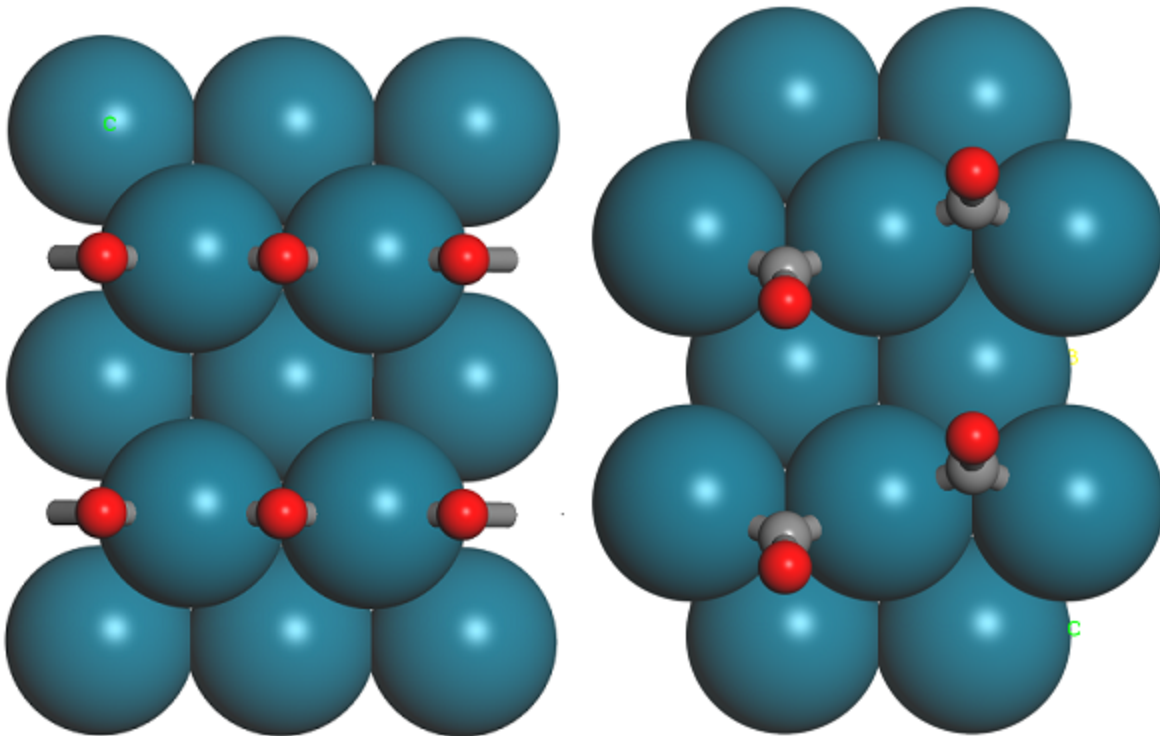
Make **(1x1) CO on Pd (110).xsd** the active document and open the **Display Style** dialog. On the **Lattice** tab set the **Max.** value of the range in the **A** direction to **2.00**, in the **B** direction to **2.00**, and in the **C** direction to **0.90**. Select the **(2x1) CO on Pd(110).xsd** document and change the **Max.** ranges to **2.00** in the **B** direction and **0.90** in the **C** direction.

To better differentiate between surface and adsorbate, you may want to change the Atom display style of all Pd atoms.

For each document, select one atom of each Pd layer. On the **Atom** tab of the **Display Style** dialog, select the **CPK** radio button and change the **CPK** scale to **0.9**. Close the Display Style dialog.

Orient both structures such that the (110) surface rows are facing the same way.

The models should look similar to the images below.




1 × 1 and 1 × 2 supercells of CO on Pd(110)

Take a note of the z-coordinate of the oxygen atoms in either case, they should be approximately 5.4 and 5.3 Å.

4. To add extra information to the STM isosurface


Now you will import the volumetric information into the two structure documents.

Click the **CASTEP** button  on the toolbar, then select **Analysis** from the dropdown list to open the CASTEP Analysis dialog. Select **STM profile** from the list.

Open **(1x1) CO on Pd (110).castep** and ensure this is listed as the **Results file**. Set the value of **STM bias** to **1.0** and uncheck the **View isosurface on import** checkbox. Make **(1x1) CO on Pd (110).xsd** the active document and click the **Import** button.

Repeat this for the **(2x1) CO on Pd (110).castep** output document and the **(2x1) CO on Pd (110).xsd** structure. Close the CASTEP Analysis dialog.

The next step will be to create simulated images to model STM experiments in the *constant height mode* for our two structures. This can be achieved by displaying slices through our simulated STM volumetric information.



On the **Volume Visualization** toolbar, click arrow for the **Slice** button  and select **Parallel to A & B axis**. Repeat for the other document.

This procedure creates a volume slice that will become our STM images. Scanning tunneling microscopy is usually done well above the actual atoms in any experiment and relies on tunneling. To mimic this setup in our simulation, we have to set our slice relatively high above the oxygen atoms, but also well away from the bottom periodic images of the Pd atoms. A value of 1.0 Å above the O atoms is a good compromise, as long as we remember to compare like with like and set the same value for both simulations.

Select the **Slice**. In the **Properties Explorer**, double-click on the **Slice Position** property and change the **Z** value to 6.4. Repeat for the other document.

Note: For high-quality STM simulations in research problems, you will have to go at least 3 Å higher above the highest atom and use an accordingly large unit cell height. To achieve a reasonable resolution of your simulations, you may have to significantly increase the plane wave cut

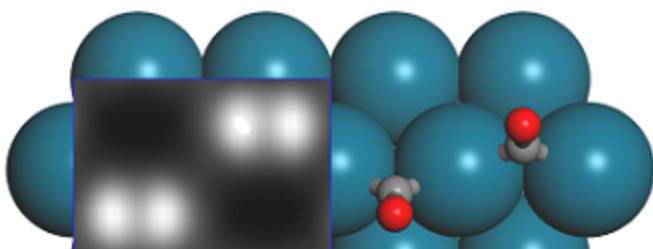
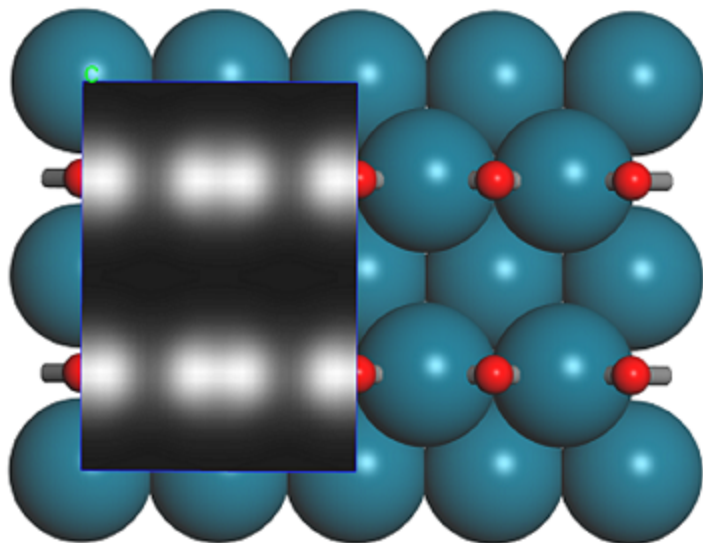
We now have to adjust the color scale to show the relevant information.

Select the **Slice** and click the **Color Maps** button . Use the **right-arrow**  buttons to set the **From** and **To** values to the **SliceMappedMin** and **SliceMappedMax** values shown in the Properties Explorer respectively. Change the **Spectrum** to **Black-White** and set **Bands** to **128**.

Repeat this for the other document and close the Color Maps dialog.

Note: In complex simulations, an estimate of the relative brightness for different adsorbates may be obtained if the color scales are identical. However, this only works if all the settings in all calculations are absolutely identical.

You may want to change the representation such that a part of the periodic surface is not covered by the slices. Your final results should look similar to this:



1×1 and 1×2 Supercells of CO on Pd(110) with simulated STM profile. The calculated volume slice on the left side of each image corresponds to the predicted STM contrast, while the extended supercell shows the location of the atoms underneath the STM image.

According to this simulation, it should be very easy to distinguish between the 1×1 and 2×1 structures of CO adsorbed on Pd(110) in an STM simulation. The shape of the STM image suggests that the contrast is mainly due to the π -orbitals of the CO molecule, which are aligned in the 1×1 supercell, but offset in the 2×1 structure. The volume slice is constructed from the density due only to orbitals corresponding to the bias, that is, those about 1 eV above the Fermi level. The color corresponds to the total density of states, with the white regions corresponding to the highest DOS.

This is the end of the tutorial.

Predicting the core level spectra of BN from first principles

Purpose: Introduces the core level spectroscopy feature in CASTEP.

Modules: Materials Visualizer, CASTEP

Time: 🕒 🕒

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Density functional theory provides a robust and reliable framework for calculations of core-level spectra. This technique has been applied to numerous systems with good results (Gao et al., [2008](#)). DFT as a method is somewhat limited, and recent developments in core-level spectroscopy calculations using the Bethe-Salpeter equation or time-dependent DFT (or a combination of the two) provide more rigorous approaches for a core level spectrum calculation. In these methods many-body effects, such as the broadening of spectra due to electron-hole lifetime, can be taken into account. While good agreement with experimental results has been achieved, this necessarily comes with a much greater computational burden in comparison to standard ground state DFT calculations.

A systematic observation of core hole effects and a quantitative estimation of the core hole strength in materials can assist in the simulation and interpretation of core level spectra. Applying empirical rules, a core-level spectrum is not likely to be heavily influenced by core-hole effects, so information on the ground electronic structure of a material can be inferred directly from the experimental spectrum. In this case, traditional ground state calculations should predict the main features of experimental results and allow interpretation of the spectrum. If this is not the case, inclusion of the influence of the core hole is essential in the theoretical simulation. Analysis of experimental results should take into account that near-edge fine structure includes influences in the core excitation processes beyond the ground state electronic structure.

For a more general discussion of the core level spectroscopy and details of its implementation see [S.-P. Gao et al., 2008](#) and references.

Introduction

CASTEP can calculate spectroscopic properties of solids that are due to electronic transitions from a core level of an ion to the conduction band (X-ray absorption) and from the valence band to a core level (X-ray emission). This can be used to describe a wide variety of experimental results connected to such processes. Core holes can be created by X-ray or electron incident radiation.

The core level is localized, so core level spectroscopy provides a detailed element-specific picture of the local electronic structure around a given atomic site. There is no contribution from the other atoms in the system, so the electronic states for a specific atom can be investigated.

In the case of anisotropic systems angular-dependent experiments enable the separation of states with different symmetries for the involved orbitals. An important consequence is that symmetry states which result solely from chemical bonding can be studied. For further information see the core level spectroscopy theory topic.

This tutorial illustrates how CASTEP can be used to determine the core level spectra of a material in Materials Studio using quantum mechanical methods. You will learn how to build a crystal structure and set up a CASTEP energy calculation, followed by core-hole spectroscopy calculations and then analyze the results.

This tutorial covers:

- [Getting started](#)
- [To set up and run a CASTEP calculation](#)
- [To set up the core holes](#)
- [To set and run a CASTEP calculation with core holes](#)
- [To analyze the results](#)
- [To compare the results with experimental data](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **BN** as the project name, click the **OK** button.

The new project is created with *BN* listed in the Project Explorer. Now you will import the BN structure for your calculation.

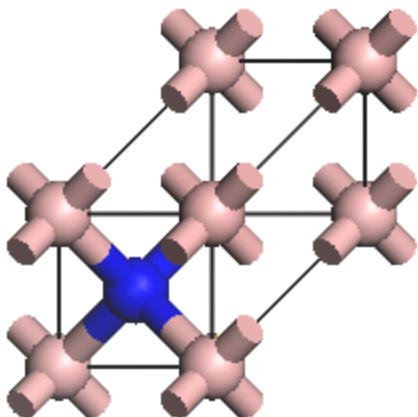
Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to the folder **Structures/semiconductors/** and select **BN.msi**. Click the **Open** button.

The crystal structure in the 3D Viewer is the conventional unit cell containing 8 atoms, which shows the cubic symmetry of the lattice. CASTEP uses the full symmetry of the lattice if any exists, so the primitive lattice, containing 2 atoms per unit cell, can be used. The charge density, bond distances, and total energy per atom will be the same no matter how the unit cell is defined, so by using fewer atoms in the unit cell, the computation time is decreased.

Note: The only time that care is needed is when a spin-polarized calculation is performed on a magnetic system, where the charge density spin wave has a period which is a multiple of the primitive unit cell.


Choose **Build | Symmetry | Primitive Cell** from the menu bar.

The 3D Viewer displays the primitive cell.

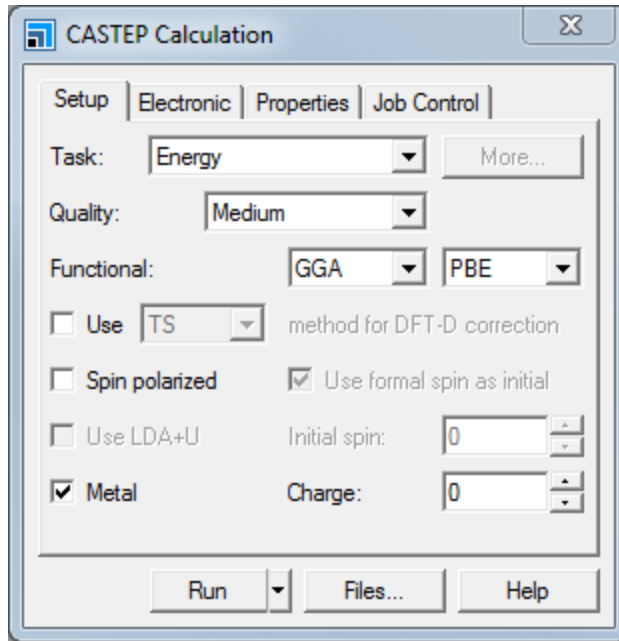


BN primitive cell

2. To set up and run a CASTEP calculation

Click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

On the **Setup** tab of the CASTEP Calculation dialog, ensure the **Task** is set to **Energy** and the **Quality** is set to **Medium**.

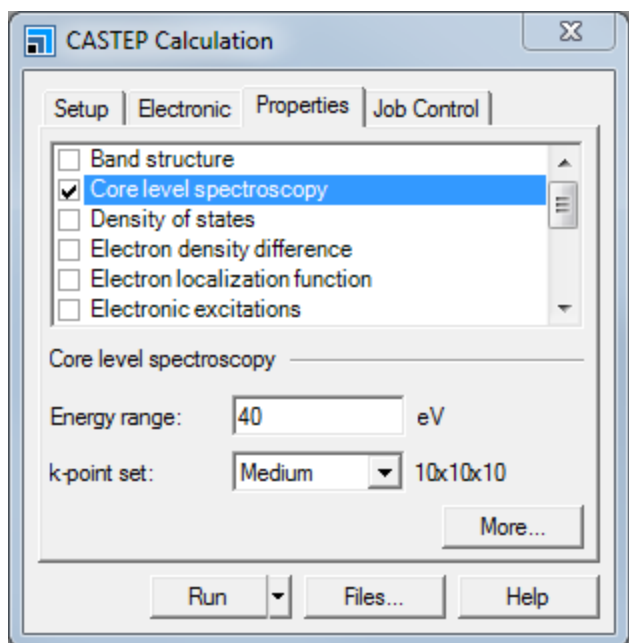
If you change the quality, the other parameters change to reflect this. Next, you will specify the electronic options for the calculation.

On the **Electronic** tab, select **OTFG ultrasoft** from the **Pseudopotentials** dropdown list.

On the fly (OTFG) pseudopotentials are required to compute the core level spectra. If you choose a different type of pseudopotential, the core level spectroscopy calculation cannot be performed.

Next, you will specify which properties you want to calculate.

On the **Properties** tab, check the **Core level spectroscopy** checkbox and set the **Energy range** to **40 eV**.



CASTEP Calculation dialog, Properties tab

An energy range of 40 eV for the core level spectroscopy will allow access to energies up to 40 eV above the Fermi level.

On the **Job Control** tab click the **More...** button to open the CASTEP Job Control Options dialog. Change the **Update interval** to **30.0 s** and close the dialog.

If you wish to run the calculation on a remote server, you can specify this on the Job Control tab.

Click the **Run** button and close the dialog.

After a few seconds, a new folder is displayed in the Project Explorer and this will contain all the results from the calculation. The Job Explorer is displayed, which contains information about the status of the job.

When the job finishes, the files are transferred back to the client and this can take some time due to the size of certain files. When the results are transferred, you should have several documents, among them:

- BN.xsd - the crystal structure
- BN.castep - an output file from the CASTEP energy calculation
- BN_EELS.castep - an output file from the CASTEP core level spectroscopy calculation
- BN.param and BN_EELS.param - input information, saving the input files before proceeding with the calculation creates these files and gives you the opportunity to edit them

You will find these files in the Project Explorer in a folder called BN CASTEP Energy once the calculation completes.

3. To set up the core holes

To simulate core hole effects you should create a supercell of sufficiently large size, so that artificial interactions between periodic images of the atoms containing core holes are reduced. However, large supercells are very computationally expensive, so a supercell of 32 atoms (6 Å) is used to strike a balance in this tutorial.

Note: For investigative experiments, where greater computational resources are available, larger supercells should be used in order to obtain more accurate results.

Now you will construct a supercell from the primitive cell by redefining the extent of the lattice.

Make **BN.xsd** in the project root the active document.

Select **Build | Symmetry | Redefine Lattice** from the menu bar to open the Redefine Lattice dialog. Enter **-3 1 1** for **A**, **-1 -1 3** for **B**, and **1 1 1** for **C**. Click the **Redefine** button and close the dialog.

Select **File | Save As...** from the menu bar and save the 3D Atomistic document as **BN_N_hole.xsd**. Repeat this to save the document as **BN_B_hole.xsd**.

Choose **Window | Close All** from the menu bar, then double-click on **BN_N_hole.xsd** in the Project Explorer.

You will create a core hole on a nitrogen atom and ensure that the symmetry is properly imposed.

Select any **N** atom in the supercell.

Select **Modify | Electronic Configuration** from the menu bar to open the Electronic Configuration dialog. On the **Core Hole** tab select **1s** from the **Shell** dropdown list and close the dialog.

Choose **Build | Symmetry | Find Symmetry...** from the menu bar to open the Find Symmetry dialog. On the **Options** tab check the **CoreShellWithHole** from the list of properties. On the **Find** tab click the **Find Symmetry** button, then the **Impose Symmetry** button. Close the dialog.

Now you should create a core hole on a boron atom and ensure that the symmetry is properly specified.

Repeat these steps for **BN_B_hole.xsd**.

Select **File | Save Project** from the menu bar.

4. To set up and run a CASTEP calculation with core holes

You will repeat the previous CASTEP energy calculation determining the core level spectra, but this time taking account of the B and N core holes.

Make **BN_N_hole.xsd** the active document.

Open the **CASTEP Calculation** dialog, on the **Electronic** tab check the **Use core hole** checkbox.

Click the **Run** button, click the **Yes** button to convert to a primitive cell and close the CASTEP Calculation dialog.

This is a rather time consuming job, depending on the machine each calculation may take several hours. When the job finishes, the files are transferred back to the client.

Make **BN_B_hole.xsd** the active document and click the **Run** button on the CASTEP Calculation dialog again.

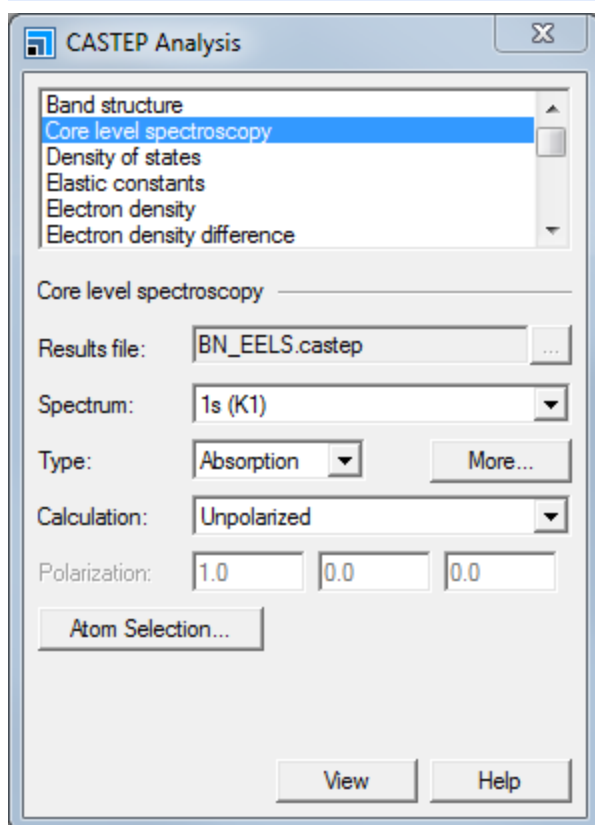
Choose **File | Save Project** from the menu bar, followed by **Window | Close All**.

5. To analyze the results

Now you can analyze and visualize the results of the CASTEP calculation.

Make **BN CASTEP Energy/BN.xsd** the active document and select the **N** atom.

Choose **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog.



CASTEP Analysis dialog, Core level spectroscopy selection

Select **Core level spectroscopy** and ensure that **BN_EELS.castep** is the specified **Results file**. Select **1s (K1)** from the **Spectrum** dropdown list and choose **Absorption** for the **Type**. Click the **More...** button to open the CASTEP EELS Analysis Options dialog. Set the **Instrumental smearing** to **0.8 eV** and close the dialog.

The 1s[K1] spectrum corresponds to the core level spectrum for a core electron in the 1s orbital. An absorption spectrum simulates the required energy absorbed during the creation of the core hole; an emission spectrum would reflect the energy of an X-ray photon emitted during relaxation of the core hole back to the ground state. The smearing applied by CASTEP is a Gaussian broadening of the calculated results. The value used in this tutorial is selected to correspond to the resolution of the

experimental spectra (Jaouen et al., 1995). For a cubic system, such as BN, both polarized and unpolarized incident radiation will produce the same core level spectrum.

Click the **View** button.

A new core level spectrum for nitrogen in BN is displayed in a chart viewer. Now create the equivalent spectrum for boron.

Select any **B** atom in **BN CASTEP Energy/BN.xsd** and, on the CASTEP Analysis dialog, click the **View** button.

The core level spectrum for boron in BN is displayed. The B and N core level spectra taking into account a 1s core hole can also be created. To ensure that the core hole is used you need to select the correct atom.

Make **BN_N_hole CASTEP Energy/BN_N_hole.xsd** the active document.

Click the **Atom Selection...** button on the CASTEP Analysis dialog to open the Atom Selection dialog. Choose **Contains Core Hole** from the **Select by Property** dropdown list and click the **Select** button.

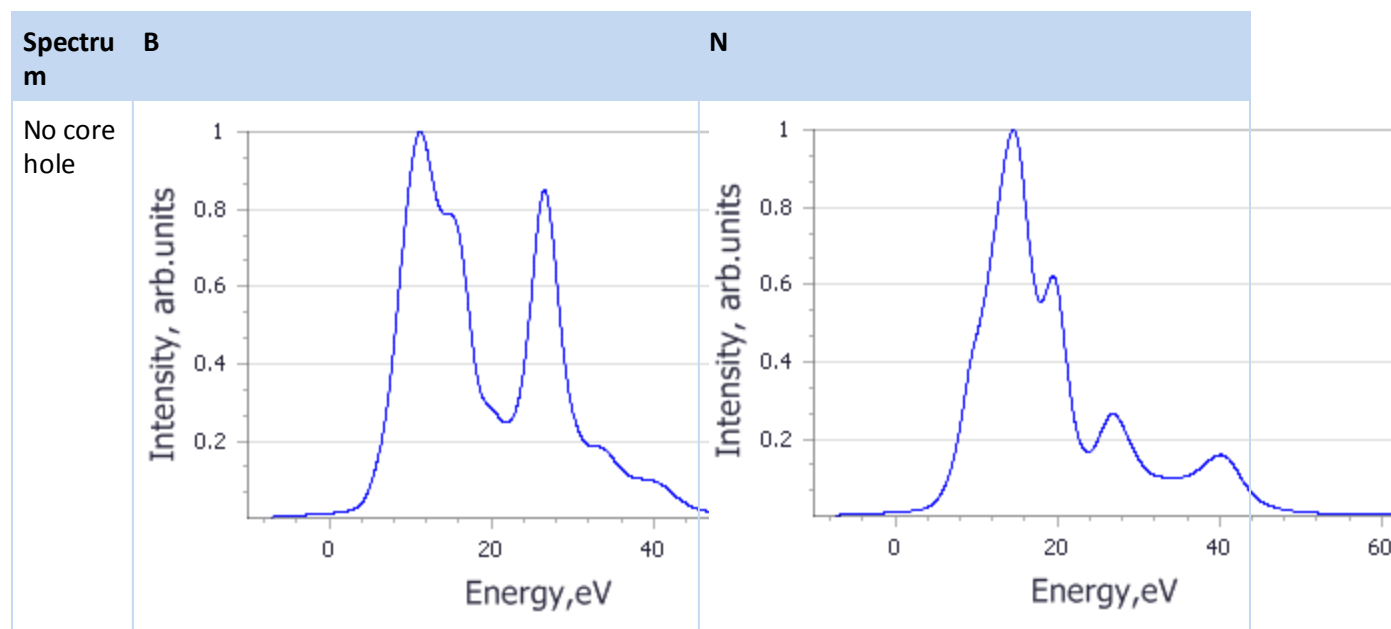
You can now view the core level spectrum for the nitrogen atom with the 1s core hole.

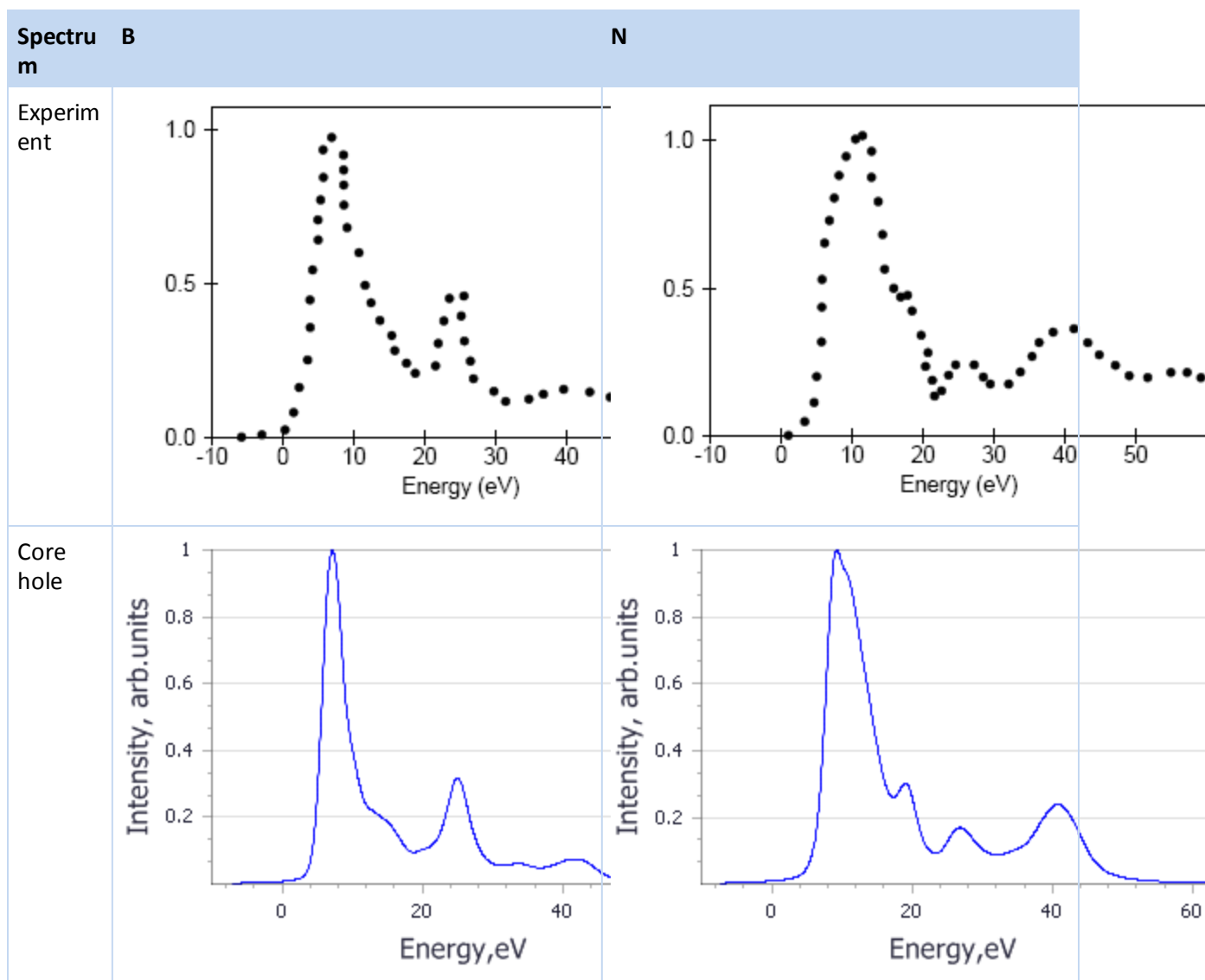
On the CASTEP Analysis dialog, click the **View** button.

Repeat the core hole atom selection and CASTEP analysis for **BN_B_hole CASTEP Energy/BN_B_hole.xsd**.

6. To compare the results with experimental data

Analysis of the core level spectroscopy properties of BN with and without consideration of a core hole effects has provided you with four spectra, which can be compared with experimentally collected data (Jaouen et al., 1995).





This is the end of the tutorial.

References

Gao, S-P.; Pickard, C.J.; Payne, M.C.; Zhu, J.; Yuan, J. "Theory of core-hole effects in 1s core-level spectroscopy of the first-row elements", *Phys. Rev. B*, **77**, 115122 (2008).

Jaouen et al., *Microsc. Microanal. Microstruct.*, **6**, 127 (1995)

CCDC tutorials

The following tutorials illustrate how to utilize CCDC's capabilities.

- [Using the CSD together with Materials Studio](#)
- [Crystal identification using CCDC and experimental powder diffraction](#)
- [Analyzing hydrogen bonds in potential polymorphs of hydantoin](#)

Using the CSD together with Materials Studio

Purpose: Illustrates the use of Materials Studio in conjunction with the CSD.

Modules: Materials Visualizer, Polymorph, VAMP, Forcite, COMPASS

Time: 🕒 🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Introduction

The Cambridge Structural Database (CSD) is a repository of small molecule crystal structures. It is the principal product of the Cambridge Crystallographic Data Centre (CCDC; <http://www.ccdc.cam.ac.uk>). The CSD records bibliographic, chemical, and crystallographic information for organic molecules and metal-organic compounds.

This tutorial illustrates how information from the CSD can be used to add value to results from Materials Studio calculations. Polymorphs of a small molecule compound are predicted and subsequently compared to known crystal structures of this compound that are registered in the CSD.

Note: This tutorial requires a license for the CSD.

Note: The results described in this tutorial were obtained using CCDC v.5.31, 2010 Release. If you have a different version of CCDC you may observe numerically different results.

This tutorial covers:

- [Getting started](#)
- [To sketch and optimize the structure](#)
- [To predict polymorphs and identify known experimental structures](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

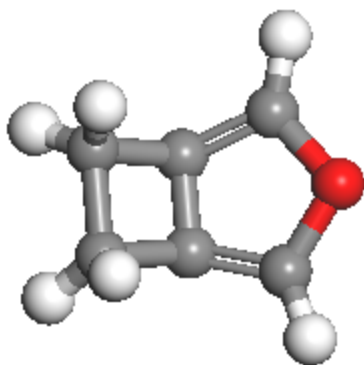
Open the **New Project** dialog and enter **CSD** as the project name, click the **OK** button.

The new project is created with *CSD* listed in the Project Explorer.

2. To sketch and optimize the structure

In this tutorial you will use Polymorph to generate a list of potential polymorphs of 3-oxabicyclo(3.2.0) hepta-1,4-diene (OHD) in the P 21/c space-group. Then you will verify that one of the low energy packing arrangements indeed corresponds to an experimentally known crystal structure.

In the Project Explorer, right-click on **CSD** and select **New | 3D Atomistic Document**. Change the name of the new structure document to **OHD-mol**. Use the Sketch tools to sketch an OHD molecule shown below.



Molecular structure of OHD

Next, you will optimize the molecule using VAMP.

Select **Modules | VAMP | Calculation** from the menu bar to open the VAMP Calculation dialog. On the **Setup** tab, change the **Task** to **Geometry Optimization**. Click the **Run** button and close the dialog.

When the calculation has finished, save the project and close all windows.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To predict polymorphs and identify known experimental structures

Now you will set up the Polymorph prediction calculation.

In the Project explorer, open **OHD-mol VAMP GeomOpt/OHD-mol.xsd**. Select **Modules | Polymorph | Calculation** from the menu bar to open the Polymorph Calculation dialog. On the **Setup** tab click the **Assign** button to make the OHD molecule a motion group.

Check that the **Task** is set to **Prediction** and click the **More...** button to open the Polymorph Prediction dialog. Check both the **Clustering** checkboxes and close the dialog.

Pre-clustering steps will be included in the prediction sequence both before and after the geometry optimization stage. Clustering before the geometry optimization means that fewer minimizations will be performed and the calculation will be less time consuming.

On the **Energy** tab of the Polymorph Calculation dialog, change the **Forcefield** to **COMPASS**. On the **Space Groups** tab deselect all space groups except for **P 21/C**. Click the **Run** button and close the dialog.

While the calculation is running you can query the CSD against the OHD-mol structure you sketched earlier. First, close all windows.

Select **File | Save Project** from the menu bar followed by **Window | Close All**.

Open the OHD-mol.xsd document you created earlier.

Select **Build | Bonds** and select **Convert representation to Kekule**. Click **Calculate** then close the dialog.

In the Project Explorer, double-click on the **OHD-mol.xsd** document in the root of the project.

Select **Modules | CCDC | ConQuest Search** from the menu bar to open the ConQuest Search dialog.

On the **Setup** tab, change the **Task** to **Substructure search** and click the **Search** button and close the dialog.

The results are returned in a study table named OHD-mol.std. You should have retrieved two structures, one in the Pbc_a and one in the P 21/c space group. Now you will extract the P 21/c structure from the study table and optimize this structure using the same forcefield as used in the polymorph prediction sequence. This is useful to account for slight deviations between experimental and predicted lattice and structural parameters.

In the OHD-mol.std study table, in the **Structures** column double-click on the entry in the row that corresponds to the **P 21/c** space group.

This opens a 3D representation of the structure in a *Detail View*. To save the structure you will have to copy and paste it into a new 3D Atomistic document.

Ensure that **OHD-mol Detail View** is the active document, press **CTRL+ C**. In the Project Explorer, right-click on the project root and select **New | 3D Atomistic Document** and press **CTRL + V**. Select **File | Save As...** from the menu bar to open the Save As dialog. Type **OHD P21c** as the filename and click the **Save** button.

Now you will use Forcite to optimize this structure.


Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog. On the **Setup** tab, change the **Task** to **Geometry Optimization** and click the **More...** button to open the Forcite Geometry Optimization dialog. Check the **Optimize cell** checkbox and **close** the dialog.

On the **Energy** tab, change the **Forcefield** to **COMPASS**. Make sure that both **Electrostatic** and **van der Waals** in the **Summation method** section are set to **Ewald**. Click the **Run** button and close the dialog.

Once the Polymorph calculation finishes, you will collect the results of the run into a study table using the analysis tool of Polymorph.

In the Project Explorer, navigate to **OHD-mol VAMP GeomOpt/OHD-mol PMP Predict**. Select **Modules | Polymorph | Analysis** from the menu bar. Select **OHD-mol P21-C.xtd** on the Insert Polymorph Results File dialog and click the **Open** button.

A study table called `Polymorph Analysis.std` is created, containing the polymorphs.

Select column **A** containing the structures and click the **Models** button  on the **QSAR Models** toolbar. Select **Crystal Similarity Measure** from the **Models** dialog and double-click on this model to open the Model Editor - Crystal Similarity Measure dialog.


On the **Inputs** tab click on the cell for **Value** in the **Reference crystal** row, select **OHD P21c Forcite GeomOpt/OHD P21c.xsd** from the dropdown list. Click the **Save** button and close the dialog.

On the **Models** dialog make sure **Crystal similarity** is still selected, click the **Run** button and close the dialog.

When the calculation has finished a new column labeled *Crystal Similarity Measure* is added to the study table. Within a range of 0.2–0.3 kcal/mol from the lowest energy structure proposed by the Polymorph prediction sequence, you should find one or more equivalent structures with a crystal similarity score of about 0.1.

Tip: If there is no structure within 0.3 kcal/mol of the lowest energy with a similarity of 0.1, you should rerun the Polymorph prediction steps. Polymorph prediction is a random process, so you may have to run the prediction sequence more than once to ensure all potential crystal structures are found.

You should also sort the results according to the crystal similarity measure, in order to confirm that there are no other structures even closer to the experimental structure.

In the study table select the column labeled **Crystal Similarity Measure**. Click the **Sort Ascending** button  on the **Study Table Viewer** toolbar.

You should see that the second lowest energy structure has by far the lowest crystal similarity score. You can further verify that the predicted structure is equivalent to the experimental structure by generating simulated powder X-ray diffraction patterns using the Reflex module or visually inspecting the packing motifs and cell volumina.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Crystal identification using CCDC and experimental powder diffraction

Purpose: Illustrates the use of Materials Studio in conjunction with the CSD.

Modules: Materials Visualizer, Reflex, QSAR

Time: 🕒 🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Introduction

The Cambridge Structural Database (CSD) is a repository of small molecule crystal structures. It is the principal product of the Cambridge Crystallographic Data Centre (CCDC; <http://www.ccdc.cam.ac.uk>). The CSD records bibliographic, chemical, and crystallographic information for organic molecules and metal-organic compounds.

This tutorial illustrates how information from the CSD can be used to add value to results from Materials Studio calculations. An experimental powder X-ray spectrum is compared to automatically generated spectra from compounds registered in the CSD that contain the chemical name of the experimental structure.

Note: This tutorial requires a license for the CSD.

Note: The results described in this tutorial were obtained using CCDC v.5.31, 2010 Release. If you have a different version of CCDC you may observe numerically different results.

This tutorial covers:

- [Getting started](#)
- [To search the ConQuest database](#)
- [To compare an experimental powder X-Ray diffraction pattern to structures available in the CSD](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **crystal_ID** as the project name, click the **OK** button.

The new project is created with *crystal_Id* listed in the Project Explorer.

2. To search the ConQuest database

In this section you will compare an experimental powder X-ray diffraction (PXRD) pattern to structures registered in the CSD using an automatic powder comparison algorithm based on the Reflex module. This allows you to check whether a compound crystallized in a lab corresponds to a known crystalline lattice.

First you will load the experimental spectrum.

Click on the **crystal_ID** project root in the Project Explorer. Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Examples/Reflex/Experimental Data**, select **Chart Files** from the file types dropdown list for the **File name**. Choose **indigo_1.3cam** and click the **Open** button.

The experimental spectrum of a crystalline form of the indigo pigment is loaded. The automatic powder comparison tool is unable to fit background functions. Therefore you will have to subtract a fitted background. You will also have to estimate the full width at half maximum (FWHM) of the peaks as this is later needed as an input.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. On the **Pattern Preparation** tab, change the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document is created, called **indigo_1(Background Removed).xsd**. Zoom in to the first peak at 10.5 and determine the FWHM which is roughly 0.4.

Now you will query the CSD.


Select **Modules | CCDC | ConQuest Search** from the menu bar to open the ConQuest Search dialog.

On the **Setup** tab, change the **Task** to **Chemical name search** and enter **indigo** as the **Chemical name**. Click the **Search** button and close the dialog.

When the search finishes, a study table named **indigo.std** is returned containing the search results.

3. To compare an experimental powder X-Ray diffraction pattern to structures available in the CSD

You will now use the automatic powder comparison model to find the closest match between the experimental PXRD and the structures in the CSD.

Ensure that **indigo.std** is the active document, select the column labeled **Structures**. Click the **Models** button  on the **QSAR Models** toolbar. Double-click the row for **Figure of merit (Powder Comparison)** to edit the input to this model.


On the Model Editor - Powder Comparison dialog select the **Inputs** tab and change the **Value** column for **Experimental data** to **indigo_1(Background Removed).xsd**. Change **Max. 2-Theta** to **80** and **Profile FWHM U** and **Profile FWHM V** to **0**. Set **Profile FWHM W** to **0.16**.

Note: The square-root of the profile parameter W describes the FWHM independent form 2-Theta, while U and V describe its variation across the 2-Theta range.

Change **Profile NA** and **Profile NB** to **0**. Click the **Save** button and close this dialog. Click the **Run** button and close the Model Editor dialog.

When the calculation has finished, three columns are added to the study table, one of them containing R_{wp} factors. You will sort the entries in the study table according to R_{wp} to determine the most likely match between the experimental PXRD and the entries in the CSD.

Ensure that **indigo.std** is the active document, select the column labeled **Rwp (Powder Comparison)**

and click the **Sort Ascending** button  on the **Study Table Viewer** toolbar.

The structure with the lowest R_{wp} (which should be around 32) has the CSD Refcode "INDIGO02". To confirm that this structure actually corresponds to the experimental powder X-ray diffraction pattern you will carry out a full Pawley refinement.

Double-click the icon for **INDIGO02** in the **Structure** column of **indigo.std** to open the Detail View. Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog. On the **Setup** tab change **2-Theta Max** to **80** in the **Range** section.

On the **Exp. Data** tab select the row with **indigo_1.xcd** in the **Document** column and **1** in the **Pattern** column.

On the **Pattern** tab check all boxes in the **Refine** column. On the **Lattice** tab check all boxes in the **Refine** section. On the **Display** tab check the **Display simulation/experiment difference** checkbox and click the **Refine** button. **Close** the Reflex Powder Refinement dialog.

The resulting R_{wp} should be between 9 and 12. You can further lower the R_{wp} by including asymmetry corrections and/or crystalline size effects. But for the purpose of identifying that the experimental structure is indeed the previously registered form, the current R_{wp} value ensures this finding.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Analyzing hydrogen bonds in potential polymorphs of Hydantoin

Purpose: Illustrates how to categorize Polymorph results based on hydrogen bond motifs.

Modules: Materials Visualizer, CCDC, Polymorph (optional), DMol³ (optional)

Time: 🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Polymorphism in crystals of organics molecules poses challenges, as well as opportunities, in solidification applications, pharmaceutical development, and the fine and specialty chemicals industries. Depending on the molecular arrangement, properties such as solubility, bioavailability, and stability can be drastically influenced. One way to characterize and categorize differences in packing is by analyzing the hydrogen bond topologies, or motifs. Figure 1 gives a schematic overview of some of the common types of hydrogen bond motifs.

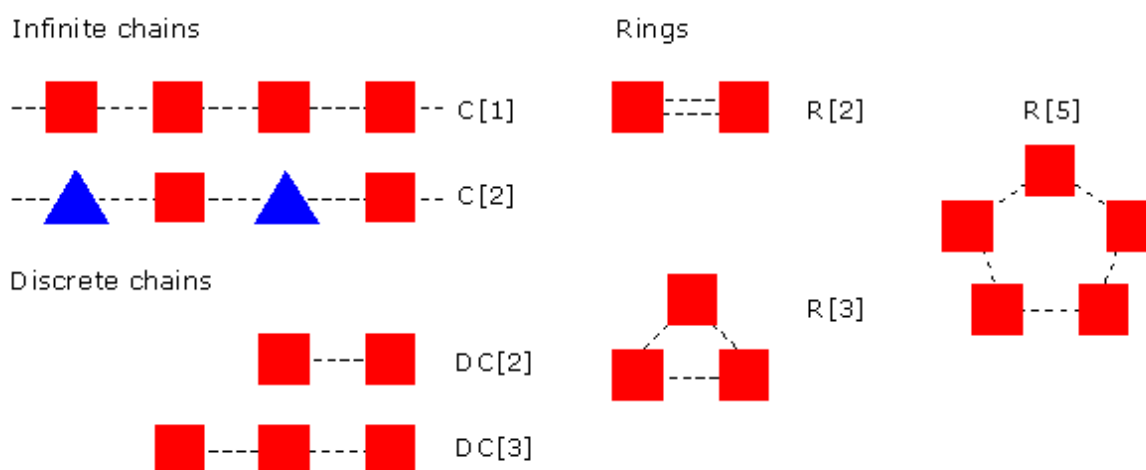


Figure 1. Schematic representation of some common hydrogen bond motifs

Motifs are annotated in Materials Studio as **nM[s]**, where **M** labels the motif type, **n** is the number of motifs of type **M**, and **s** is the size of the motif of type **M**. CCDC distinguishes the following motif types, **M**:

- R = ring
- C = infinite chain
- DC = discrete chain
- S = intramolecular contact
- M = intermolecular contact

This tutorial discusses the basic steps needed to generate motif information from Polymorph calculations. First, the molecule is characterized in terms of functional groups that represent key features of the molecular architecture. Next, hydrogen bond donors and acceptors are assigned within these functional groups. When the molecule has been prepared for analysis, the CCDC module queries

the CSD for compounds containing the defined functional groups. The resulting matches are analyzed in terms of their motif information. Finally, a scoring step analyses the results of a Polymorph calculation and compares the motif information of each suggested polymorph against the results of the CSD query.

Note: Motif makes use of CCDC's CSD ([Allen et al., 2002](#)) and Mercury ([McRae et al., 2006](#)) functionality. These tools are directly available from the CCDC.

Introduction

Hydantoin was one of the molecules used in the third CCDC blind test for polymorph prediction ([Day et al., 2005](#)). When Polymorph is used to predict the packing of hydantoin, the experimentally observed crystal structure is predicted along with two additional structures with lower lattice energies. In this tutorial you will use the CCDC Motif Search to generate a statistical measure of how close the predicted hydrogen bond motifs are to the known structure.

This tutorial covers:

- [Getting started](#)
- [To sketch the molecular structure of hydantoin](#)
- [To prepare the structure and define functional groups and donor/acceptor sites](#)
- [To query the CSD for related structures](#)
- [To assign motif information to Polymorph output and score the top ranked Polymorph structures](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.


1. Getting started

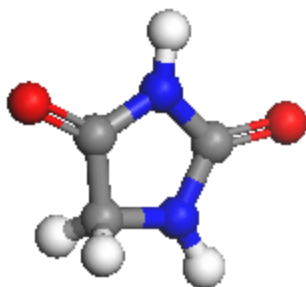
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **hydantoin** as the project name, click the **OK** button.

The new project is created with *hydantoin* listed in the Project Explorer.

2. To sketch the molecular structure of hydantoin


In the Project Explorer, right-click on the project root and select **New | 3D Atomistic Document**. Change the name of the new structure document to **hydantoin-mol**. Use the Sketch tools to sketch a hydantoin molecule (shown below) and clean the structure by clicking the **Clean** button .

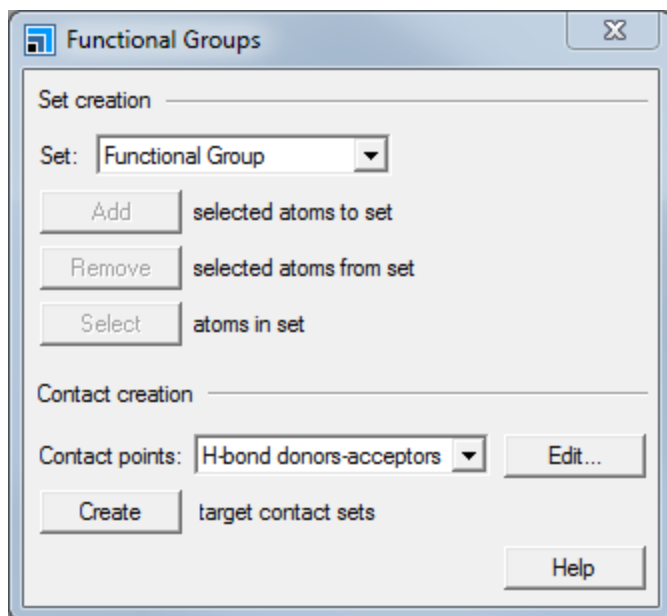


Molecular structure of hydantoin

3. To prepare the structure and define functional groups and donor/acceptor sites

In this section you will use the *Functional Groups* dialog to define functional groups and donor/acceptor sites. Functional groups are essential to define what constitutes a similar structure when querying the CSD.

Select **Modules | CCDC | Functional Groups** from the menu bar or click the  button on the **Modules** toolbar and select **Functional Groups** to open the Functional Groups dialog.

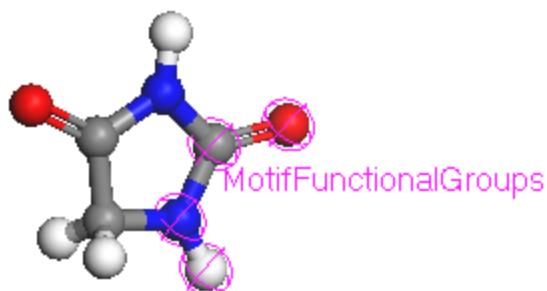


Functional Groups dialog

The hydantoin molecule contains two equivalent donor and acceptor sites. To run a meaningful CCDC Motif Search you should select a functional group that contains both the donor (oxygen) and the acceptor (nitrogen) sites. The smallest functional group that fulfills this requirement is O=C-N, however the O=C-NH-C fragment captures more of the molecular topology. You could also select the entire molecule as a functional group. The type of functional group you define will control what results are retrieved from the CSD and depends on the intended application of the search. For the purpose of this tutorial you will try to retrieve as many relevant structures as possible to maximize the statistical relevance of the scoring function to rank Polymorph results.

Select an **O=C-NH** fragment in **hydantoin-mol.xsd**. On the **Functional Groups** dialog, make sure that **Functional Group** is selected as the **Set**. Click the **Add selected atoms to set** button and click anywhere in the 3D Viewer to deselect everything.

Your hydantoin molecule should look like the one below:



Functional groups in hydantoin

Next, you will define the donor and acceptor sites.

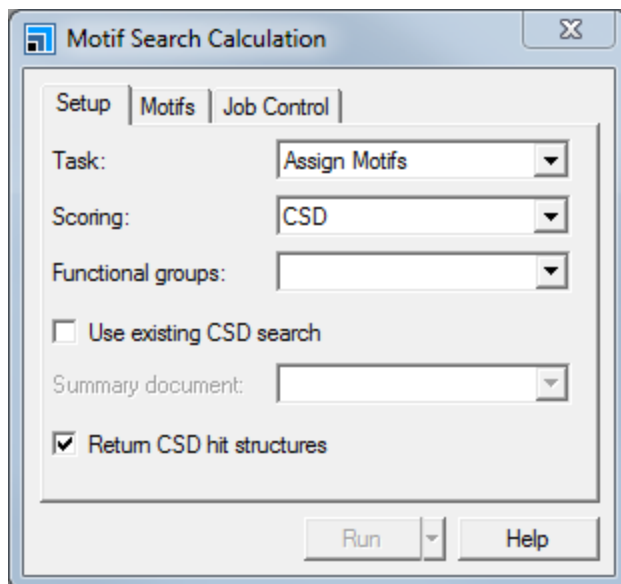
On the **Functional Groups** dialog change the **Set** to **Acceptors**. Select the **oxygen** atom in your defined functional group and click the **Add selected atoms to set** button.

Change the **Set** to **Donors**, select the **nitrogen** atom in your functional group and click the **Add selected atoms to set** button. Close the dialog.

4. To query the CSD for related structures

In this section you will query the CSD for structures containing the defined functional groups and extract the connectivity information between the acceptor and donor sites.

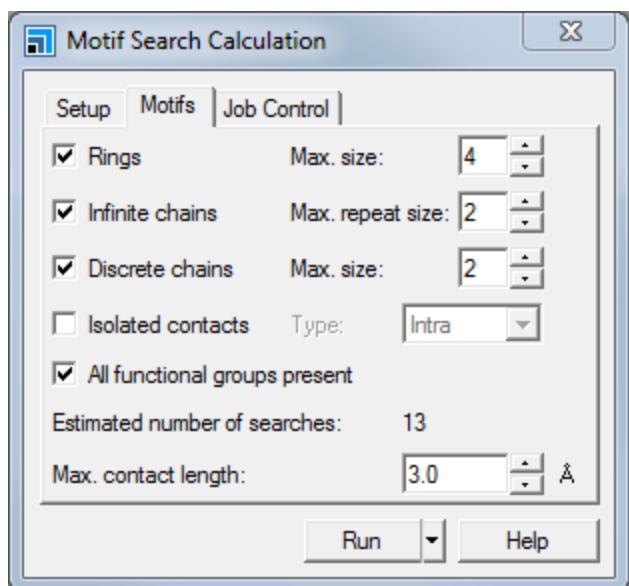
Select **Modules | CCDC | Motif Search** from the menu bar to open the **Motif Search Calculation** dialog.



Motif Search Calculation dialog, Setup tab

On **Setup** tab change the **Task** to **CSD Search** and make sure that the **Return CSD hit structures** checkbox is checked.

On the **Motifs** tab check the **Rings**, **Infinite chains**, **Discrete chains**, and **All functional groups present** checkboxes. Set the **Max. size** for **Rings** to **4** and the **Max. repeat size** for **Infinite chains** and **Max. size** for **Discrete chains** both to **2**. Set the **Max. contact length** to **3.0 Å**.



Motif Search Calculation dialog, Motifs tab

On the **Job Control** tab select an appropriate server from the **Gateway location** dropdown list. Click the **Run** button.

When the query has finished, results will be automatically downloaded from the server and stored in a folder named *hydantoin-mol Motif Search*. The matching structures together with their motif formulae are collected in a study table document. A summary document *hydantoin-mol Summary.txt* is also created. In the next section you will use this summary document as an input to the scoring task when comparing the Polymorph predicted structures to the CSD hit structures.

5. To assign motif information to Polymorph output and score the top ranked Polymorph structures

Since you will not run a polymorph prediction sequence in this tutorial you will import results from a previous prediction sequence into this project. If you would like to try to predict the packing arrangements yourself, it is suggested that you perform a DMol³ GGA-PBE optimization of hydantoin to determine the ESP charges and then to run Polymorph using these charges together with the Dreiding force-field. On more details on how to run polymorph prediction sequences please refer to the Polymorph tutorials section.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Examples/StudyTables**, choose **All Files** file types dropdown list for the **File name**, and select **M8_all_Polymorph.std**. Click the **Open** button.

Next, you will set the input parameters to assign and score the predicted packing arrangements. Note that to run the assignment/scoring the study table document containing the predicted structures have to be in focus and the document containing the fragment/contact point information needs to be selected in the interface.

On the **Motif Search Calculation** dialog, change the **Task** to **Assign Motifs** and select **CSD** from the **Scoring** dropdown list. Select **hydantoin-mol.xsd** from the **Functional groups** dropdown list. Check the **Use existing CSD search** checkbox and select the **hydantoin-mol Summary.txt** file from the **Summary document** dropdown list.

On the **Motifs** tab make sure that the settings are the same as in the previous section. Click the **Run** button and close the dialog.

Once the calculation finishes, results are returned. The main results document is the study table called **M8_all_Polymorph.std** in the **M8_all_Polymorph Motif Assign** folder. It lists the original structures along with their motif formulas. The first two structures share the same motif formula, **R[3] C[1] C[2]** and have the lowest energies calculated by Polymorph. The motif formula of the third and fourth structures is **R[2]**. Inspecting the *Matching score* and *Averaged score* indicates that the motif of the third and fourth structures is significantly more representative of previously known structures that contain the same fragment. Note that the third structure is the experimentally known structure.

	A	B	C	J	K	L	M	N	O	P
	Structures	Space group name	Space group number	Cell volume	Motif Formula	Rings	Chains	Matching score	Averaged score	Scoring
1	M8Dreiding P21-C - 1	P 21/c	14	418.51500000	R[3] C[1] C[2]	1	2	4.284323e-004	0.01998233	Score Probabilities
2	M8Dreiding P21-C - 2	P 21/c	14	417.31400000	R[3] C[1] C[2]	1	2	4.284323e-004	0.01998233	Score Probabilities
3	M8Dreiding P21-C - 3	P 21/c	14	414.80000000	R[2]	1	0	0.01688413	0.04687583	Score Probabilities
4	M8Dreiding C 2/c	C 2/c	15	833.59600000	R[2]	1	0	0.01688413	0.04687583	Score Probabilities
5	M8Dreiding P 21 21 21	P 21 21 21	19	426.56400000	R[3] C[1] C[2]	1	2	4.284323e-004	0.01998233	Score Probabilities
6	M8Dreiding C 2/c	C 2/c	15	844.52500000	R[2] C[1]	1	1	0.00218111	0.05781841	Score Probabilities

Results from scoring the top 6 Polymorph predicted structures using Motif Search

Note: The values in the study table may differ depending on your version of CSD System Software.

Double-click in the **Structure** cells for the third and fourth structures, with the **R[2]** motif formula.

A new 3D Viewer opens, containing the Polymorph predicted unit cells for the structure, the assigned hydrogen bonding motifs are displayed as pink dashed lines.

The scoring values obtained from the CCDC Motif search calculation indicate that the third and fourth structures are candidates for further investigation and should not be discounted because there are other structures with lower energies. For example, X-ray powder diffraction patterns could be simulated and compared with experimental patterns using the Reflex module.

This is the end of this tutorial.

References:

F. H. Allen, *Acta Cryst. B*, **58**, 380 (2002)

C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, **39**, 453 (2006).

G. M. Day, W. D. S. Motherwell, H. L. Ammon, S. X. M. Boerrigter, R. G. Della Valle, E. Venuti, A. Dzyabchenko, J. D. Dunitz, B. Schweizer, B. P. van Eijck, P. Erk, J. C. Facelli, V. E. Bazterra, M. B. Ferraro, D.W. M. Hofmann, F. J. J. Leusen, C. Liang, C. C. Pantelides, P. G. Karamertzanis, S. L. Price, T. C. Lewis, H. Nowell, A. Torrisi, H. A. Scheraga, Y. A. Arnautova, M. U. Schmidt and P. Verwer, *Acta Cryst. B*, **61**, 511 (2005).

Conformers tutorials

The following tutorial illustrates how to utilize Conformers' capabilities.

Using Conformers to probe geometry-energy relationships

Purpose: Introduces the Conformers module for searching low energy conformations and probing conformation-property relationships.

Modules: Materials Visualizer, Conformers

Time: 🕒

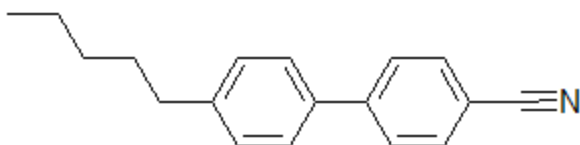
Prerequisites: Sketching simple molecules Visualizer Tutorial

Introduction

The potential energy surface of a given molecule becomes increasingly complex as the number of atoms in the molecule increases. Although modern geometry optimization methods are stable enough to find low energy conformers, they may not necessarily find the global energy minimum of a structure. For example, whilst the lowest energy conformation for a chain may be known, when you attach this to a ring, you need to find the lowest energy conformation of the chain relative to the ring. Conformers is a tool that allows you to change a set of defined torsions either systematically, randomly, or with temperature jumps, whilst keeping the rest of the molecule unchanged. Using the previous example, this allows you to set a chain to be all-trans whilst varying the connecting torsion to a ring.

By using systematic searches around particular torsion angles Conformers allows you to build up a picture of the energy barriers to rotation for a torsion angle, this is coupled with the ability to predict properties such as dipole moments for the molecule. Thus Conformers provides a suite of tools to systematically study the effects of conformation on key properties.

In this simple example, you will examine the change in the energy barrier as you rotate the interannular torsion in the biphenyl moiety of a liquid crystal molecule, 5CB, with varying substituents on the ring. You will also use the analysis tools to study the dependency of the dipole moment on the conformation and energy.



5CB - a simple liquid crystal molecule

This tutorial covers:

- [Getting started](#)
- [To perform a systematic conformational analysis for 5CB](#)
- [To substitute fluorines on the rings and the effect on the energy barrier](#)
- [To analyze the effect of conformation on the dipole moment](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.


1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **5CB** as the project name, click the **OK** button.

The new project is created with *5CB* listed in the Project Explorer.

The first step is to load in a pre-defined structure, the liquid crystalline molecule *5CB*.

Click the **Import** button  on the toolbar and navigate to **Examples\Documents\3D Model**. Double-click on **5CB.xsd**.

2. To perform a systematic conformational analysis for 5CB

Once you have imported the molecule, you need to define the torsions that you want to vary. You can do this by either adding torsions to the molecule or by using the Torsions functionality of the Conformers tool. Initially, you will use the Torsions functionality.

Click the **Conformers** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

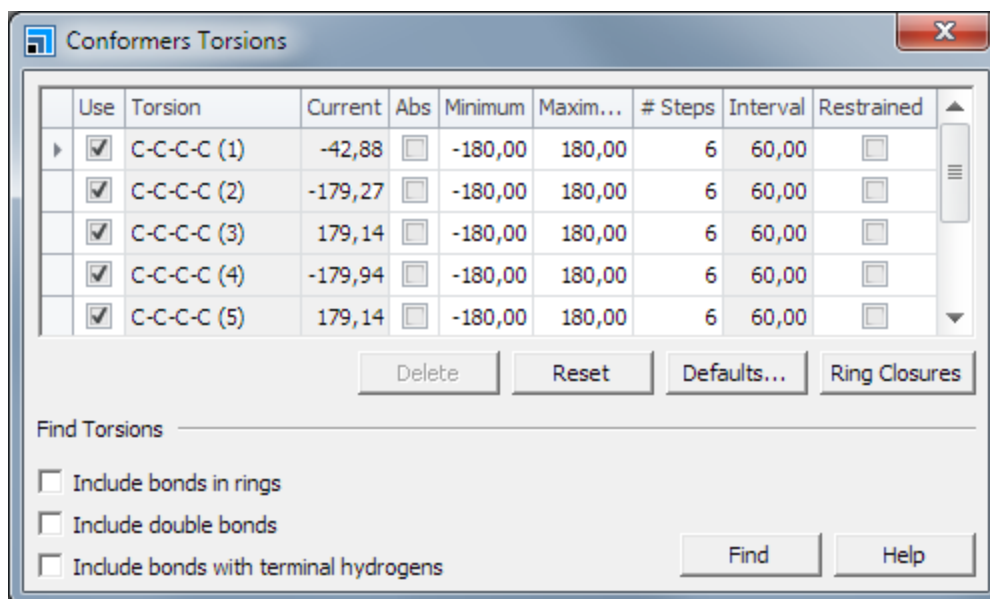
This opens the Conformers Calculation dialog.

Click the **Torsions...** button to open the Conformers Torsions dialog.

This displays all the rotatable torsions in the molecule. You can choose to include bonds in rings, double bonds, and bonds with terminal hydrogen atoms

Move the open dialog boxes so that you can see *5CB*. Click the **Find** button.

The Conformers Torsions dialog lists all the rotatable torsions.



Conformers Torsions dialog

You can select the torsions you want to rotate by checking the Use checkbox. The Absolute column allows you to select either absolute or relative values for the torsion angles. You can also edit the minimum and maximum angles, the number of steps, and whether the angle is restrained.

Click on the left row heading cell for a torsion so that the entire row is selected.

As you click on the box, the torsion is selected in the molecule. For this calculation, you are going to vary the torsion between the two benzene rings which has a current value of -42.88.

Click on the row heading cell for the topmost row. Scroll to the bottom, hold down SHIFT, and click on the row heading cell for the bottommost row. This will select all the torsions. Uncheck the **Use** checkbox for any torsion; all the checkboxes will be unchecked. Click anywhere and check the **Use** checkbox for **C-C-C-C(1)**.

Note: If you want to study the conformations of rings, you need to break a bond using the Ring Closures tool.

As you are doing a systematic search, the number of conformers will be dependent upon the number of steps you define.

Change the **# Steps** value to **36**.

The Interval changes to 10, indicating that you will be performing an energy calculation every 10 degrees. On the Conformers Calculation dialog, the Estimated conformers updates to 36.

Close the **Conformers Torsions** dialog.

As this is a classical simulations calculation, you need to specify the forcefield and charges that you will use in the simulation.

On the **Conformers Calculation** dialog, select the **Energy** tab.

For this simulation, you will use the Universal forcefield. Universal has no charges defined so you should calculate the charges using QEq.

Set the **Charges** option to **Charge using QEq**.

You can also use filtering to remove conformers before they are returned from the server.

Select the **Filters** tab.

Conformers allows you to filter by Energy difference, RMS difference for coordinates or torsions, and radial distribution function. Filters are very useful if you are sampling thousands of conformers and wish to eliminate similar conformers in order to produce a diverse conformer set.

As you are running a very quick calculation with a small number of conformers, you can do this without filtering.

Click the **Run** button and close the dialog.

When the calculation is complete, the *Job Completed* dialog will appear. A new folder, entitled 5CB Conformers Calculation, opens in the Project Explorer and contains the results files.

Tip: You can output to either the study table, trajectory, or both. If you are generating many thousands of conformers, you should use a trajectory document.

There are several files returned:

5CB.xsd the input structure updated with the results from the calculation.

5CB - Calculation the saved settings for the calculation.

5CB Energies.xcd is the live update of the conformer energies.

5CB reference.xsd is the structure that contains the sets, atoms, and torsions that can be used in an extended search.

5CB RMS Deviation.xcd is a plot of the RMS deviation of the Cartesian coordinates.

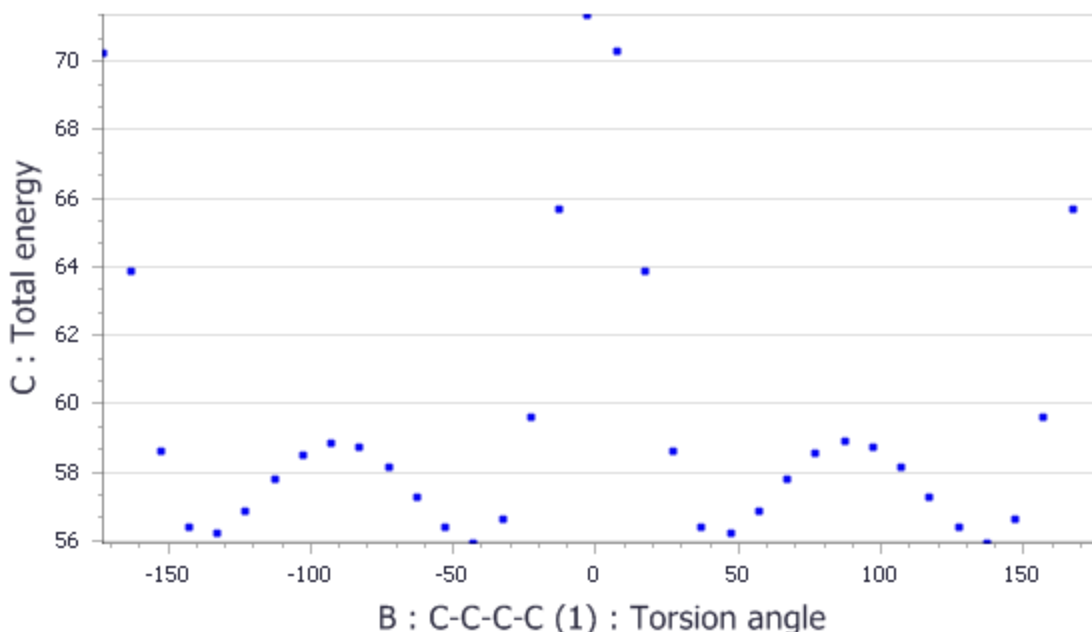
5CB.std is the study table containing the results of the calculation.

5CB.txt and Status.txt are text files containing information about the calculation.

You will focus on the study table for your initial analysis.

Make **5CB.std** the active document. Select columns **B** and **C** and click the **Quick Plot**  button.

You will have a plot showing two main peaks indicating larger barriers to rotation and, in the valleys, two other energy minima.



On the chart document **5CB Scatter plot.xcd**, select several points around the high energy peaks. Change focus to the **5CB.std**.

The high energy conformers are highlighted in the study table. You can extract these to a collection document to overlay them.

Right-click in one of the selected cells in column A and choose **Extract To Collection** from the shortcut menu.

In the new collection document *Extracted From 5CB.xod*, you can see that the high energy conformers had high steric hindrance. When you look at the chart, you can see that the potential energy surface goes through a smaller maximum as well.

On the chart document **5CB Scatter plot.xcd**, select a few points at one of the smaller maximums. On the study table **5CB.std**, extract the selected structures to a new collection document - this will be named **Extracted From 5CB(2).xod**.

The structures near the second energy maximum place the rings perpendicular to each other. This shows that the rings prefer to sit slightly off-plane to each other but not to flip completely.

3. To substitute fluorines on the rings and the effect on the energy barrier


You can begin to substitute some halogens for hydrogens on the biphenyl ring system to see the effect this has on the energy barrier to rotation.

Import **5CBF.xsd** and **5CB2F.xsd**.

5CBF.xsd contains the 5CB structure with an added fluorine on one of the benzene rings. **5CB2F** contains fluorine on both benzene rings. Initially, you will work with **5CBF.xsd**.

Make **5CBF.xsd** the active document.

Previously you used the Torsions tool to find all the rotatable torsions, this can be very useful if you are sampling many torsions using Boltzmann jump or random sampling. However, if you wish to just rotate one torsion, you can define it using the geometry monitors.

Click the **Measure/Change** arrow  on the **Sketch** toolbar and select **Torsion** from the dropdown list. Click on the bond connecting the two phenyl rings.

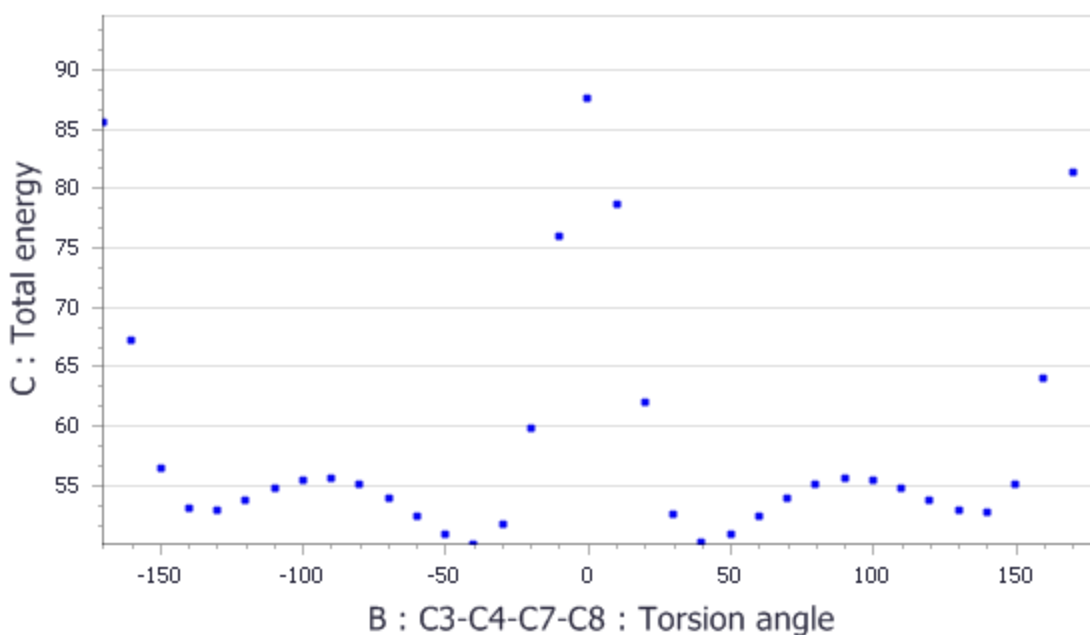
A torsion monitor is added to the structure. Now you can select this from the Conformers Calculation, Torsions dialog.

Open the **Conformers Calculation** dialog and click **Torsions...** button on the Search tab.

The *Use* checkbox should already be checked, you should increase the number of steps and run the calculation.

Change the **# Steps** to **36**. Close the **Conformers Torsions** dialog and click the **Run** button.

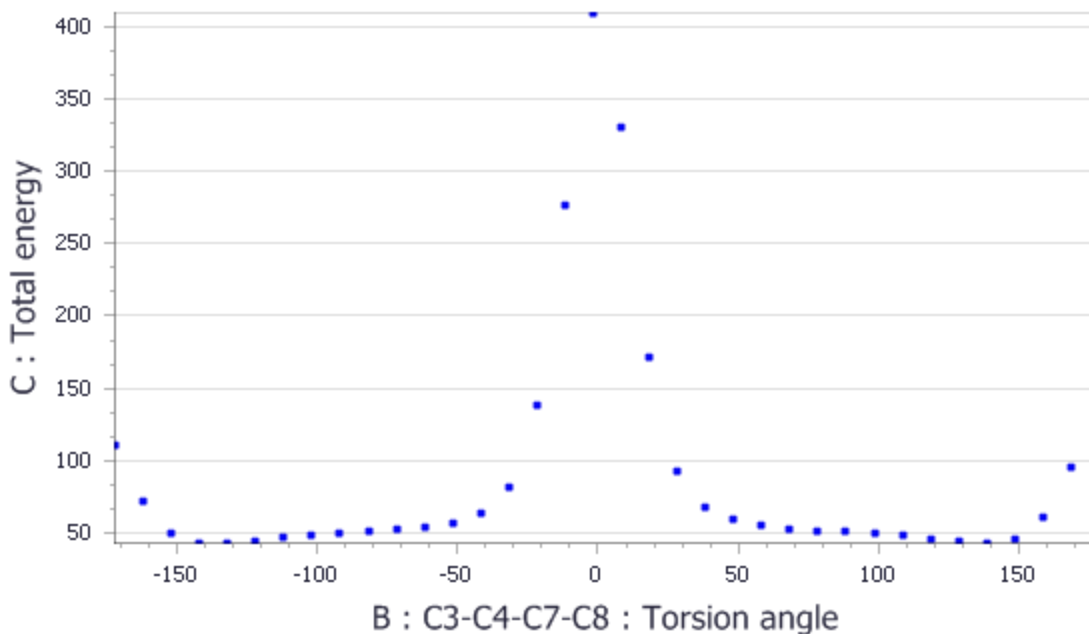
When the calculation is complete click the **OK** button on the Job Completed dialog. In the study table, **5CBF.std**, plot the **Torsion angle** (column B) against the **Total energy** (column C).



5CBF Scatter plot.xcd

The addition of the fluorine increases the energy barrier to rotation by a factor of two due to the increased steric interactions.

Repeat the above calculation for **5CB2F.xsd** and plot the **Torsion angle** against the **Total energy**.




5CB2F Scatter plot.xcd

Adding in the second fluorine further increases the energy barrier to rotation by a factor of approximately ten.

4. To analyze the effect of conformation on the dipole moment

You can use the Conformers analysis tool to perform clustering and calculate different properties. For this tutorial, you will calculate the change in the dipole moment for 5CB2F and plot it against the energy.

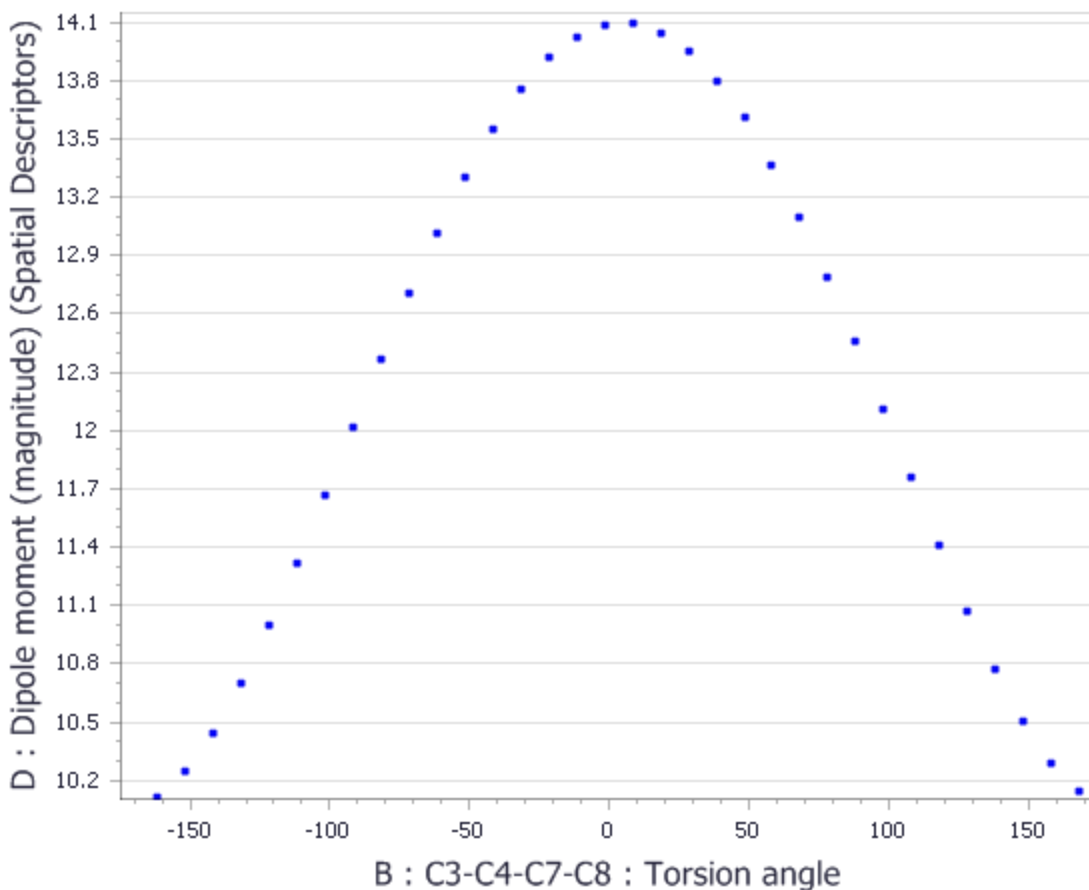
Make sure that the study table **5CB2F.std** is in focus. Select the structures column, **A**. Click the **Conformers** button  on the **Modules** toolbar and select **Analysis** to open the Conformers Analysis dialog.

The Dipole moment analysis functionality uses the current charges on the atoms to calculate the dipole moment for the system.

Select **Dipole moment** and click the **Analyze** button.

A job is submitted to the server and, when complete, a new column is added to the study table.

Plot the **Torsion angle** against the **Dipole moment**.




5CB2F Scatter plot (2).xcd

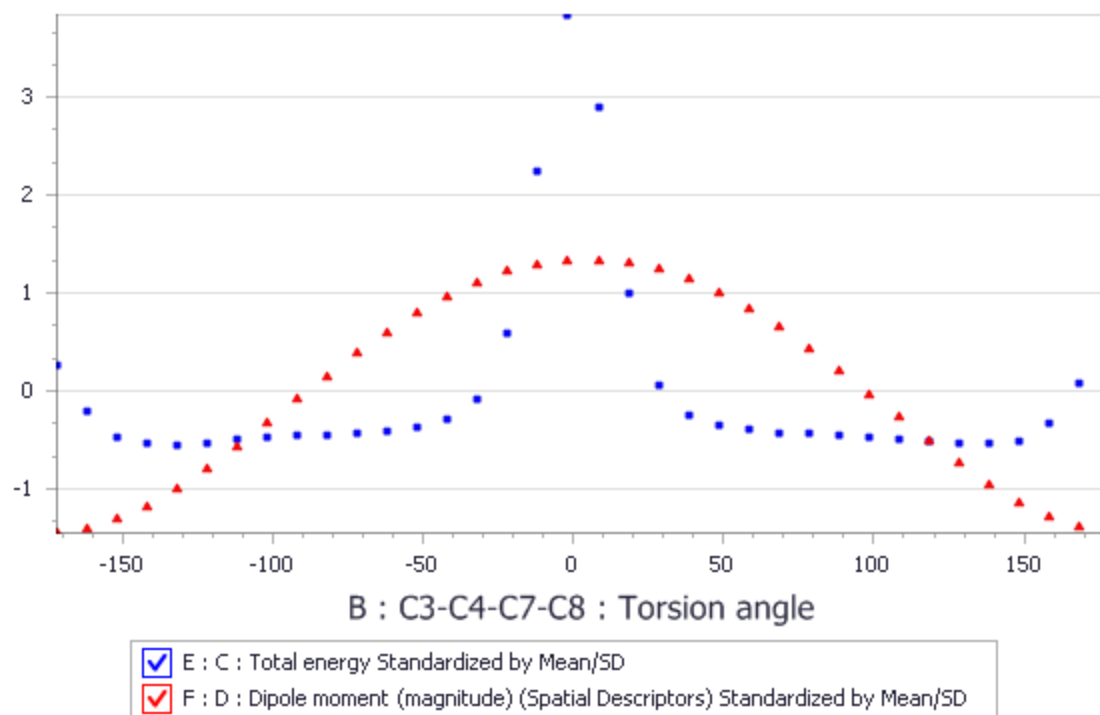
You should see that the dipole moment reaches a maximum at about 0 degrees. This makes sense as at 0 degrees, the fluorines are aligned.

To compare the change in dipole moment with the energy of the conformer, you need to scale the energies and dipoles so that they can be plotted on the same chart. You can use the Standardize data tool to automate this.

In the study table **5CB2F.std**, click on columns **C** and **D** to select them. Select **Statistics | Initial Analysis | Standardize Data...** to open the Standardize Data dialog and click the **OK** button.

Two new columns have been added to the study table, *Total energy Standardized by Mean/SD* and *Dipole moment (magnitude)*.

Select columns **B**, **E**, and **F** by pressing the **CTRL** key and clicking on each column heading, then click the **Quick Plot**  button.



5CB2F Scatter plot (3).xcd

You should now see that the maximum dipole moment is at the energy maximum. Again, this makes sense as the fluorine atoms are coincident and hence the steric hindrance will be very high.

This is the end of the tutorial.

DFTB+ tutorials

The following tutorials illustrate how to utilize DFTB+'s capabilities.

- [Geometry optimization of a carbon nanotube](#)
- [Creating parameters for DFTB+](#)
- [Simulating electron transport with DFTB+](#)

Geometry optimization of a carbon nanotube

Purpose: To introduce basic DFTB+ calculations of structural and electronic properties

Modules: Materials Visualizer, DFTB+

Time: 

Prerequisites: None

Background

DFTB+ is a semi-empirical tight binding method based on a two-centered approach to density functional theory (DFT). The use of a tight binding approach makes it faster than ordinary DFT methods but it also makes it dependent on parameter sets known as Slater-Koster libraries. Libraries are provided for standard organic molecules and semi-conductors.

Interactions with carbon nanotubes (CNT) are typically handled better by quantum mechanics techniques than by classical forcefield-based approaches. However, the system size limitations imposed by using quantum mechanics techniques narrows the range of applications that can be handled. DFTB+ represents a good compromise between classical and quantum simulation techniques for studying carbon nanotubes, giving the accuracy and electronic information of the quantum calculation but applying it to system sizes outside the reach of standard quantum techniques.

Introduction

In this tutorial you will use the DFTB+ module to do a geometry optimization for a carbon nanotube and calculate its band structure.

This tutorial covers:

- [Getting started](#)
- [Initial preparation](#)
- [To set up a Geometry optimization job:](#)
- [To select properties](#)
- [To control the job settings and run the job](#)
- [To analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DFTB CNT** as the project name, click the **OK** button.

The new project is created with DFTB CNT listed in the Project Explorer.

2. Initial preparation

The first step is to use the nanostructure building tools to create a 10×10 carbon nanotube.

Select **Build | Build Nanostructure | Single-Wall Nanotube** from the menu bar to open the Build Single-Wall Nanotube dialog. Set **N** and **M** to **10** and click the **Build** button. Close the **Build Single-Wall Nanotube** dialog.

To avoid interactions between periodic images of the CNT you should increase the lattice parameters perpendicular to the CNT.

Select **Build | Symmetry | Lattice Parameters** from the menu bar to open the Lattice Parameters dialog. On the **Advanced** tab, uncheck the **Keep fractional coordinates fixed during changes to the lattice** checkbox. On the **Parameters** tab, set the lengths **a** and **b** to **30** and close the dialog.


You will perform a geometry optimization of the CNT, including optimization of the cell lengths. To keep the periodic lattice lengths that you have just set, you should constrain these axes.

Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. On the **Lattice** tab, check the **a**, **b**, **α** , **β** , and **γ** checkboxes and close the dialog.

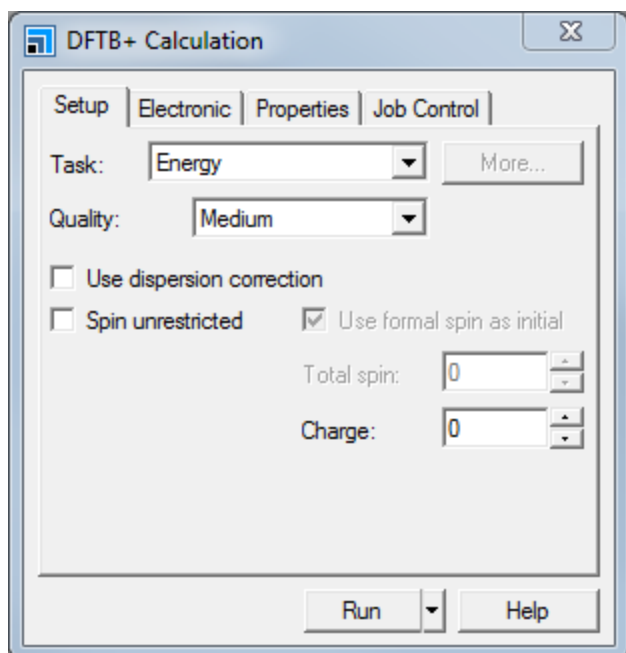
When you perform the calculation, the a and b cell lengths will remain fixed.

3. To set up the DFTB+ job

You are now ready to begin setting up the DFTB+ job.

Click the **DFTB+**  button on the **Modules** toolbar and select **Calculation** or choose **Modules | DFTB+ | Calculation** from the menu bar.

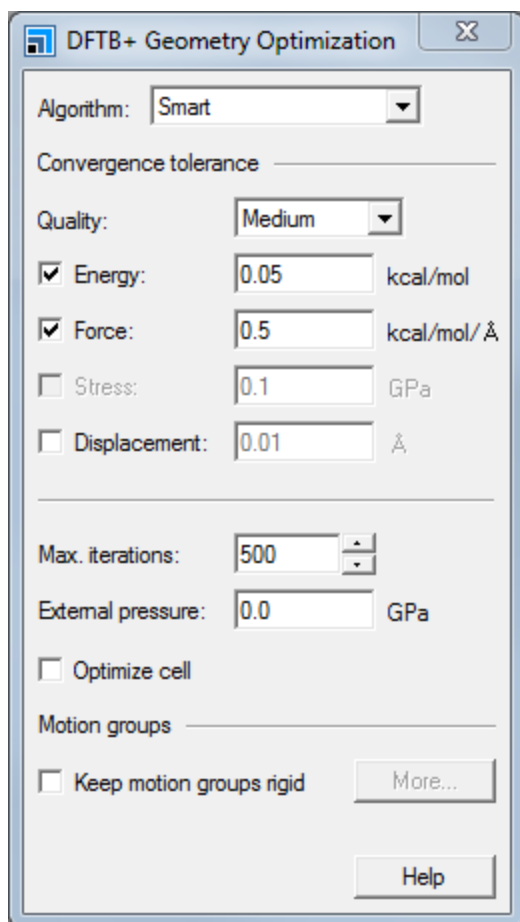
This opens the DFTB+ Calculation dialog.



DFTB+ Calculation dialog, Setup tab

Select **Geometry Optimization** from the **Task** to dropdown list.

Click the **More...** button to open the DFTB+ Geometry Optimization dialog.



DFTB+ Geometry Optimization dialog

You will use the *optimize cell* option to relax the lattice parameters. As you have constrained the *a* and *b* lattice lengths, the *Optimize cell* option will only optimize the *c* lattice length.

Check the **Optimize cell** checkbox and close the dialog.

In order to run a DFTB+ job a valid Slater-Koster library must be selected. DFTB+ requires interactions between all available elements in the target structure to be defined in the library. A quick overview for each library can be displayed by clicking the **View** button. In this tutorial you will use the **CHNO** library.

On the **Electronic** tab of the DFTB+ Calculation dialog, select the **CHNO** library from the **Slater-Koster library** dropdown list.

Note: If you want to use DFTB+ with a structure that contains atom interactions that are not supported in any of the available parameter sets, you can use the DFTB+ Parameterization task for creating your own parameters. This uses DMol³ to perform the DFT calculations. For more information, see the [Creating parameters for DFTB+](#) tutorial.

4. To select properties

As well as performing a geometry optimization, you can also select from a range of properties that will be calculated on the optimized structure. For this tutorial, you will calculate the band structure of the CNT.

On the **Properties** tab, check the **Band structure** checkbox in the list of properties and set the **k-point set** to **Fine**.

Since you are calculating the band structure for a 1D object, you should create the Brillouin zone paths and only keep the one corresponding to the direction of the nanotube.

Click the **Path...** button to open the Brillouin Zone path dialog, click the **Create** button and then delete all Brillouin zone paths except the **Z to G** path.

Note: If you generate a trajectory using the Dynamics task, you can use Forcite Trajectory Analysis to perform further analysis.

5. To control the job settings and run the job

You can use the commands on the *Job Control* tab on the DFTB+ Calculation dialog to control the calculation.

You can choose the gateway location where you will run your calculation and set various options such as the job description. You can also specify live update settings and job completion options.

You are now ready to run your DFTB+ Geometry optimization job.

Click the **Run** button and close the dialog.

A text document named `Status.txt` is displayed, reporting the status of the calculation. This document is updated regularly until the calculation is complete, it can be a useful aid to indicate the progress of your calculation.

6. To analyze the results


When the calculation is complete, the results are returned to the `SWNT DFTB+ GeomOpt` folder in the Project Explorer.

In the `SWNT DFTB+ GeomOpt` folder, double-click on `SWNT.txt`.

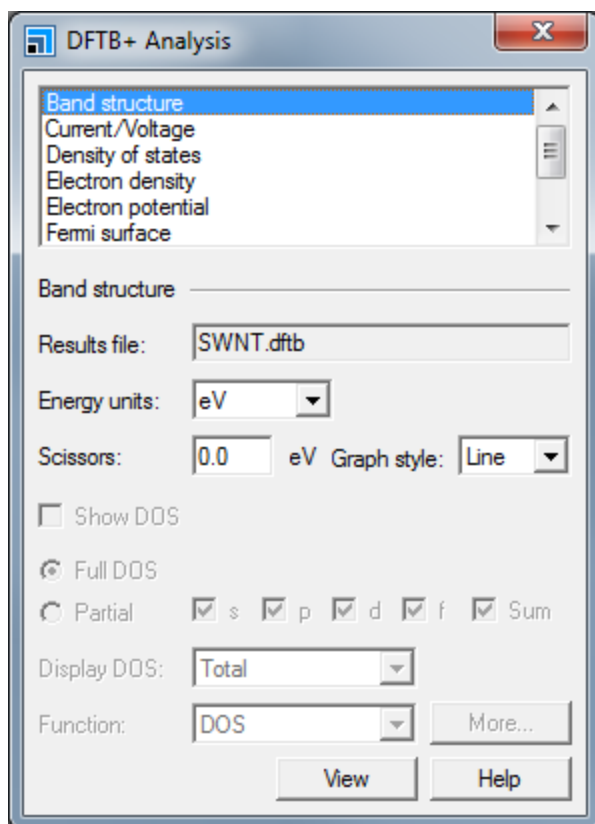
The `SWNT.txt` document contains an overview of the job and the result. The `SWNT.dftb` file contains the output from the last single point energy DFTB+ calculation. This file can contain helpful information if there are issues with a calculation.

Change focus to the optimized `SWNT.xsd`.

To visualize the band structure, you need to analyze the output documents.

Click the **DFTB+**  button on the **Modules** toolbar and select **Analysis** or choose **Modules | DFTB+ | Analysis** from the menu bar.

This opens the DFTB+ Analysis dialog.



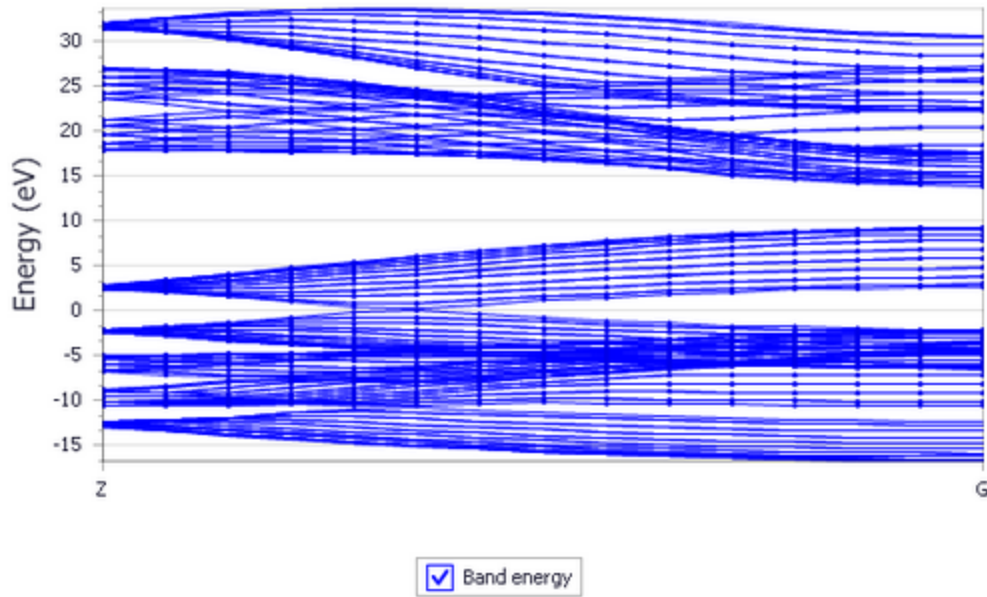
DFTB+ Analysis dialog

Select **Band structure** and click the **View** button.

This generates and displays a chart showing the band structure for the CNT, note the characteristic band crossing at the Fermi level.

DFTB Band Structure

Band gap is 0.271 eV



DFTB+ Analysis view, Band structures

This is the end of the tutorial.

Creating parameters for DFTB+

Purpose: To introduce the use of the DFTB+ parameterization tool for creation of DFTB+ parameter libraries.

Modules: Materials Visualizer, DMol³, DFTB+

Time: 🕒🕒🕒

Prerequisites: Sketching molecules Visualizer Tutorial

Background

DFTB+ requires atomic parameters for the interaction between atoms. A number of parameter sets are available in Materials Studio. If you want to use DFTB+ with a structure that contains atom interactions that are not supported in any of the available parameter sets, Materials Studio supplies a tool for creating your own parameters.

The parameters created by the DFTB+ parameterization tool will be contained in a Slater-Koster Library file (.skflib) and will contain the following:

- README.txt file with information about the parameters
- Slater-Koster files (.skf) for the element pairs in question, containing:
 - Electronic parameters
 - Short range potential
 - Hubbard terms
- Spin constants for the elements
- Wave plot data for each element
- An skf.aux file containing extra settings

Introduction

In this tutorial you will use the DFTB+ parameterization tool to create a carbon and hydrogen parameter set.

This tutorial covers:

- [Initial preparation](#)
- [To set up the DFTB+ parameterization:](#)
 - Defining conformation systems
 - Defining electronic settings
 - Defining settings for the fitting
- [To control the job settings and run the job](#)
- [To evaluate the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CHparameters** as the project name, click the **OK** button.

The new project is created with CHparameters listed in the Project Explorer.

2. Initial preparation

The first step in a DFTB+ parameterization is to decide what systems to use for the fitting. In this project you will try to create a parameter set which will work well for most hydrocarbons. To achieve this you will need to fit against the different types of bonds that these systems can contain.

You will use the following systems:

- hydrogen-hydrogen bonds
 - hydrogen molecule
- carbon-carbon bonds
 - ethane, single bond
 - ethene, double bond
 - benzene, hybrid bond
- carbon-hydrogen bonds
 - methane


Ethane, methane, and benzene can be imported from Materials Studio's collection of structures.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Structures\organics** and select the **ethane.xsd**, **methane.xsd**, and **benzene.xsd** structure files, click the **Open** button.

The hydrogen and ethene molecules will have to be created using the sketching tools.

In two new 3D Atomistic documents, create an H-H and a $\text{H}_2\text{C}=\text{CH}_2$ molecule and rename the documents **H2.xsd** and **ethene.xsd**.

You now have all molecules necessary to set up the parameterization. However, before you start using them you need to perform a geometry optimization on each molecule using DMol³. This ensures that the unperturbed molecule has the optimized structure that the parameterization aims to reproduce.

Click the **DMol3**  button on the **Modules** toolbar and select **Calculation** or choose **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.

Set the **Task** to **Geometry optimization**, the **Quality** to **Fine**, the **Functional** to **GGA PBE**, and on the Electronic tab set the **Basis file** to **4.4**.

Ensure that **ethene.xsd** is the active document and click the **Run** button.

You should run this geometry optimization with the same settings for all the input structures.

Make **H2.xsd** the active document and click the **Run** button on the DMol3 Calculation dialog.

Repeat this for **ethane.xsd**, **methane.xsd**, and **benzene.xsd**.

When the jobs are all complete, you should save the project and then close all the windows.

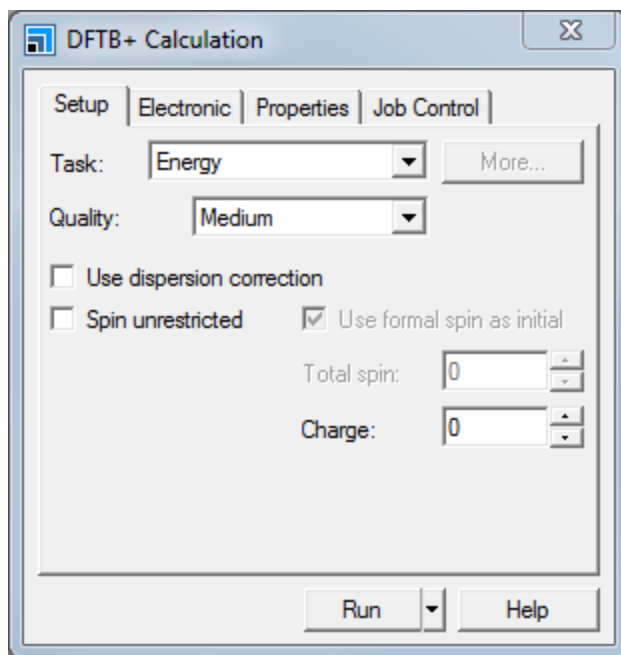
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To set up the DFTB+ parameterization

You are now ready to begin setting up the parameterization job.

Click the **DFTB+** button on the **Modules** toolbar and select **Calculation** or choose **Modules | DFTB+ | Calculation** from the menu bar.

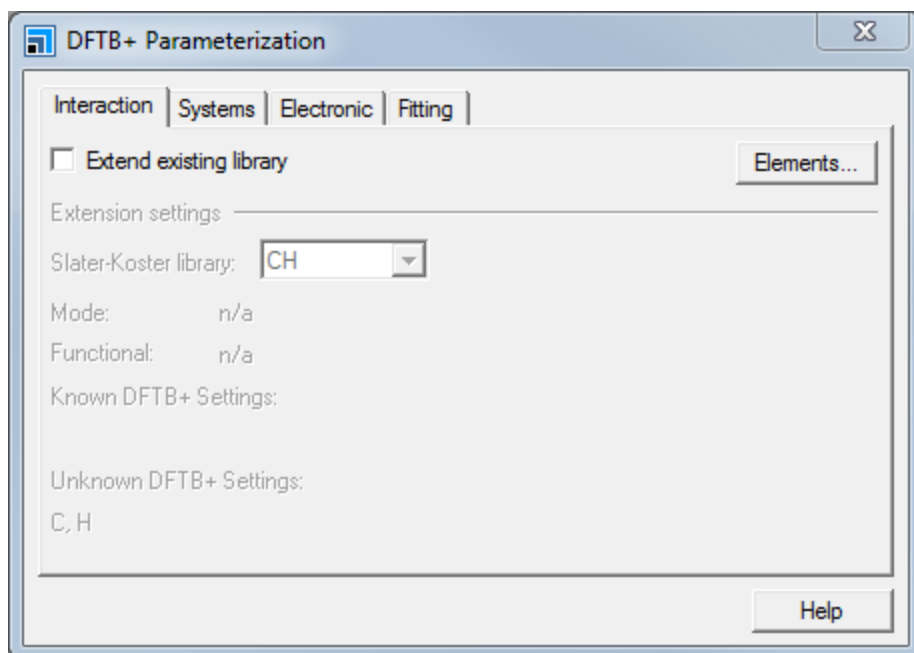
This opens the DFTB+ Calculation dialog.



DFTB+ Calculation dialog, Setup tab

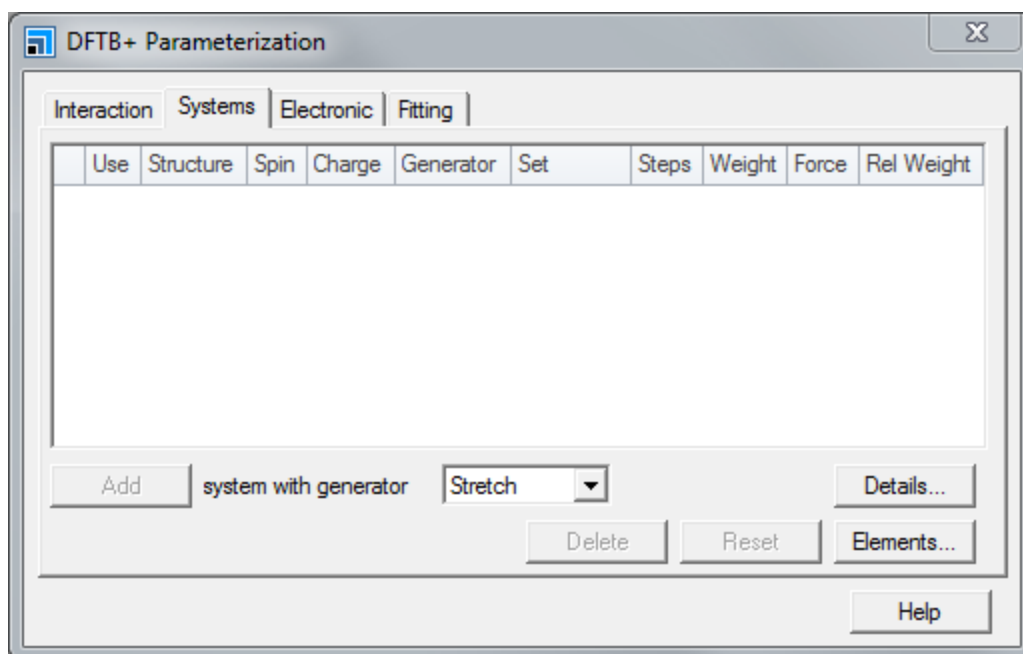
Set the **Task** to **Parameterization**. Change the **Quality** from Medium to **Fine**.

Click the **More...** button to open the DFTB+ Parameterization dialog.



DFTB+ Parameterization dialog

The DFTB+ Parameterization dialog facilitates the setup of a parameterization. Select the **Systems** tab to begin setting up the system conformation paths that will be used for the fitting.



There are four different conformation generators:

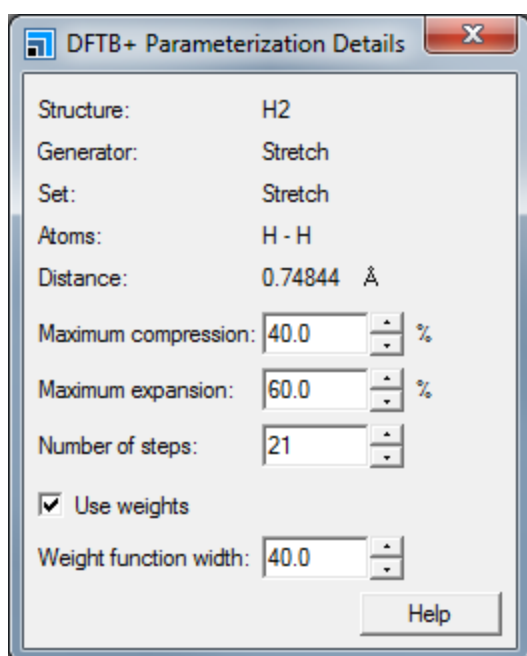
- Stretch - moves a selected set of atoms along a selected direction.
- Perturb - randomly moves an atom around its original position.
- Scale - uniformly scales the size of the system.
- Trajectory - uses the conformations contained in a trajectory file.

For more details about generators refer to the Systems tab - DFTB+ Parameterization dialog topic.

Make **H2 DMol3 GeomOpt/H2.xsd** the active document and select the bond and one of the hydrogen atoms. On the **Systems** tab select **Stretch** as the generator, click the **Add** button.

This will create a stretch definition for the hydrogen molecule, where the selected atom will be moved along the direction of the bond. Details about the path of conformations that will be generated can be reviewed on the DFTB+ Parameterization Details dialog.

Click the **Details...** button to open the DFTB+ Parameterization Details dialog.



DFTB+ Parameterization Details dialog

The DFTB+ Parameterization Details dialog contains detailed information about the selected path. For a stretch generator you can set *Maximum compression*, *Maximum expansion*, the *Number of steps* to be generated, and the *Weight function width*. Since the minimum fitting distance is about 0.65 Å you should reduce the *Maximum compression*.

Set the **Maximum compression** to **20%** and the **Number of steps** to **31** then close the dialog.

Next you will prepare a perturbation of the methane molecule.

Make **methane DMol3 GeomOpt/methane.xsd** the active document and select a hydrogen atom. Select **Perturb** as generator and click the **Add** button.

This will create a perturb definition for the hydrogen atom, where the selected atom will be moved randomly around the original position. Details about the path that will be generated can be reviewed on the DFTB+ Parameterization Details dialog.

For a perturb generator you can set *Maximum perturbation*, *Number of shells* to be generated and the *Weight function width*. Each shell will have four positions with a fixed radius. With the current setting you will cover a bond distance of approximately 0.55-1.65 Å which will cover the range of interest for the C-H bond. However, in order to get a better accuracy around the equilibrium position you will create a second path with a smaller maximum perturbation and a sharper weight function.

Select another hydrogen atom in the methane molecule and create a new perturb path. On the DFTB+ Parameterization Details dialog change the **Maximum perturbation** to **30** and the **Weight function width** to **15**.

Creating the paths for the H-H and the C-H interactions is simple because these paths only have single bonds. Setting up the paths for the C-C interaction will be more complicated since there will be overlap between potentials of different bond orders. You will try to solve this problem by setting up paths with sharp weight functions, such that when there is an overlap the bond which is closest to its equilibrium will dominate. You will start with the longest bond as it will need to cover the tail of the short range potential.

Make **ethane DMol3 GeomOpt/ethane.xsd** the active document and create a distance measurement between the two carbon atoms and select the distance measurement.

Select **Stretch** as generator and click the **Add** button, reduce the **Weight** to **0.5**. On the DFTB+ Parameterization Details dialog change the **Maximum expansion** to **70** and the **Number of steps** to **31**.

Create a perturb path for one of the carbon atoms and change the **Maximum perturbation** to **30** and the **Weight function width** to **15**.

Now that you have ensured that there is coverage for the tail you can add the remaining bond types with sharp weight functions only. The maximum perturbation should be about 0.3 Å and the width of the weight function will be about half the maximum perturbation.

Create a perturb path for a carbon atom in each of the ethene and benzene molecules.

You have now created paths that cover all the important bonds for a hydrocarbon system.

To ensure that you have enough coverage on all element pairs, click the **Elements...** button on the Systems tab of the DFTB+ Parameterization dialog.

This opens the DFTB+ Parameterization Elements dialog.



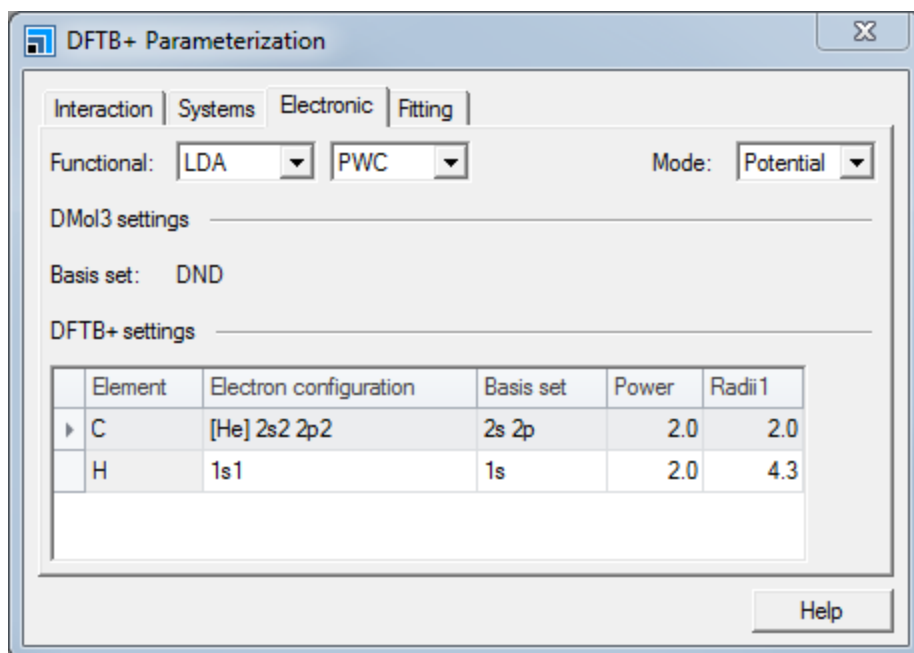
DFTB+ Parameterization Elements dialog

The DFTB+ Parameterization Elements dialog provides an overview of how many conformations will be created for each element pair. If the number of conformations for a pair is deemed to be sufficient the cell will be green. You can change the view to show percentage contribution per element pair, useful when your parameterization uses different weights for different paths.

Close the **DFTB+ Parameterization Details** and **DFTB+ Parameterization Elements** dialogs.

You are now ready to set up the electronic settings for the parameterization.

Select the **Electronic** tab of the DFTB+ Parameterization dialog.



DFTB+ Parameterization dialog, Electronic tab

The same functional that will be used for the creation of the electronic parameters in the Slater-Koster files, will also be used by DMol³ when calculating the total energy and forces for your path conformations. The basis set used by DMol³ is determined by the *Quality* setting.

Set the Functional to GGA PBE.

The *Mode* determines how the electronic parameters in the Slater-Koster files are determined. In **Potential** mode the potential of each single atom is used to create the pair potential. In the **Density** mode the electron densities of each atom are added and used to determine the potential for each pair. The choice of *Mode* affects the settings for the elements, the **Potential** mode has one compression radii, while the **Density** mode has two compression radii per element. The compression radii are used to compress the wavefunction and the electron density so that they avoid areas far away from the nucleus. In literature reports the **Potential** mode is commonly used for band structures and the **Density** mode is often used for bio-molecules and energetic calculations. For more details about the two modes refer to the DFTB+ theory section.

In this case you will use the **Density** mode to make it easier to obtain good geometries after fitting.

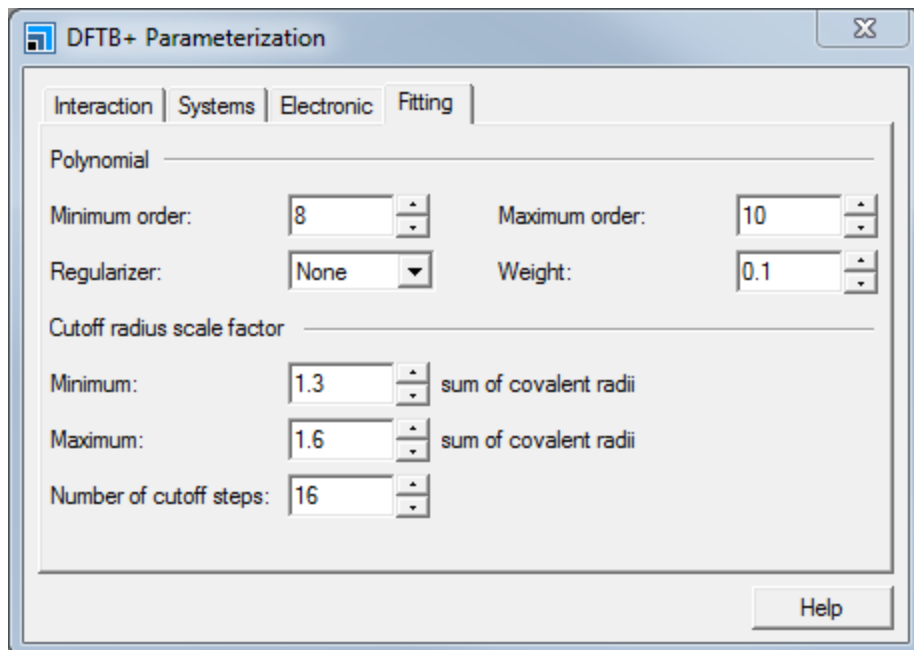
Set the Mode to Density.

Now you need to set the DFTB+ settings for each atom. The default settings will give a good starting point but can be changed to improve electronic properties of the target systems. The *Electron configuration* and the *Basis set* can be used to improve the electronic properties. Often the conduction band and LUMO will depend on excited orbitals, for example in silicon an 3s3p basis set will provide good valence bands but poor conduction bands, this can be alleviated by changing the basis set to 3s3p3d where the excited d-orbital will interact with the conduction bands. The settings for the compression radii will not only affect electronic properties but also how good geometry agreement you can get. Unfortunately it is often the case that the settings that give good electronic agreement are not the same as those that will result in the best geometry, so a compromise is often required. In this tutorial you will use values that are known to give good results. The default hydrogen settings are already appropriate.

For Carbon, change **Radii1** to **1.9** and **Radii2** to **4.8**.

You will now modify the settings used for the fitting of the short ranged potential.

Select the **Fitting** tab.



DFTB+ Parameterization, Fitting tab

The fitting is performed using a polynomial basis set where each term in the polynomial has a cut-off radii:

Eq. 1

$$f_v(r) = \begin{cases} (r - r_0)^v & \text{If } r < r_0 \\ 0 & \text{otherwise} \end{cases}$$

Short range potentials are generated for a defined set of cutoff factors. For each cutoff factor fittings are performed using different maximum polynomial orders. The best fit for each cutoff factor is returned.

In the Polynomial section set **Maximum order** to **12**.

The cutoff factor is typically around 1.5 times the bond length. If the cutoff factor extends too far, for example into second neighbor atoms, it can have an adverse impact on the transferability of the parameters.

Close the **DFTB+ Parameterization** dialog.


Before you start the parameterization you should save the project and then close all the windows.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To control the job settings and run the job

Before launching the job, you should save these settings.

Select the **CHparameters** item in the Project Explorer.

Click the **DFTB+**  button on the **Modules** toolbar and select **Save Settings...**, enter **CH Para1** as the name and click the **OK** button.

You will use the commands on the *Job Control* tab on the DFTB+ Calculation dialog to control the calculation.

Select the **Job Control** tab on the DFTB Calculation dialog.

You can choose the gateway location where you will run your calculation and set various options such as the job description. You can also specify live update settings and what happens when the job completes.

Uncheck the **Automatic** checkbox and enter **CH Para1** as the **Job description**.

You are now ready to run your DFTB+ parameterization.

Click the **Run** button and close the dialog.

A text document named `Status.txt` is displayed, containing the status of the calculation. This document is updated regularly until the calculation is complete. It can be a useful aid to indicate the progress of your calculation.

The **CH Para1** job will only use the total energies to fit the short range potential this will ensure good energy accuracy for the fitting but will not necessarily result in very good geometries. You can improve the accuracy of the fitting by fitting towards both energies and forces.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Tip: The location of the job folder will depend on the current selection in the Project Explorer. If there is no selection the job will appear under the project folder.

Double-click on **CH Para1 - Calculation** in the Project Explorer to open the saved settings. Open the **DFTB+ Parameterization** dialog and, on the **Systems** tab, check all the **Force** checkboxes and set the **Rel weight** values to **5**. Close the DFTB+ Parameterization dialog.

On the **Job Control tab** of the DFTB+ Calculation dialog set the **Job description** to **CH Para2**. Save these new settings as **CH Para2** and click the **Run** button on the DFTB+ Calculation dialog.

In a final run you will assess the effects of the selected mode.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Open the **CH Para2 - Calculation** job settings and on the **Electronic** tab of the DFTB+ Parameterization dialog change the **Mode** to **Potential** and close the dialog. On the **Job Control tab** of the DFTB+ Calculation dialog set the **Job description** to **CH Para3**. Save these settings as **CH Para3** and run a new calculation.

5. To evaluate the results

When the calculations are complete, the results for the first job are returned to the CH Para1 DFTB+ Parameterization folder in the Project Explorer.

In the **CH Para1 DFTB+ Parameterization** folder, double-click on **CH Para1.txt**.

```
#####
## CALCULATING ELECTRONIC PARAMETERS ##
#####
Mode : Density

Computing spin constants for C
Computing spin constants for H
Begin Pair C H
    Computing orbital energies for C
    Hubbard terms: C=(0.39910 0.36467 0.00000)
    Computing electronic parameters for C-C
    Computing orbital energies for H
    Hubbard terms: H=(0.41962 0.00000 0.00000)
    Computing electronic parameters for H-H
    Computing electronic parameters for C-H
    Creating .coef and .skf files.
End Pair
Assembling waveplot data in CH_Para1.hsd
Electronic parameter creation finished

#####
## CALCULATING REPULSIVE PARAMETERS ##
#####
DFT code : DMol3
    Basis : DNP
    Functional : PBE
    Integration grid : fine
Fitting basis : cutoffpoly
    Lowest degree : 3
    Highest degree : From 8 to 12
Regularizer : None


Fit    Cutoff    Polynomial    Total error    Regularization penalty
      factor  degree        (Ha^2)        (Ha^2)
-----
1      1.300    11            3.903e-03     0.000e+00
2      1.320    11            3.304e-03     0.000e+00
3      1.340    11            3.036e-03     0.000e+00
4      1.360    11            2.578e-03     0.000e+00
5      1.380    11            2.291e-03     0.000e+00
6      1.400    11            1.892e-03     0.000e+00
7      1.420    11            1.744e-03     0.000e+00
8      1.440    11            1.459e-03     0.000e+00
9      1.460    11            1.312e-03     0.000e+00
```

10	1.480	11	1.143e-03	0.000e+00
11	1.500	10	1.061e-03	0.000e+00
12	1.520	10	9.673e-04	0.000e+00
13	1.540	10	8.084e-04	0.000e+00
14	1.560	10	7.415e-04	0.000e+00
15	1.580	10	6.278e-04	0.000e+00
16	1.600	10	5.777e-04	0.000e+00

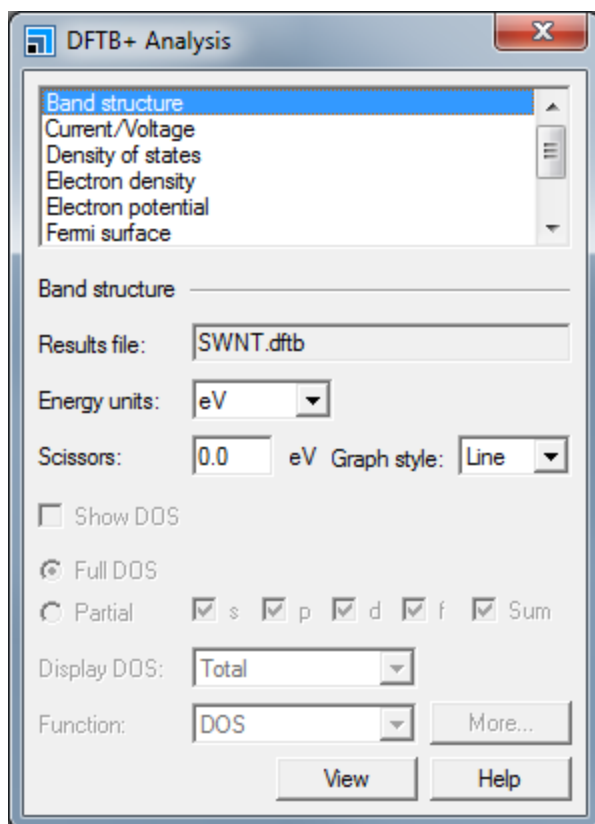
Repulsive parameter creation finished
Returned parameterization found in Fit16

The CH Para1.txt document contains the job output (there could be slight numerical differences compared to the sample output above). At the bottom of the document you will find a table with fitting results for the different cut-off factors used. The total error is the accumulated squared fitting error in Hartree for all conformations. Notice that the fit with the lowest error is not necessarily going to give the best results when tested since the error measurement is for the total error while you want good accuracy around the equilibrium points. So it is worthwhile testing more than one of the returned parameter sets. The fitting with the lowest total error will be returned in the job folder, while a collection of all fittings can be found in the [Alternatives](#) sub folder.

To visualize the parameters, you need to analyze the **.skflib** output documents.

Click the **DFTB+**  button on the **Modules** toolbar and select **Analysis** or choose **Modules | DFTB+ | Analysis** from the menu bar.

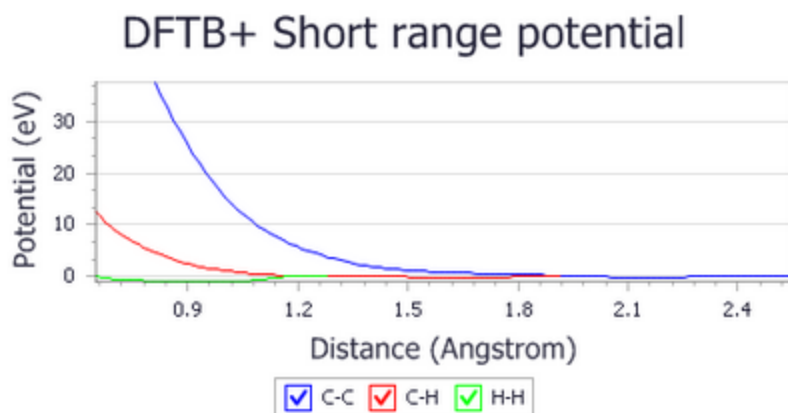
This opens the DFTB+ Analysis dialog.



DFTB+ Analysis dialog, Slater Koster Parameters

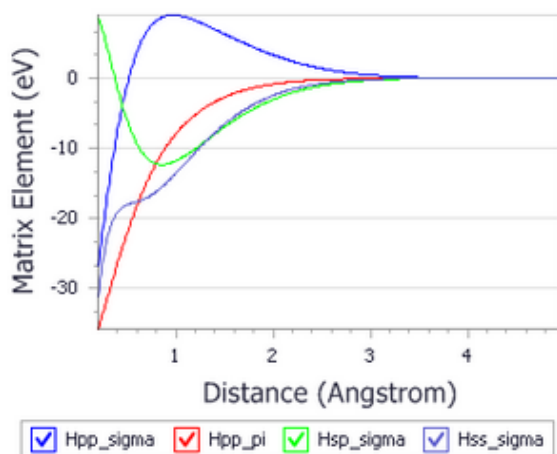
Select **Slater Koster parameters** and ensure the CH Para1.skflib file is available. The filename is displayed as the **Results file**. Check the **View Hamiltonian matrix elements** and the **View overlap matrix elements** checkboxes. Click the **View** button.

This will open two charts, one showing the short range potentials and one showing the Hamiltonian and overlap matrix elements.

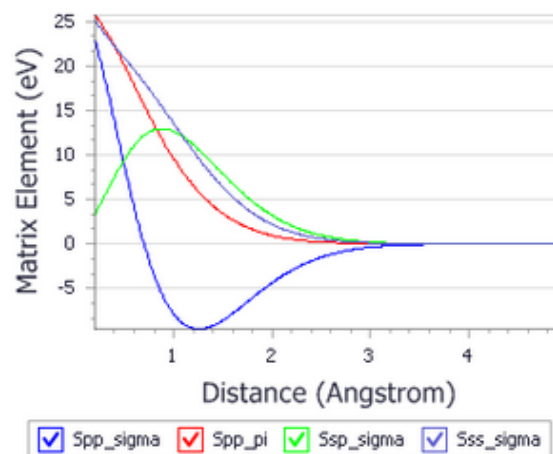


DFTB+ Analysis view, Short range potential

DFTB+ Hamiltonian Matrix Elements - C-C



Overlap Matrix Elements - C-C



DFTB+ Analysis view, Slater Koster Parameters

The Short range potential chart is important, oscillations in the tail indicate that not enough data to fit against in this region. If the curve oscillates around zero you are likely better off with a shorter cut-off radii, otherwise you will need to extend the conformation path responsible for the data in that region.

Zoom in at the tail of the curves and check for oscillations.

Generate the same analysis charts for the other two jobs and compare the results.

To evaluate your parameterization you will perform a geometry optimization on hydrocarbon structures using both DFTB+ and DMol³ and compare the results. Since a parameter evaluation is likely to be repeated many times it is good practice to script the test. For this tutorial a Materials Studio script is supplied which compares geometry optimization results between DMol³ and DFTB+.

Select the CHparameters root in the Project Explorer and create a new folder named **Testing**. Import **DFTBEval.pl** from the **Examples\Scripting** folder.


Move the un-optimized **methane.xsd**, **ethane.xsd**, **ethene.xsd**, and **benzene.xsd** structures into the Testing folder.

Open CH Para1.skflib in the **CH Para1 DFTB+ Parameterization** results folder. Open the **Save As** dialog and navigate to the Testing folder, append **.skflib** to the filename and click the **Save** button.

The DFTBEval.pl Perl script will perform geometry optimization on all 3D Atomistic documents in the folder and compare any distance and angle measurements in the files. It will also calculate the atomization energy for the structures. The results will be returned in an output .txt file with detailed data for each structure and a statistical analyses of the results.

Create a distance measurement for each bond type and an angle measurement for each angle type in each of the structures.

In **DFTBEval.pl** change the name of the **\$skflibFile** variable to **CH Para1.skflib** and save the file.

Ensure that **DFTBEval.pl** is the active document and click the **Run on Server**  button.

The calculations will take a few minutes. You should also save **.skflib** files for the other two parameterizations in the **Testing** folder and start a calculation for each.

Save the **CH Para2.skflib** and **CH Para3.skflib** parameterization result files to the **Testing** folder.

Change the name of the **\$skflibFile** variable in **DFTBEval.pl** to **CH Para2.skflib**, save the file, and click the **Run on Server**  button.

Change the name of the **\$skflibFile** variable in **DFTBEval.pl** to **CH Para3.skflib**, save the file, and click the **Run on Server**  button.

The evaluation script generates an output **.txt** file containing the comparisons between each of the geometry monitor lengths or angles after optimization with DFTB+ and DMol³, for example using **CH Para2.skflib**:

```
benzene
-----
DMol3 C3-C2 = 1.39838   C3-H9 = 1.09097
DFTB+ C3-C2 = 1.41183   C3-H9 = 1.10388
Diff   C3-C2 = 0.01345   C3-H9 = 0.01291

DMol3 C2-C7-C6 = 120.00000   H12-C7-C6 = 120.00000
DFTB+ C2-C7-C6 = 119.99743   H12-C7-C6 = 120.00193
Diff   C2-C7-C6 = -0.00257   H12-C7-C6 = 0.00193
```

```
Atomization Diff = -111.42031
=====
```

```
ethane
-----
DMol3 C2-C1 = 1.52883   C2-H6 = 1.10051
DFTB+ C2-C1 = 1.53114   C2-H6 = 1.10342
Diff   C2-C1 = 0.00232   C2-H6 = 0.00292

DMol3 C1-C2-H6 = 111.46185   H3-C1-H4 = 107.40931
DFTB+ C1-C2-H6 = 110.80505   H3-C1-H4 = 108.09995
Diff   C1-C2-H6 = -0.65681   H3-C1-H4 = 0.69064
```

```
Atomization Diff = -64.02598
=====
```

ethene

DMol3 C2-C1 = 1.33543 C2-H5 = 1.09169

DFTB+ C2-C1 = 1.33113 C2-H5 = 1.09893

Diff C2-C1 = -0.00430 C2-H5 = 0.00724

DMol3 C1-C2-H6 = 121.65149 H4-C1-H3 = 116.69702

DFTB+ C1-C2-H6 = 121.55766 H4-C1-H3 = 116.88250

Diff C1-C2-H6 = -0.09383 H4-C1-H3 = 0.18548

Atomization Diff = -48.44674

=====

methane

DMol3 C2-H3 = 1.09771

DFTB+ C2-H3 = 1.09173

Diff C2-H3 = -0.00598

DMol3 H1-C2-H5 = 109.47122

DFTB+ H1-C2-H5 = 109.47021

Diff H1-C2-H5 = -0.00101

Atomization Diff = -39.03390

=====

Bond Error Statistics:

C-C = 6.68714e-003

C-H = 7.26190e-003

=====

Total Average = 7.01557e-003

Angle Error Statistics:

HCH = 2.92376e-001

CCC = 2.56980e-003

HCC = 2.50853e-001

=====

Total Average = 2.33180e-001

Your results will vary as the conformations for the perturb paths are randomly generated. An error for a bond distance below 0.02 Å is acceptable.

If you compare the evaluation data between the three parameterizations you will find that, as expected, the CH Para2 gives the best results. The CH Para1 parameterization shows acceptable results for all test structures. The CH Para3 parameterization performs very well but not as well as the CH Para2 parameterization.

The accuracy for bond types that give poor results can be improved by adding more data or, if the number of steps is already high, the weight for the corresponding path can be increased. It is also

possible that data from neighboring bond types disturb the fitting, in this case a decrease in the conformation width and the weight function width could counteract the problem.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Suggested further studies:

- Compare carbon nanotube band structures between DMol³ and the DFTB+ potential and density generated parameters. Notice that the band structure is independent of the short range potential so the CH Para1 and CH Para2 parameterizations should give the same result. You expect to see better results for the parameters generated using the potential mode.
- Expand the evaluation set, locate and try to correct poorly performing structures. Notice that sometimes the poor performance is due to missing physics and cannot be corrected.
- Expand the parameterization setup with a third element.

Simulating electron transport with DFTB+

Purpose: To introduce DFTB+ calculations on transport devices

Modules: Materials Visualizer, DFTB+

Time: 🕒🕒🕒

Prerequisites: Building transport devices for electron transport calculations Visualizer Tutorial, and Sketching a porphyrin, Working with isosurfaces and slices, Geometry optimization of a carbon nanotube

Background

DFTB+ is a semi-empirical tight binding method based on a two-centered approach to density functional theory (DFT). The use of a tight binding approach makes it faster than ordinary DFT methods but it also makes it dependent on parameter sets known as Slater-Koster libraries. Libraries are provided for standard organic molecules and semi-conductors.

The Electron Transport task in DFTB+ applies the non-equilibrium Green's function (NEGF) formalism to model electron transport between two or more electrodes. The Electron Transport task allows you to calculate properties such as transmission function and current voltage characteristics as well as potential charge density distributions.

Introduction

In this tutorial you will use the DFTB+ module to calculate transport properties for graphene nano ribbons.

This tutorial covers:

- [Getting started](#)
- [Initial preparation](#)
- [To set up the electron transport job](#)
- [To analyze the transmission](#)
- [To analyze the electron potential](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DFTB Transport** as the project name, click the **OK** button.

The new project is created with DFTB Transport listed in the Project Explorer.

2. Initial preparation

The first step is to import a graphene unit cell.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Examples\Documents\3D Model\Graphene.xsd**, then click the **Open** button.

From the graphene unit cell you will create a zig-zag graphene nanoribbon.

Select **Build | Symmetry | Supercell** to open the Supercell dialog. Set **B** to **6** and click the **Create Supercell** button. Close the dialog.

Delete the top-most hexagon and cap the edges with hydrogen atoms by clicking the **Adjust Hydrogen** button.




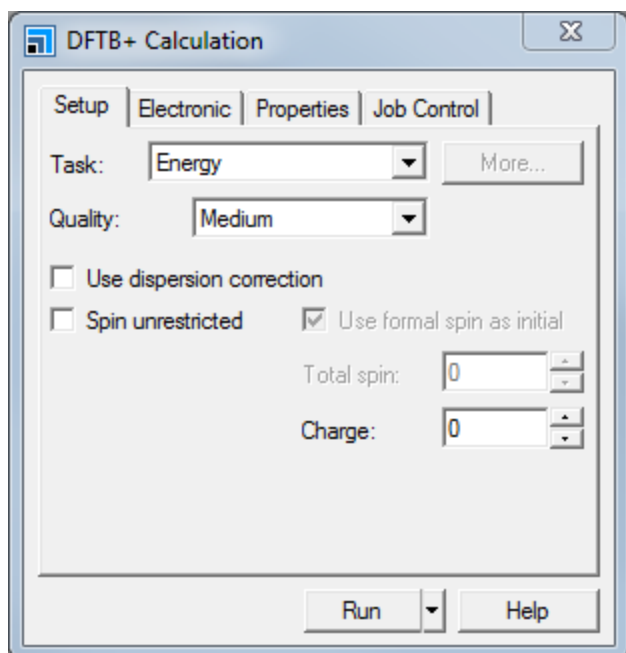
Graphene unit cell

Increase the lattice constants to avoid interaction between periodic copies.

Right-click in the document and select **Lattice Parameters**. On the **Advanced** tab uncheck the **Keep fractional coordinates fixed during changes to the lattice** checkbox. On the **Parameters** tab, set **b** to **80 Å** and **c** to **50 Å**. Close the dialog.

Optimize the geometry of the nano ribbon using the DFTB+ Geometry optimization task.

Click the **DFTB+**  button on the **Modules** toolbar and select **Calculation** or choose **Modules | DFTB+ | Calculation** from the menu bar.



DFTB+ Calculation dialog, Setup tab

Change the **Task** from Energy to **Geometry Optimization**. Click the **More...** button to open the Geometry Optimization dialog, check the **Optimize cell** checkbox and close the dialog.

Ensure the **Quality** is set to **Medium**.

On the **Electronic** tab set the **Slater-Koster library** to **mio**.

To improve the SCC convergence it is good to use a non-zero temperature for the calculation.

Check the **Use smearing** checkbox and set the **Smearing** to **0.001 Ha**.

Start the geometry optimization calculation.

Click the **Run** button and close the dialog.

A folder is created, Graphene DFTB+ GeomOpt, which will contain the optimized structure when the calculation is complete.

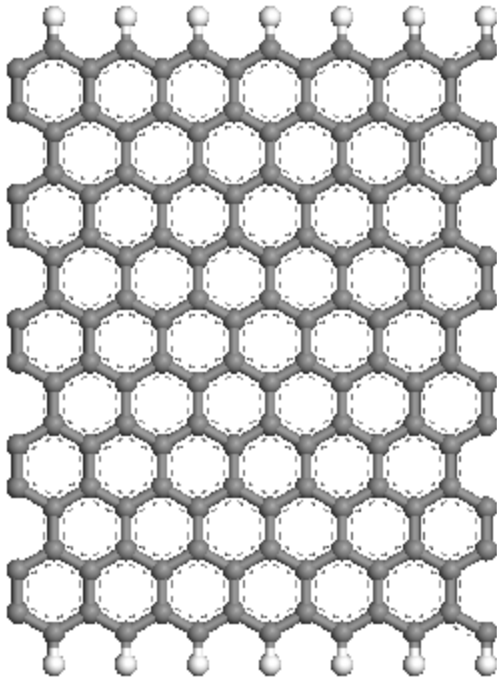
You will now use the optimized nanoribbon to create an ideal nanoribbon and a nanoribbon containing a quantum dot for transport.

Use copy and paste to create two copies of the optimized **Graphene.xsd** document in the top level of the project. Rename them **GrapheneWireIdeal.xsd** and **GrapheneWireQD.xsd**.

Ensure that **GrapheneWireIdeal.xsd** is the active document. Open the **Supercell** dialog and set **A** to **7**. Click the **Create Supercell** button.

Open the **Display Style** dialog, on the **Lattice** tab change the **Style** to **Original**.

Select **Build | Symmetry | Nonperiodic Superstructure** from the menu bar. Ensure the ends are straight and remove atoms until they are aligned as shown in this image.



Nanoribbon

The structure is now ready to have electrodes added to it.

Select **Build | Build Transport Device | Build Electrode** to open the Build Electrode dialog. Set **Electrode direction** to **-X** and click the **Build** button. Then set **Electrode direction** to **+X** and click the **Build** button again.

Use the optimized nano ribbon to create a nanoribbon with a central quantum dot.

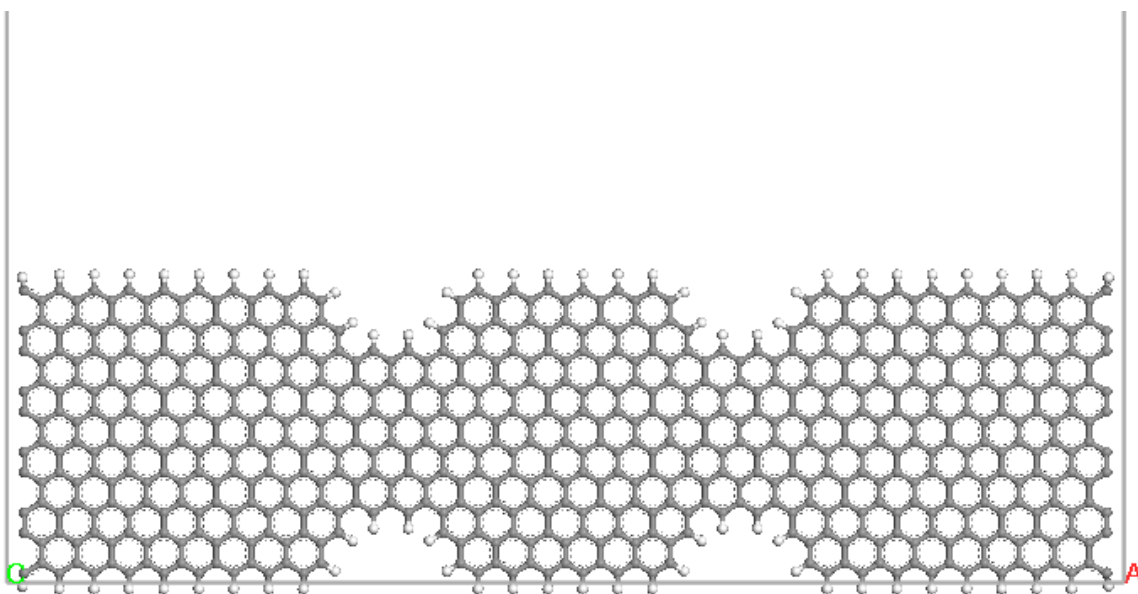
Make **GrapheneWireQD.xsd** the active document. On the **Supercell** dialog set **A** to **32** and click the **Create Supercell** button. Close the dialog.

Change the display style for the lattice to **Original** and close the Display Style dialog.

Remove atoms and cap the edges with hydrogen atoms using the **Adjust Hydrogen** tool to create the nanoribbon in the image below. Do not adjust the hydrogens for the terminal carbon atoms at the limits of the unit cell.

Tips:

- There are 18 carbons (9 hydrogens) on the left edges before the first defects and 18 carbons (9 hydrogens) on the right after the second defects.
- The central sections have 13 carbons (6 hydrogens) along the edge.
- You may need to remove some carbon atoms along the left side to obtain a structure matching the image below.



Nanoribbon with quantum dot

Tip: If you wish to geometry optimize the new structure it can be done now. Remember to constrain the atoms on both sides of the central structure to ensure that they remain periodic.

Once you are happy with the structure remove the periodicity and add electrodes to the end of the device.

Select **Build | Symmetry | Nonperiodic Superstructure** from the menu bar. Ensure the ends are straight, remove atoms until they are straight.

On the **Build Electrode** dialog, set **Electrode direction** to **-X** and click the **Build** button. Then set **Electrode direction** to **+X** and click the **Build** button again. Close the Build Electrode dialog.

Tip: If the *Build* button on the Build Electrode dialog is disabled, this means that the structure's periodicity is not sufficient. To improve the organization of the structure, click the *Clean* button (you may need to do this more than once before the Build button becomes enabled).

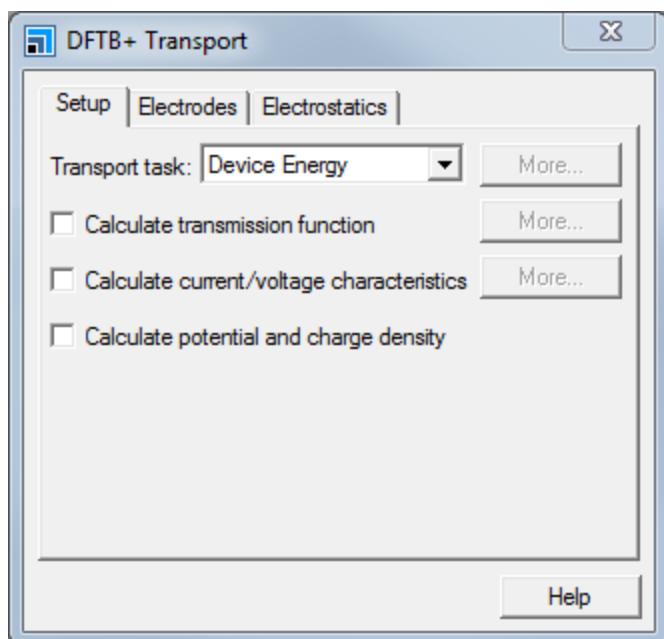
3. To set up the electron transport job

You now have two device structures ready for use with the DFTB+ Electron transport task.

Begin by setting up a calculation of the transmission for the ideal nanoribbon.

Make **GrapheneWireIdeal.xsd** the active document.

Open the **DFTB+ Calculation** dialog, on the **Setup** tab select **Electron Transport** from the **Task** to dropdown list. Click the **More...** button to open the DFTB+ Electron transport dialog.

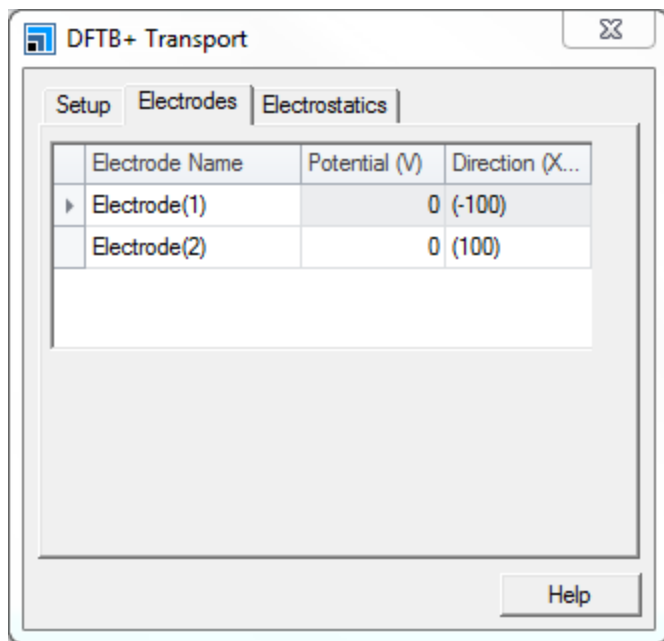


The DFTB+ Electron transport dialog contains settings specific to the Electron transport task.

Check the **Calculate transmission function** and **Calculate potential and charge density** checkboxes.

The job will now calculate the transmission functions between the electrodes and return data for electron potential and charge density.

Select the **Electrodes** tab.



The Electrodes tab shows information about and allows you to modify settings for the electrodes. Change the name of the electrodes.

Change the name of **Electrode(1)** to **source** and **Electrode(2)** to **drain** . Close the DFTB+ Transport dialog.

The names of the electrode objects are also modified in the 3D Atomistic document.

Note: If you use the Properties Explorer to change the name of electrodes, the electrode will use any settings related to *new* name. If no settings exist the default settings will be applied. When the name is changed on the DFTB+ Transport dialog the current settings will be used with the new name.

As part of the calculation each electrode will be modeled as a semiperiodic structure in order to calculate charge, potential and Fermi level. You need to set the k-point settings to be used for the calculation. For 2D periodic devices you also need to set the k-points perpendicular to the device. Employing the *Separation* setting allows you to specify a custom value of 0.02, this provides better sampling than the *Fine Quality* option.

Systems with open boundary conditions often have problems with convergence for the self consistent convergence. To improve the convergence reduce the mixing parameter for the charge mixing.

On the **Electronic** tab of the DFTB+ Calculation dialog click the **More...** button to open the DFTB+ Electronic Options dialog.

On the **SCC** tab set the **Max. SCC cycles** to **500** and the **Mixing amplitude** to **0.05**.

On the **k-points** tab select the **Separation** radio button and set a value of **0.02** 1/Å. Close the dialog.

You are now ready to start the transport job.

Click the **Run** button.

A text document named `Status.txt` is displayed, reporting the status of the calculation. This document is updated regularly until the calculation is complete, it can be a useful aid to indicate the progress of your calculation.

You will now set up a calculation for the nano ribbon with the central quantum dot.

First change the name of the electrodes to source and drain.

Make **GrapheneWireQD.xsd** the active document. Open the **DFTB+ Transport** dialog, on the **Electrodes** tab change the name of **Electrode(1)** to **source** and **Electrode(2)** to **drain**.

Since we expect the transmission spectra of this device to be more complex you should increase the number of steps for the transmission function.

On the **Setup** tab of the DFTB+ Transport dialog, click the **More...** button for **Calculate transmission function** and set the number of **Steps** to **401**. Close both dialogs.

You are now ready to launch the job.

Click the **Run** button and close the dialog.


4. To analyze the transmission function

When the calculations are complete the results are returned in the `GrapheneWireideal DFTB+ Transport` and `GrapheneWireQD DFTB+ Transport` folders in the Project Explorer.

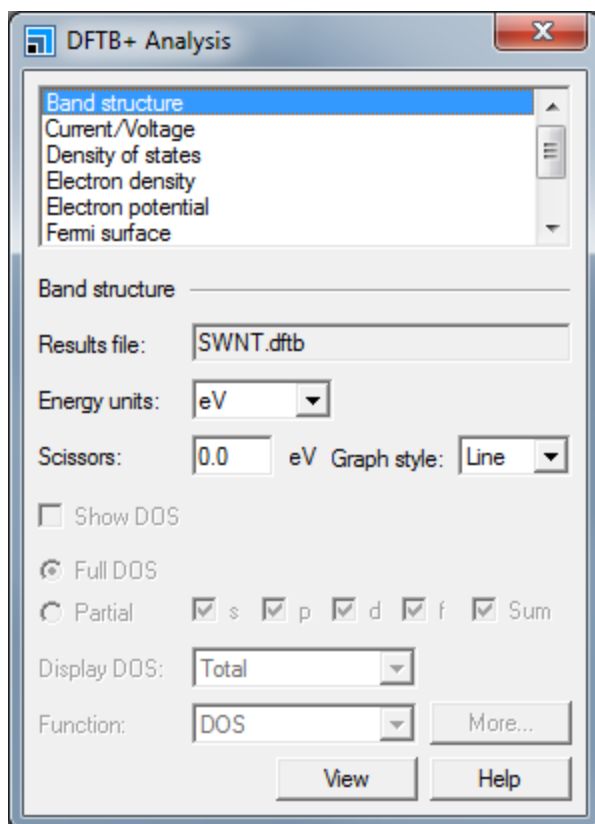
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

In the **GrapheneWireideal DFTB+ Transport** folder double-click on **GrapheneWireideal.xsd**

You will now analyze the results using the DFTB+ Analysis module.

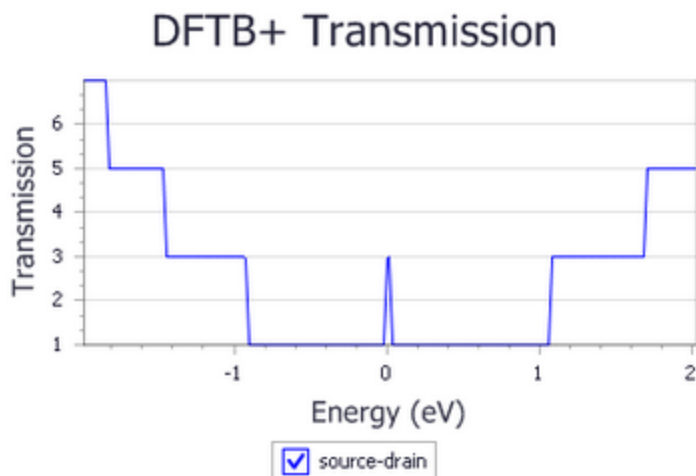
Click the **DFTB+**  button on the **Modules** toolbar and select **Analysis** or choose **Modules | DFTB+ | Analysis** from the menu bar.

This opens the DFTB+ Analysis dialog.



Select **Transmission** from the list and click the **View** button.

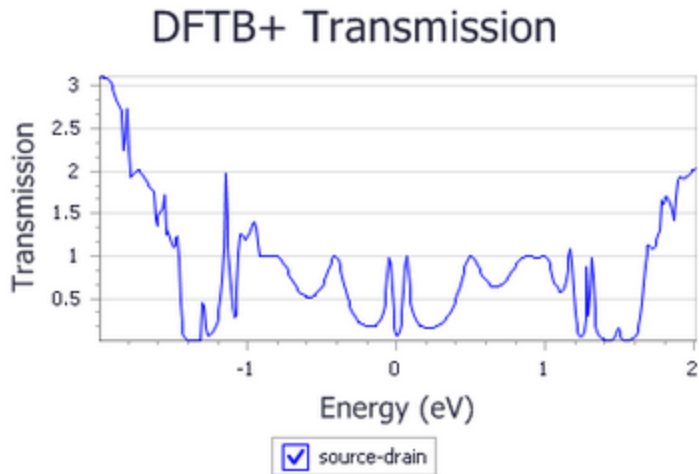
A plot of the transmission function is shown.



The transmission for an ideal wire will have a step like structure where the transmission value is equal to the number of available bands in the band structure for the wire. The energies of the transmission function are plotted relative to the lowest chemical potential of the electrodes. Notice that zig-zag nanoribbons have a characteristic peak at the Fermi level.

In the **GrapheneWireQD DFTB+ Transport** folder double-click on **GrapheneWireQD.xsd** and click the **View** button on the **DFTB+ Analysis** dialog.

This shows the transmission function for the nanoribbon with a quantum dot.



Note: If your Transmission chart has two graphs plotted (one for drain-source and the other for source-drain) this indicates that your electrodes are not symmetric. In this case the graphs correspond to transmission in each direction, a single graph indicates that transmission is identical in both directions.

The quantum dot causes electrons to scatter and creates a more complicated transmission function.


5. To analyze the electron potential

Further insight into the electron transport properties of the structure can be gained.

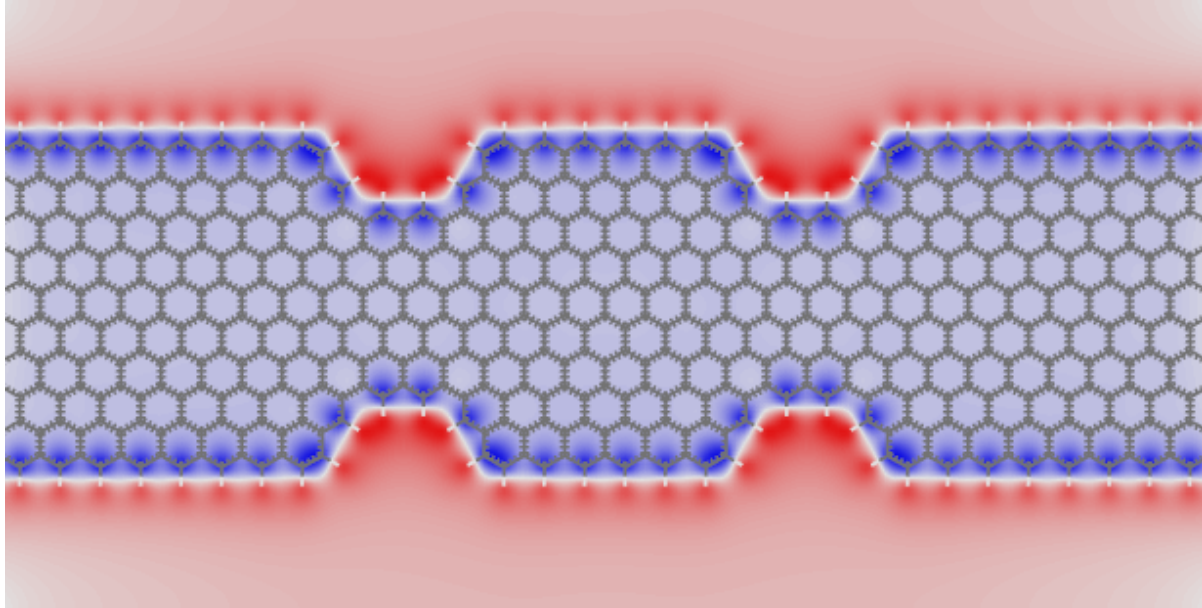
Select **Electron potential** from the list and uncheck the **View isosurface on import** checkbox. Make **GrapheneWireQD.xsd** the active document and click the **Import** button.

This imports the electron potential field to the document.

Click the arrow for the **Create Slices** button  on the toolbar and select **Parallel to A & B axis**.

Click the **Color Maps** button  to open the Color Maps dialog, change the range to **-0.85** and **0.85** and set the **Spectrum** to **Blue-White-Red**.

This creates a slice along the X and Y plane of the structure where blue is negative potential and red is positive potential.



The hydrogen atoms have a large positive potential while the carbon atoms have a large negative potential at the surface and a potential close to zero in the central region.

This is the end of the tutorial.

DMol³ tutorials

The following tutorials illustrate how to utilize DMol³'s capabilities.

- [Computing band structure and density of states with DMol³](#)
- [Geometry optimization for solids using delocalized internal coordinates in DMol³](#)
- [Transition state searching using LST/QST tools](#)
- [Calculating the free energies of chemical reactions](#)
- [Exploring the minimum energy path of chemical reactions using DMol³'s LST/QST and NEB tools](#)
- [Calculating optical properties of Coumarin](#)
- [Kinetics of a Diels-Alder reaction](#)
- [Simulating electron transport with DMol³](#)

Computing band structure and density of states with DMol³

Purpose: To introduce the electronic properties of band structures and density of states.

Modules: Materials Visualizer, DMol³

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Extended periodic systems can be characterized by their energy bands, which are analogous to orbital eigenvalues in molecular systems. Unlike the orbital eigenvalues, the energy of each band varies at different points in *reciprocal space*. The bands are conventionally plotted in the reciprocal space to show the dispersion of eigenvalues in different directions. There are a limited number of unique high symmetry directions in reciprocal space, so only a finite number of points are needed to characterize the bands. By observing the energy gaps between bands at various points, it is possible to draw conclusions about the nature of a material; whether it is an insulator, a conductor, or a semiconductor.

Another way of characterizing the electronic structure of a material is by the density of states (DOS). The DOS counts the relative number of energy levels in each energy range. In a molecule, there are distinct energy eigenvalues, so the DOS has a value of 1 at each of these values and a value of 0 elsewhere. In contrast, for a crystal the energy levels constitute a continuum, and DOS charts provide a useful tool for qualitative analysis of the electronic structure of the material. Examining the DOS also allows you to see whether a system is conducting or insulating. In addition, the partial density of states (PDOS) allows you to characterize the DOS in terms of the contributions from particular atomic orbitals, s, p, d, or f.

Introduction

In this tutorial, you will use DMol³ to compute and analyze the band structure, DOS, and PDOS of a semiconductor.

This tutorial covers:

- [Getting started](#)
- [To set up the DMol³ calculation](#)
- [To control the job settings and running the job](#)
- [To analyze the band structure](#)
- [To analyze the DOS and PDOS](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **AIAs_DOS** as the project name, click the **OK** button.

The new project is created with *AIAs_DOS* listed in the Project Explorer. Now you will import the input file you will be studying.

The next step is to import the structure that you will analyze. Materials Studio includes a wide range of prebuilt structures. In this tutorial, you will perform calculations on AIAs (a semiconductor).

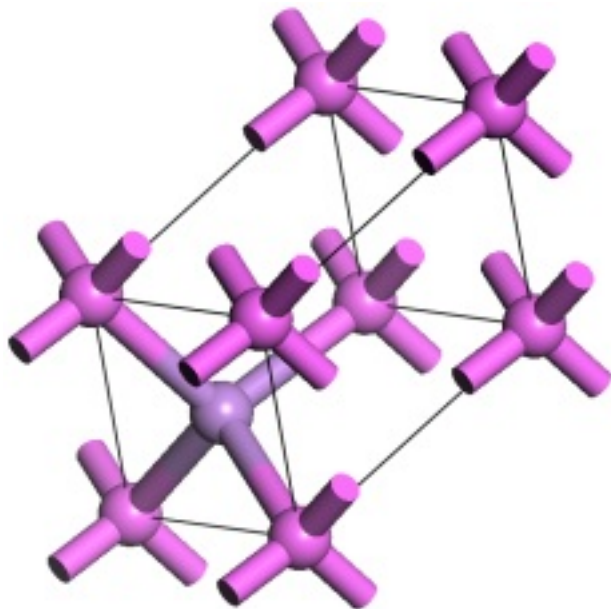
Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Structures\semiconductors\AIAs.msi**, then click the **Open** button.

The structure of AIAs is displayed. The crystal structure in the 3D Viewer is the conventional unit cell, which shows the cubic symmetry of the lattice.


2. To set up the DMol³ calculation

DMol³ uses the full symmetry of the lattice, if any exists. The primitive lattice, containing 2 atoms per unit cell, can be used instead of the conventional cell, which contains 8 atoms. The charge density, bond distances, and total energy per atom will all be the same no matter how the unit cell is defined. By using fewer atoms in the unit cell, the computation time will be decreased.

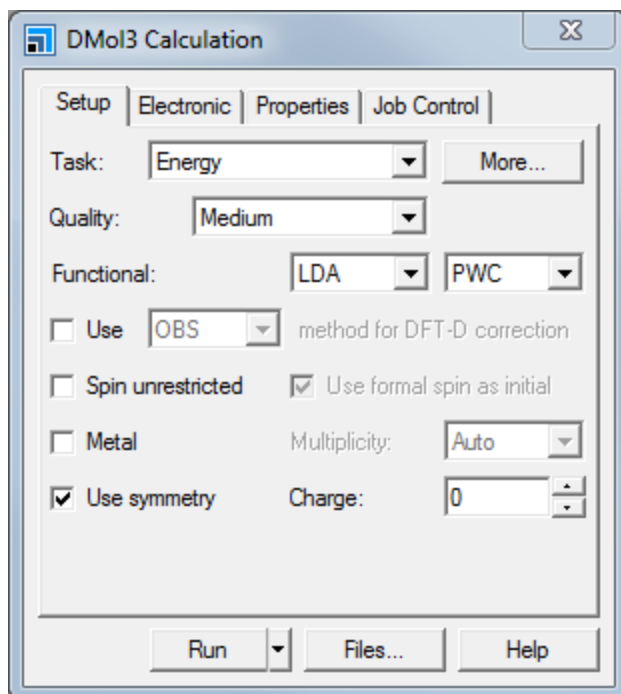
Choose **Build | Symmetry | Primitive Cell** from the menu bar.



The primitive cell of AlAs

Click the **DMol3** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.



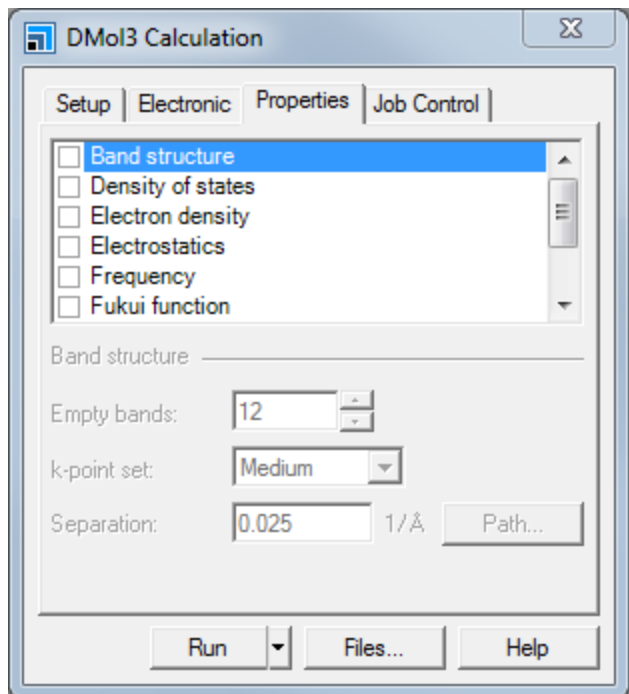
DMol3 Calculation dialog, Setup tab

Select **Energy** from the **Task** dropdown list. Set the **Functional** to **LDA** and **PWC**, and the **Quality** to **Medium**.

You will use all the default options for the *Medium* quality setting, there is no need to change any of the other calculation parameters.

Select the **Properties** tab.

This tab allows you to calculate certain properties after the structure is optimized.



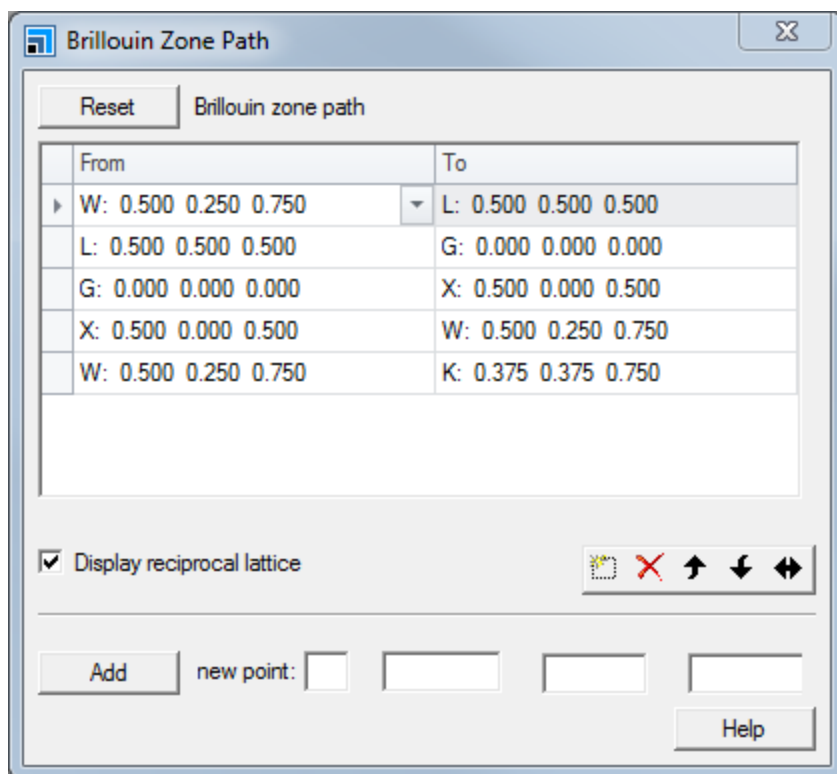
DMol3 Calculation dialog, Properties tab

Check the **Band structure** checkbox.

Notice that the default number of *Empty bands* to be included is 12 and the default value of *k-point set* is *Medium*. These values are suitable for most applications. However, you should examine the k-point set in more detail.

Click the **Path...** button to display the Brillouin Zone Path dialog. Click the **Create** button.

The button name changes to **Reset** when the Brillouin Zone has been created.



Brillouin Zone Path dialog

The structure in the 3D Viewer is updated to display the reciprocal lattice in light blue and the Brillouin zone paths in magenta, the k-points are labeled with the letters reported on the Brillouin Zone Path dialog.

Each row of the table indicates a path through symmetry-unique points in the Brillouin zone. The coordinates are given in fractional coordinates in reciprocal space. In row 1, for example, a path will be traced from $[0.5, 0.25, 0.75]$ to $[0.5, 0.5, 0.5]$. The energy will be computed at a number of points along the path, and the results will be displayed as a plot of electron energy vs k-vector. By convention, each of the high symmetry points in Brillouin zone is assigned a letter. As you can see, for example, *W* corresponds to $[0.5, 0.25, 0.75]$. The gamma point, Γ , represented here by *G*, corresponds to $[0, 0, 0]$.

Using the controls at the bottom of the panel, you can add or delete rows or you can change the value of the coordinates. You could also change the number of divisions along each segment of the path by changing the value of *k-point set* on the *Properties* tab. However, you do not need to change any of these values for this tutorial.

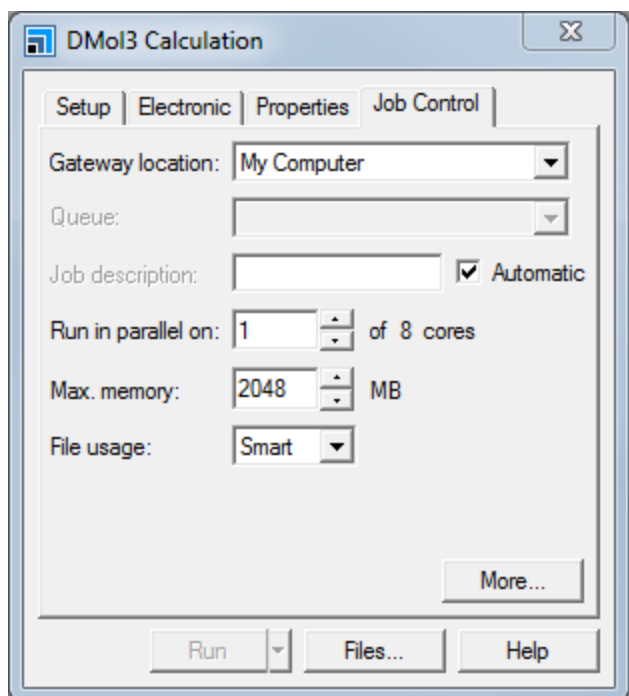
Close the Brillouin Zone Path dialog.

On the **Properties** tab check the **Density of states** and **Calculate PDOS** checkboxes to compute the full and partial density of states.

3. To control the job settings and running the job

You will use the commands on the *Job Control* tab to control the DMol³ calculation.

Select the **Job Control** tab.



DMol3 Calculation dialog, Job Control tab

Here, you can choose the gateway location where you will run your calculation and set various options, such as the job description, whether the job will be launched using multiple cores, and the number of cores to employ. You can access further job options by clicking the *More...* button, including live update settings and controls that determine what happens when the job completes.

You are now ready to run your DMol³ calculation.

Click the **Run** button and close the dialog.

The Job Explorer opens, containing information about status of the calculation.


A text document called `Status.txt`, containing the DMol³ run status opens. This document is updated regularly until the calculation is complete.

4. To analyze the band structure

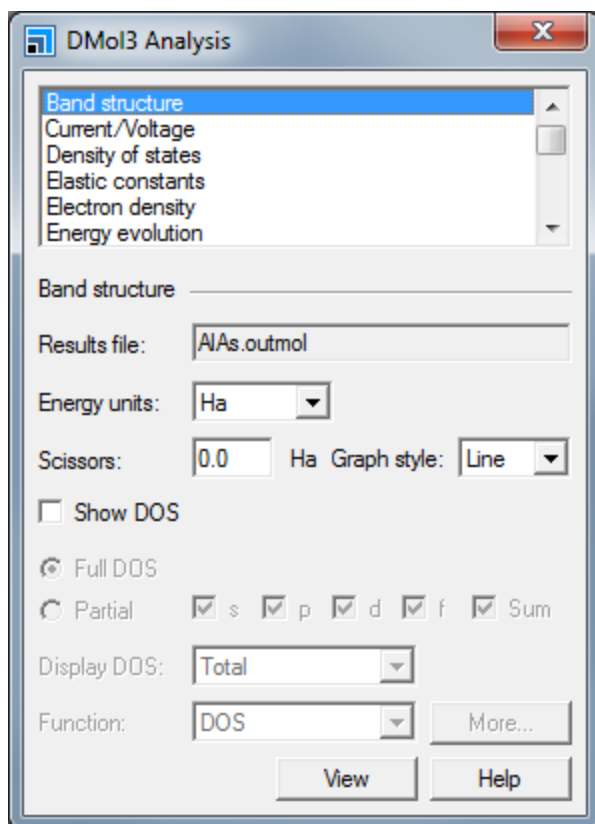
When the calculation is complete, the results are returned to the A1As DMol3 Energy folder in the Project Explorer.

In the **A1As DMol3 Energy** folder, double-click on **A1As.xsd**.

The A1As structure is displayed. The crystal structure is the same as that of the original, but this structure has results associated with it from running a DMol³ calculation. In the remainder of this tutorial, you will analyze the band structure and DOS results.

Click the **DMol3** button  on the **Modules** toolbar and choose **Analysis** or select **Modules | DMol3 | Analysis** from the menu bar.

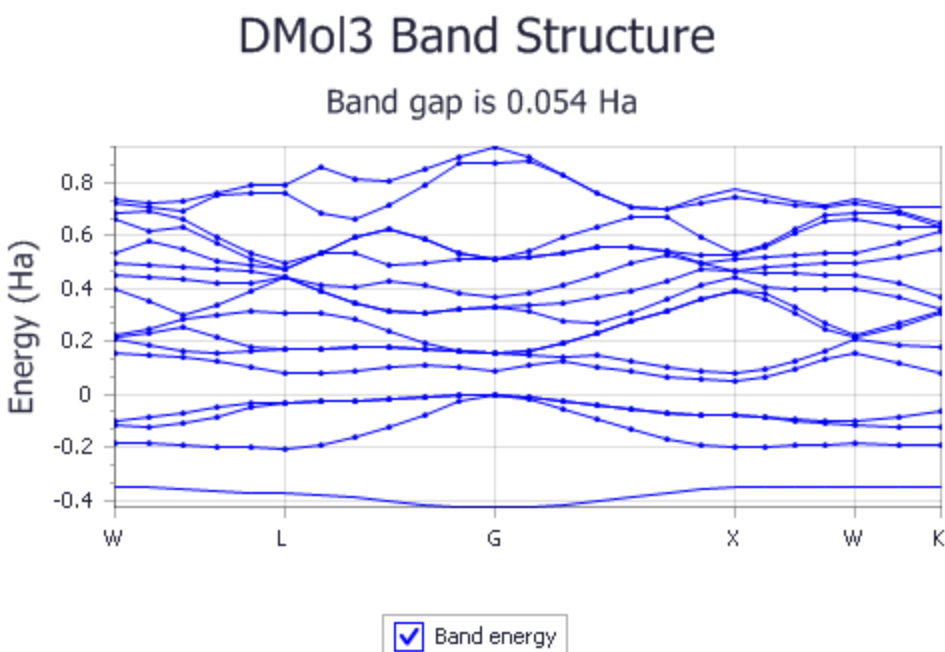
This opens the DMol3 Analysis dialog.



DMol3 Analysis dialog, Band structure selection

Select **Band structure** from the list and click the **View** button.

A band structure plot is displayed.



DMol³ band structure for AIAs

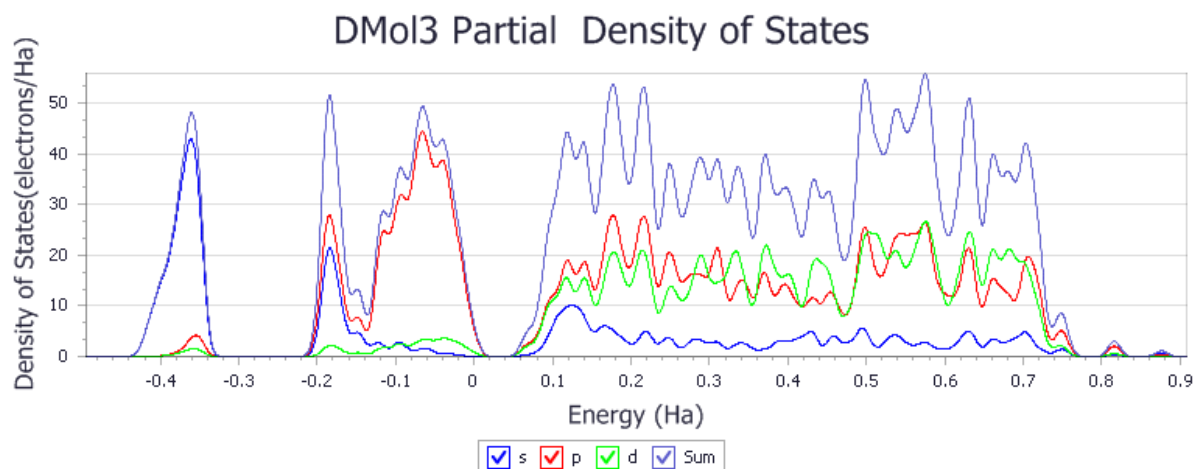
The energies of the bands are plotted with respect to the Fermi level, which is assigned a value of zero. Notice that the band gap at the Γ point, (G), is only about 0.1 Hartree, indicating that this is a semiconductor. You can use the zoom controls to expand this area of the chart and measure the band gap more precisely. The actual band gap is reported in the chart as 0.054 Ha (1.5 eV) and you can see from the plot that AIAs has an indirect band gap in qualitative agreement with experimental findings [1]. The absolute value of the band gap is underestimated by the density functional approach, with the experimental band gap at low temperatures being about 2.2 eV.

5. To analyze the DOS and PDOS

In the **AIAs DMol3 Energy** folder, double-click on **AIAs.xsd**.

Select **Density of states** on the DMol3 Analysis dialog. Click the **Partial** radio button and check the **s**, **p**, **d**, and **Sum** checkboxes. Click the **View** button.

A PDOS plot is displayed.



DMol³ PDOS for AIAs

Examine the number of energy states at the Fermi level, where Energy = 0. An insulator will have a distinct gap, while a conductor will have many states. The plot here is typical of a semi-conductor. Notice that you can see how many of the states arise from each type of orbital, s, p, or d.

It also is possible to see how many of the states are associated with a particular atom in the structure.

In the **AIAs DMol3 Energy** folder, double-click on **AIAs.xsd**.

Select one of the Al atoms by clicking on it (the Al atoms are at the corners of the cell).

Recreate the PDOS chart using the same procedure as above.

Now, select the As atom in AIAs and create another PDOS plot for this atom.

Compare the results for Al, As, and for the entire unit cell.

Tip: In order to improve the quality of DOS and PDOS plots you can change the integration method employed for the density of states calculation.

Click the *More...* button on the DMol3 Analysis dialog when *Density of states* is selected, this opens the *DMol3 DOS Analysis Options* dialog. Select **Interpolation** from the *Integration method* dropdown list and **Fine** as the *Accuracy level*. Click the *OK* button and then the *View* button on the DMol3 Analysis dialog. This will produce more accurate DOS, with sharper features and more clearly defined band gap.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

[1] [Semiconductors Information](#)

Geometry optimization for solids using delocalized internal coordinates in DMol³

Purpose: To introduce the use of the delocalized internal coordinate optimizer for periodic systems and the volume visualization tools.

Modules: Materials Visualizer, DMol³

Time: 🕒🕒🕒

Prerequisites: Working with isosurfaces and slices Visualizer Tutorial

Background

DMol³'s delocalized internal coordinate optimization scheme for molecules provides good performance for large molecular systems. This scheme has been extended to periodic systems in DMol³ in Materials Studio.

The new optimizer, built on the delocalized internal coordinates, also has the capability to handle:

- Highly coordinated systems such as close packed solids
- Fragmented systems, such as molecular crystals, in which the internal coordinates do not span the optimization space
- The inclusion of Cartesian constraints during the optimization process

In-house validation work shows that this state-of-the-art delocalized internal coordinate optimization scheme for periodic systems is typically 2-5 times more efficient than the Cartesian approaches that are the standard in solid-state calculations today.

Introduction

In this tutorial you will use the DMol³ optimizer, employing delocalized internal coordinates to perform a geometry optimization on a zeolite structure.

This tutorial covers:

- [Getting started](#)
- [To set up the DMol³ calculation](#)
- [To control the job settings and run the job](#)
- [To examine the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

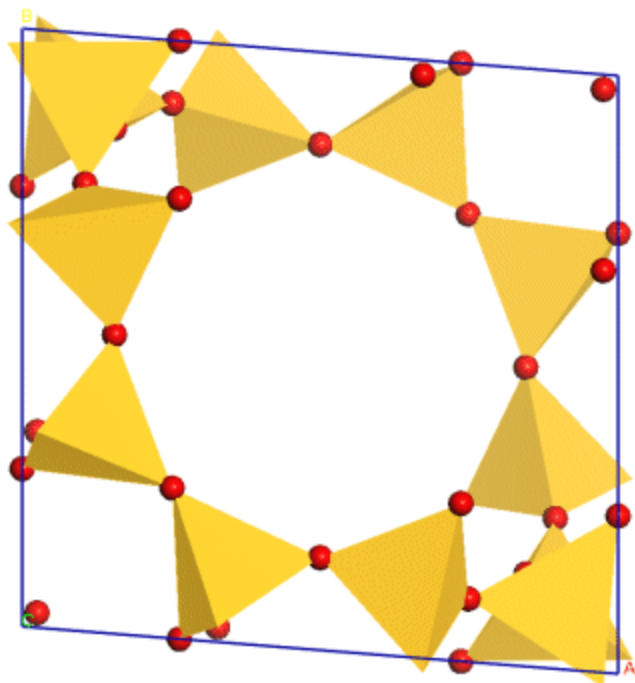
Open the **New Project** dialog and enter **Chabazite** as the project name, click the **OK** button.

The new project is created with *Chabazite* listed in the Project Explorer. The next step is to import the zeolitesheet structure that you want to optimize. Materials Studio has a wide range of prebuilt zeolite structures. In this tutorial you will optimize chabazite.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Examples\Documents\3D Model\CHA.xsd**, then click the **Open** button.


Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Click the **Polyhedron** radio button and close the dialog.

The structure of CHA is displayed as polyhedra in the 3D Viewer.

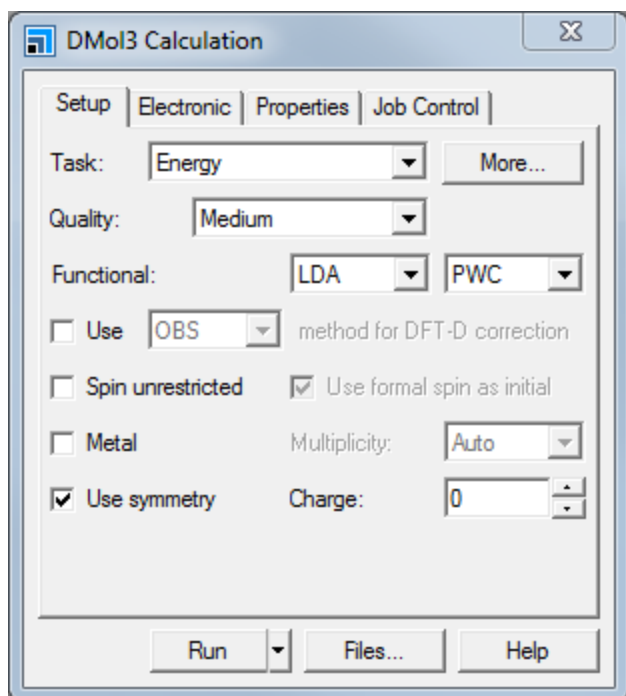


A unit cell of chabazite

2. To set up the DMol³ calculation

Click the **DMol3**  button on the **Modules** toolbar and select **Calculation** or choose **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.

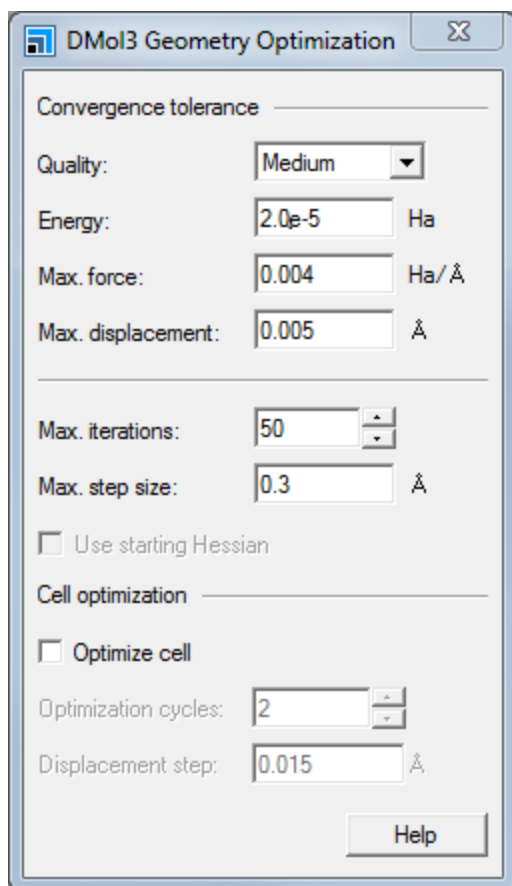


DMol3 Calculation dialog, Setup tab

Set the **Task** to **Geometry Optimization**. Change the **Functional** from LDA, PWC to **LDA, VWN**.

The LDA/VWN functional is adequate for covalent solids like a zeolite.

Click the **More...** button to open the DMol3 Geometry Optimization dialog,

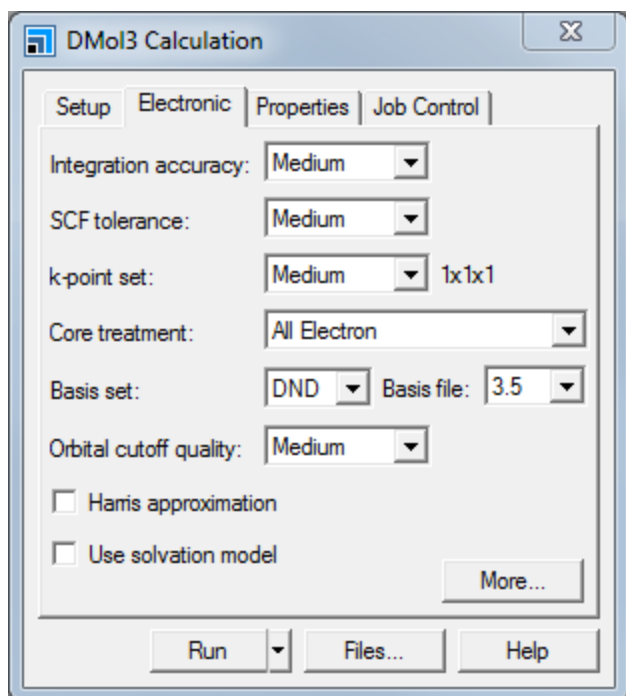


DMol3 Geometry Optimization dialog

You can set your convergence tolerance by changing the *Quality* level or by editing the values individually. The default **Medium** setting for the *Quality* selects various options such as basis set, integration grid, and convergence thresholds. These are selected to yield reliable results in most cases, while keeping computational costs reasonable.

Leave the **Quality** at **Medium** and close the dialog. On the **DMol3 Calculation** dialog, select the **Electronic** tab.

The *Electronic* tab on the DMol3 Calculation dialog is displayed. This tab contains parameters associated with the electronic Hamiltonian.



DMol3 Calculation dialog, Electronic tab

You will explore some of the options that are available to reduce the computational cost of a calculation. The options you will change on this tab are the *k-point set* and the *Orbital cutoff quality*.

Set the **k-point set** to **Gamma** and the **Orbital cutoff quality** to **Coarse**. Click the **More...** button to display the DMol3 Electronic Options dialog.

On the **Orbital Cutoff** tab the orbital cutoff is set to **3.5 Å**.

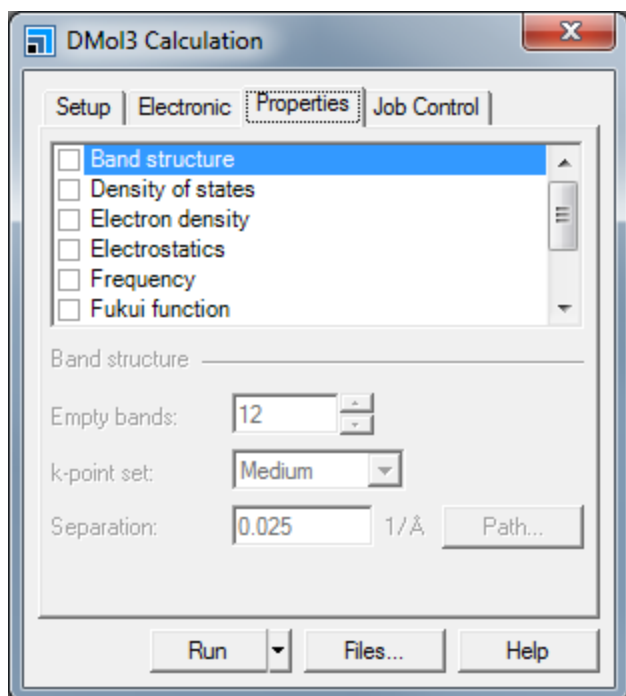
This text box allows you to customize the orbital cutoff value, giving access to more precise values than the *Orbital cutoff quality* dropdown list on the Electronic tab of the DMol3 Calculation dialog.

Close the DMol3 Electronic Options dialog.

Tip: The DMol3 Electronic Options dialog also allows you to exercise greater control over the SCF and k-point electronic Hamiltonian parameters.

Select the **Properties** tab on the DMol3 Calculation dialog.

The *Properties* tab is displayed and this allows you to calculate certain properties after the structure is optimized.



DMol3 Calculation dialog, Properties tab

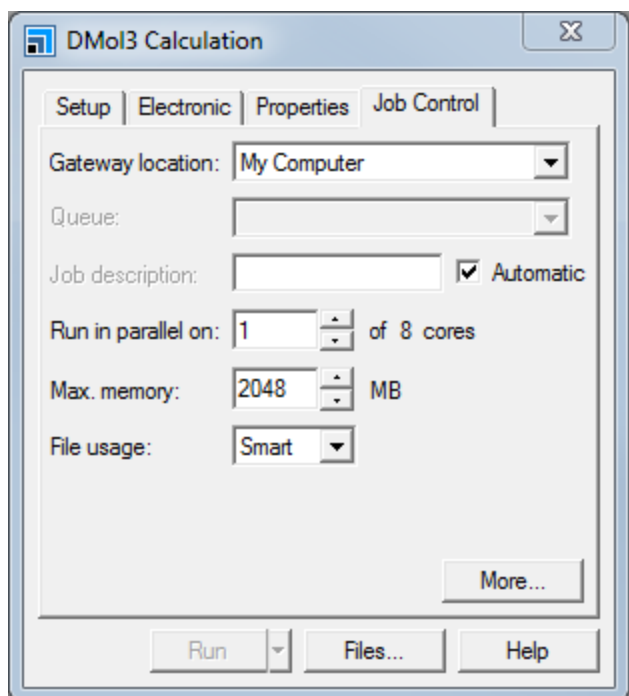
Check the **Electron density** and **Electrostatics** checkboxes.

3. To control the job settings and run the job

You will use the commands on the *Job Control* tab to control the DMol³ calculation.

Select the **Job Control** tab on the DMol3 Calculation dialog.

The *Job Control* tab is displayed.



DMol3 Calculation dialog, Job Control tab

From this tab, you can choose the gateway location where you will run your calculation and set various options such as the job description, whether the job will be launched using multiple processors, and the number of processors to employ. You can access further job options by clicking the *More...* button to open the DMol3 Job Control Options dialog. You can specify live update settings and what happens when the job completes.

You are now ready to run your DMol³ geometry optimization.

Click the **Run** button and close the dialog.

The Job Explorer opens, containing information about status of the calculation.

A text document called *Status.txt* containing the DMol3 Run Status opens. This is a live document that is updated regularly until the calculation is complete. Shortly after that, two chart documents are displayed, *CHA Energies.xcd* and *CHA Convergence.xcd*, which refer to the optimization and convergence status of the calculation. These can be useful visual aids to indicate the progress of your calculation.



4. To examine the results


When the calculation is complete, the results are returned to the *CHA DMol3 GeomOpt* folder in the Project Explorer.

In the **CHA DMol3 GeomOpt** folder, double-click on **CHA.xtd**.

The zeolite CHA structure is displayed in a 3D model window. This is a trajectory document containing the geometry optimization progress. Its history can be viewed using the controls on the Animation toolbar.

If the **Animation toolbar** is not visible, select **View | Toolbars | Animation** from the menu bar.

On the Animation toolbar, click the **Play** button  to view the sequence of changes in the optimization process. When you have finished viewing the animation, click the **Stop** button .

Tip: Click the **Animation Mode** arrow  on the Animation toolbar and select **Options** to open the Animation Options dialog. You can use this to view individual frames, change the playback speed, and the start and end frames.


The final total energy can be viewed in the `.outmol` file document.

Use the **Project Explorer** to change the focus to **CHA.outmol**. Scroll down the document to find the total energy.

The `.xsd` document contains the optimized structure.

In the **Project Explorer**, double-click on **CHA.xsd** in the **CHA DMol3 GeomOpt** folder.

To visualize the properties that you calculated, you need to analyze the output documents.

Click the **DMol3**  button on the **Modules** toolbar and select **Analysis** or choose **Modules | DMol3 | Analysis** from the menu bar.

This opens the DMol3 Analysis dialog.

Select **Electron density** and check that the correct `.outmol` file is displayed in the **Results** box. Set the **Density field** to **Total density** and check the **View isosurface on import** checkbox. Click the **Import** button.

The total electron density is displayed on the zeolite.

Zoom in and rotate to inspect the structure.

You can change the display style of the isosurface but first you should change the atom display style.

Open the **Display Style** dialog and, on the **Atom** tab, choose the **Stick** display style. Select the **Isosurface** tab.

You can change the transparency of your displayed isosurface with the *Transparency* ruler. You can also change the display style of your isosurface by checking the *Dots* or *Solid* options.

Change the **Transparency** by dragging the ruler to the next mark.

You can also control the size of the isosurface.

Change the **Isovalue** to **0.1** and press the **TAB** key. Change it back to **0.2** and press the **TAB** key again.

Once you have the electron density isosurface, you can map other calculated properties onto it.

On the **DMol3 Analysis** dialog, select **Potentials** and uncheck the **View isosurface on import** checkbox. Click the **Import** button and close the dialog.

On the **Display Style** dialog, select the **Isosurface** tab. Select **DMol3 electrostatic potential Ha*electron(-1)** from the **Mapped field** dropdown list and close the dialog.

The electrostatic potential is mapped onto the electron density isosurface. You can change the color of the mapped field by using the Color Map dialog.

Right-click in the 3D Viewer and select **Color Maps** from the shortcut menu.

This opens the Color Maps dialog; you can change the color scheme, mapped values, and number of bands displayed.


Change the **Spectrum** to **Blue-White-Red**. Click the **right-arrow** for **From** and select **Mapped Minimum**. Click the **right-arrow** for **To** and select **Mapped Maximum**. Close the dialog.

The colors on the isosurface change to reflect the minimum and maximum values associated with the field you have mapped onto the electron density.

You can access more volumetric visualization tools from the Volume Visualization toolbar.

Select **View | Toolbars | Volume Visualization** from the menu bar.

You can add a slice to the structure.

Click the **Create Slices** arrow  and select **Best Fit** to open the **Choose Fields to Slice** dialog. Select **DMol3 electrostatic potential** and click the **OK** button.

A slice is displayed through the electrostatic potential. This slice uses the minimum and maximum values of the entire field. To see the maximum and minimum in the specific area covered by the slice, you need to use the Color Maps dialog again.

Click the **Color Maps** button  and select the slice.

When you select a slice, a dashed yellow line is displayed around the edge of it and a cross is displayed in the middle of the selected slice.

Click the **right-arrow** for **From** and select **Mapped Minimum**. Click the **right-arrow** for **To** and select **Mapped Mean**. Change the **Spectrum** to **Blue-White-Red**.

There are some high maximum values in this section of the grid that you do not need to view and this is why you selected *Mapped Mean* rather than *Mapped Maximum*. You can remove the display of certain values from the field by using the Color Maps dialog.

Click the **Red right-arrow** for the color bar.

All the data points above the mean value are removed from the slice. You can also remove individual colors from the color bar by clicking on them, change the colors from the *Spectrum* dropdown and increase the number of bands.

Click the **| |** button on the right of the color bar so that colors are displayed above the mean value.
Close the **Color Maps** dialog.

You can change the display styles of the slice from the *Slice* tab on the Display Style dialog.

Open the **Display Style** dialog and, on the **Slice** tab, drag the **Transparency** to the right.

As you drag the *Transparency* ruler, the transparency of the slice changes.

When you have finished working with the slices and isosurfaces, you can remove them by selecting them in the 3D Viewer and pressing the DELETE key.

Select the slice and press the **DELETE** key. Repeat this for the **isosurface**.

More information about manipulating slices, including translation and rotation of them can be found in the Creating and customizing slices topic.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Transition-state searching using LST/QST tools

Purpose: Introduces the use of DMol³ and the Reaction Preview tool to perform a transition-state search calculation. The transition state of a simple reaction is calculated and validated.

Modules: Materials Visualizer, DMol³

Time: 🕒 🕒

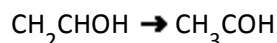
Prerequisites: [Geometry optimization for solids using delocalized internal coordinates in DMol3](#)

Background

Exploring the potential energy surface of any reaction requires both structural and energetic, or kinetic and thermodynamic, snapshots of each step in the reaction process. Of particular importance is the rate determining step, which usually involves finding the elusive transition-state structure. A few techniques have been well validated for finding a transition-state structure and among the better known of these are linear synchronous transit (LST) and quadratic synchronous transit (QST).

Introduction

This tutorial aims to introduce to you the LST/QST tool in DMol³. In this tutorial, you will learn how to use the LST/QST tool to find a transition-state structure for a hydrogen transfer reaction from vinyl alcohol to acetaldehyde.



This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculation](#)
- [To define the atom pairing](#)
- [To calculate the transition state using the LST/QST/CG method](#)
- [To refine the transition state](#)

Note: Completion of this tutorial entails running a DMol³ transition-state search. Depending on the configuration of your compute server, this calculation could take a considerable amount of time.

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.



Open the **New Project** dialog and enter **vinylOH** as the project name, click the **OK** button.

The new project is created with *vinylOH* listed in the Project Explorer.

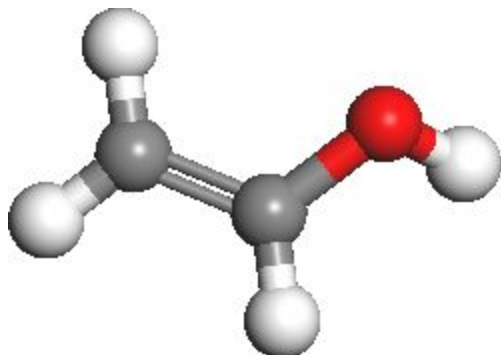
2. To prepare the structures for the calculation

In this section of the tutorial, you will build the reactants and products in two different 3D Atomistic documents. The first step is to open a new 3D Atomistic document and sketch the reactant, vinyl alcohol.


Click the **New** button  on the **Standard** toolbar and select **3D Atomistic Document** from the dropdown list.

Use the **Sketch** tools to draw a vinyl alcohol molecule. Click the **Adjust Hydrogen** button  and then the **Clean** button .

Move the structure so it looks similar to the one shown below (shown in ball and stick display style).



Rename the new document **reactant.xsd**.

Choose the **Selection** tool  on the **3D Viewer** toolbar. Double-click on any of the atoms in the vinyl alcohol structure to select all of the atoms.

Now all the vinyl alcohol atoms are selected and colored yellow.

Press the **CTRL + C** keys.

This copies the contents of the document to the clipboard.

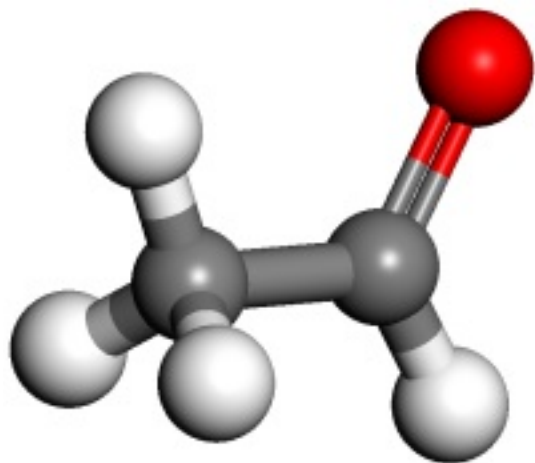
Use the **New** button to create a new 3D Atomistic document. Press the **CTRL + V** keys.

The structure is pasted into the new 3D Atomistic document. Now you have to change the bonding and rearrange the atoms to obtain the product structure.

In the new 3D Atomistic document, select the **O-H** bond and press the **DELETE** key. Click the **Sketch Atom** button, then click the lone **H** atom followed by the terminal **C** atom.

Click once on the **C-O** bond to change the bond type from single to double. Click twice in succession on the **C-C** bond to toggle the bond type from double to triple to single. Click the **Clean** button.

The structure should look similar to the one shown below.



Before continuing, you need to change the name of the document.

Rename the document **product.xsd**.

3. To define the atom pairing

For DMol³ to perform a transition-state search, all the atoms in the reactant and product documents need to be paired. This is performed using the Reaction Preview functionality on the *Tools* menu.

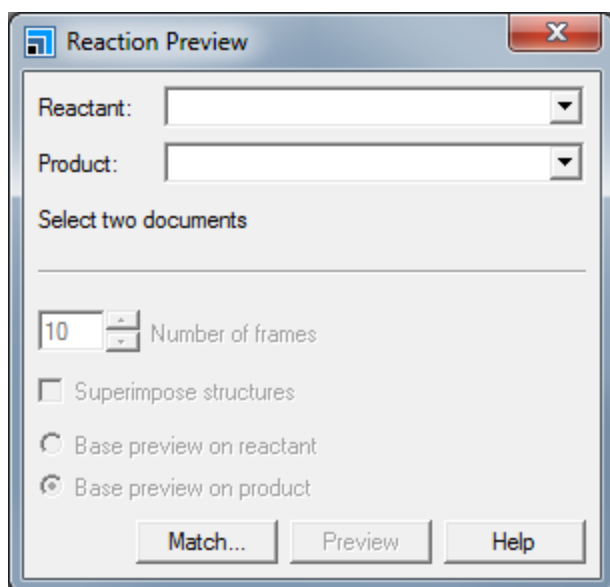
First, you should display the reactant and product structures side-by-side.

Select **Window | Tile Vertically** from the menu bar.

Now you are ready to start pairing atoms in the reactant and product structures.

Select **Tools | Reaction Preview** from the menu bar.

This opens the Reaction Preview dialog.



Reaction Preview dialog

Select the **reactant.xsd** and **product.xsd** documents from the **Reactant** and **Product** dropdown tree views. Click the **Match...** button to open the Find Equivalent Atoms dialog.

You should see that one atom is matched and six atoms are unmatched.

Double-click on **2xC** in the reactant column.

The corresponding folder in the product column also opens. The reactant column should contain **1:C** and **2:C**. These should map directly onto their counterparts in the products window, but take the following steps to make sure.

Click on **1:C** in the reactant pane and **1:C** in the product pane.

The carbon atoms in both panes should be selected and these should be identical in the two 3D Atomistic documents.

If they represent equivalent atoms, click the **Auto Find** button.

The Find Equivalent Atoms algorithm matches all of the remaining heavy atoms.

Tip: If some unmatched atoms remain, repeat the manual pairing step above on the next unmatched atom pair, but now click on *Set Match* instead. Repeat this procedure for the rest of the unmatched atom pairs or click on *Auto Find*.

You can review the matched atoms list between reactant and product.


Click on one of the atoms in the list in either the reactant or product column to review the proper pairing until you are satisfied with the matches. **Close** the Find Equivalent Atoms dialog.

To perform a transition-state search with the DMol³ LST/QST functionality, you need to create a pathway between the reactant and product as it is required as input to the DMol³ calculation.

Click on the project root in the Project Explorer. On the Reaction Preview dialog, increase the **Number of frames** to **100** and check the **Superimpose structures** checkbox. Click the **Preview** button and close the dialog.

Within a few seconds, a new 3D Atomistic Trajectory document entitled `reactant-product.xtd` is displayed. You will run the DMol³ calculation on this file. You can animate the trajectory document using the tools on the *Animation* toolbar. The animation looks best in *Bounce* mode. You can switch on bond monitoring so that it recalculates the bonds after each step.

Select **Build | Bonds** from the menu bar to open the Bond Calculation dialog. Check the **Monitor bonding** checkbox and close the dialog.

Click the **Play** button .

When you have finished watching the animation, click the *Stop* button.

4. To calculate the transition state using the LST/QST/CG method

Note: The `reactant_product.xtd` file contains important information needed by DMol³ where the first frame is reactant and the last frame is product.

You are now ready to set up the DMol³ calculation to calculate the transition state.

Open the **DMol3 Calculation** dialog, on the **Setup** tab change the **Task** to **TS Search**. Make sure that the **Quality** is set to **Medium** and set the **Functional** to **GGA** and **BP**.

Click the **More...** button to display the DMol3 Transition State Search dialog. Make sure the **Search protocol** is set to **Complete LST/QST** and set the **Quality** to **Medium**. Check the **Optimize reactants and products** checkbox and close the dialog.

You have just specified the Hamiltonian to be used and the quality level of the calculation. The quality determines both the basis set used - in this case, it is DND - and the orbital cutoff. You can check these parameters by clicking on the *Electronic* tab. Now you need to optimize the convergence behavior by applying some thermal smearing.

On the **Electronic** tab, ensure that **Medium** is selected from the **SCF Tolerance** dropdown list. Click the **More...** button to open the DMol3 Electronic Options dialog. On the **SCF** tab, check the **Use smearing** checkbox and close the dialog.

The electronic Hamiltonian settings are the same as for the geometry optimization calculation. This time you need to calculate the *Frequency* property.

On the **Properties** tab of the DMol3 Calculation dialog check the **Frequency** checkbox.

Finally, you should set the *Job Description*.

On the **Job Control** tab uncheck the **Automatic** checkbox. Type in **TS** as the **Job description**.

You are now ready to run the calculation.

Click the **Run** button and close the dialog.

Note: During the calculation, several different documents and a LST/QST graph are displayed in the workspace. These report the status of the calculation. In particular, an LST/QST graph monitors the progress of the TS search by showing a plot of energy vs. path coordinate for LST, QST, and CG (conjugate gradient).

After job completion, you can view text results in the *TS.outmol* file.

If the document is not automatically displayed, double-click on **TS.outmol** in the Project Explorer. Press **CTRL + F** and search for **Energy of barrier**.

The energy of reaction is about $-14 \text{ kcal mol}^{-1}$ and the energy barrier should be around 52 kcal mol^{-1} .

At a transition state one imaginary frequency appears in the IR spectrum. This frequency corresponds to the reaction mode, which can be animated.

You can view the transition state by opening the document *TS.xsd*.

If the document is not displayed automatically, double-click on **TS.xsd** in the Project Explorer.

A 3D Viewer opens displaying the structure of the transition state for this reaction obtained using the BP/DND level of theory.

Select **Tools | Vibrational Analysis** from the menu bar to display the Vibrational Analysis dialog and click the **Calculate** button.

The calculated normal modes appear in the grid on the dialog. There is one imaginary frequency at about -2000 cm^{-1} .

Select the imaginary frequency and click the **Animation** button. When the trajectory animation begins, click the **Stop** button. Select **Build | Bonds** from the menu bar to open the Bond Calculation dialog. Check the **Monitor bonding** checkbox and close the dialog. Click the **Play** button.

A new window is opened and the corresponding reaction mode is animated with the bonds recalculated for each frame.

Stop the animation and close the Vibrational Analysis dialog.

The **TS Search** task also generates a collection document containing the reactant, transition state, and products. You can look at the energies of the reactant, transition state, and products by labeling by their total energy.

Change focus to **TS.xod**. Right-click and select **Label** from the shortcut menu, click the **Remove All** button. Change the **Object type** to **Energy**, select **TotalEnergy** and click the **Apply** button. Close the Label dialog.

Tip: The displacements of the reactant, transition state, and product in the Y-axis indicate their relative energy differences.

Note: You can also animate the vibrational modes directly from the collection document.

5. To refine the transition state

Now the transition state found in the previous section will be refined.

Select **File | Save Project** then **Window | Close All** from the menu bar. Double-click on **TS.xsd** in the Project Explorer.

Open the **DMol3 Calculation** dialog and change the **Task** to **TS Optimization**. Leave everything else unchanged and click the **Run** button.

The transition-state optimization is now launched.

The calculation finishes after a short time since you were already very close to the fully optimized transition state. Examine the `.outmol` file of the TS optimization and search for the total final energy. Write this energy down and compare it to the energy of transition state of the LST/QST/CG optimization. Using the conversion factor $1\text{ Hartree} = 627.51\text{ kcal mol}^{-1}$, you will find that the energies differ by only about 0.6 kcal mol^{-1} , the optimized energy barrier therefore is about 53 kcal mol^{-1} .

Note: The actual energies obtained in your calculations may deviate by few kcal mol^{-1} from the numbers quoted above and vibrational frequencies can be different by few tens of cm^{-1} . In order to obtain more accurate and better reproducible results you should set the **Quality** to **Fine** and investigate the convergence of the results with respect to the calculation parameters.

Finally you can animate the reaction mode corresponding to the imaginary frequency again as described in [section 4](#).

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Calculating the free energies of chemical reactions

Purpose: Introduces DMol³ as a tool for predicting thermodynamic properties of molecular systems.

Modules: Materials Visualizer, DMol³

Time: 🕒🕒🕒

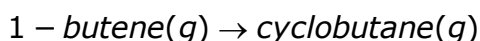
Prerequisites: [Geometry optimization for solids using delocalized internal coordinates in DMol3](#)

Background

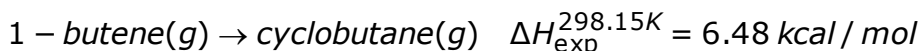
The results of a vibrational analysis calculation can be used to compute important thermodynamic properties such as enthalpy (H), entropy (S), free energy (G) and heat capacity at constant pressure (C_p) as functions of temperature. The DMol³ total energy yields the total electronic energy at 0 K. The various translational, rotational, and vibrational components are used to compute H , S , G , and C_p at finite temperatures, as discussed below.

Introduction

In this tutorial, you will use DMol³ to calculate the free energy of a simple reaction, the isomerization of 1-butene to cyclobutane:



The heat of combustion of each hydrocarbon has been measured and subtraction of the results gives [1]:

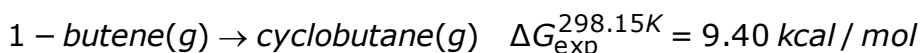


The entropy of each substance is reported in the same document [1] as $\Delta S_{\text{exp}}^{298.15K} = -9.8 \text{ cal/mol/K}$.

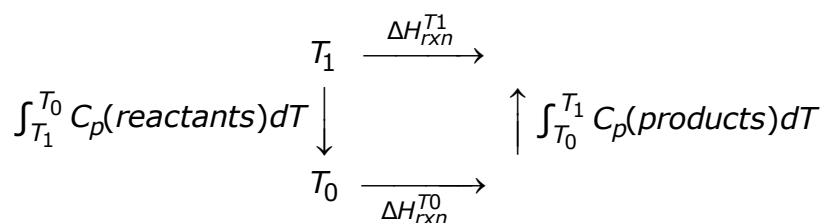
These results can be used to calculate the free energy at $T = 298.15 \text{ K}$ using:

$$\Delta G_{\text{exp}}^{298.15K} = \Delta H_{\text{exp}}^{298.15K} - T\Delta S_{\text{exp}}^{298.15K}$$

resulting in:



To determine the reaction enthalpy or free energy from first principles calculations, the thermodynamic cycle is used, as shown below, where the reaction enthalpy at temperature T_1 can be calculated if the reaction enthalpy at T_0 and the heat capacities of the products and reactants between the two temperatures are known:



resulting in the following equation:

$$\Delta H_{rxn}^{T1} = \int_{T1}^{T0} \sum_{reactants} C_p dT + \Delta H_{rxn}^{T0} + \int_{T0}^{T1} \sum_{products} C_p dT$$

The results obtained from a geometry optimization using DMol³ give the total electronic and ionic energy (E_{tot}) of the system. The enthalpy difference is given by:

$$\Delta H = \Delta U - P\Delta V$$

Note: In certain cases, the possible changes in volume of the system must be included.

The internal energy (U) of the system arises from the electronic, vibrational, translational, and rotational contributions, and is given by the following equation:

$$\Delta U = \Delta E_{tot} + \Delta E_{vib} + \Delta E_{trans} + \Delta E_{rot}$$

The Gibbs free energy difference is given by:

$$\Delta G = \Delta H - T\Delta S$$

where ΔS is given by the following equation:

$$\Delta S = \Delta S_{vib} + \Delta S_{trans} + \Delta S_{rot}$$

DMol³ can calculate all the above terms once the ground-state structure is determined and the vibrational frequencies for the $3N - 6(5)$ normal modes are obtained using statistical mechanics.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculations](#)
- [To optimize the geometry and performing a vibrational analysis calculation](#)
- [To calculate free energies at finite temperature from data contained in the DMol³ output document](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.


Open the **New Project** dialog and enter **butene** as the project name, click the **OK** button.

The new project is created with *butene* listed in the Project Explorer.



2. To prepare the structures for the calculations

In this section of the tutorial, you will build the reactants and products in separate documents. The first step is to create two new 3D Atomistic documents.

Click the **New** arrow  on the **Standard** toolbar and select **3D Atomistic Document** from the dropdown list. Repeat this procedure so that two new 3D Atomistic documents are created.

Ensure that the first 3D Atomistic document is active. Select the **Sketch Atom** tool  from the **Sketch** toolbar. Draw a chain of four carbon atoms, then press the **ESC** key to cancel sketching. Click on one of the terminal C-C bonds to increase the bond order to two.

To complete the structure, you need to add hydrogens and arrange the structure into a sensible initial geometry.


Click the **Adjust Hydrogen** button  and then the **Clean** button  on the **Sketch** toolbar.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Atom** tab select the **Ball and stick** option.

You should rename this document to avoid confusion later.

Rename the new document **1-butene.xsd**.

Now build the other molecule involved in the reaction, cyclobutane.

Click in the 3D Viewer for **3D Atomistic (2).xsd** to make it the active document. Click the **Sketch Ring** arrow  on the **Sketch** toolbar and select **4 Member** from the dropdown list. Click once in the document to insert a cyclobutane ring.

Click the **Adjust Hydrogen**  and **Clean**  buttons.

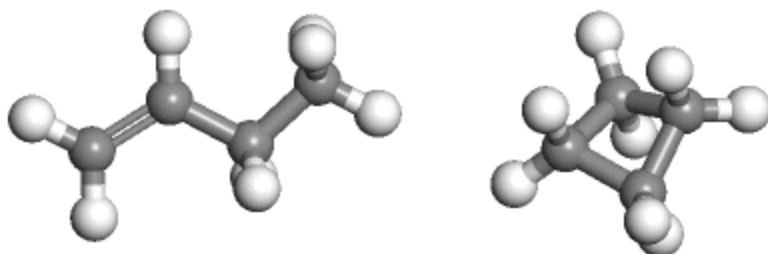
On the Display Style dialog, select the **Ball and stick** option and close the dialog.

You should rename this document.

Rename the second new document **cyclobutane.xsd**.

Click the **3D Viewer Selection Mode** button  on the **3D Viewer** toolbar.


When you have finished, you should have the two molecules shown below in separate 3D Atomistic documents.



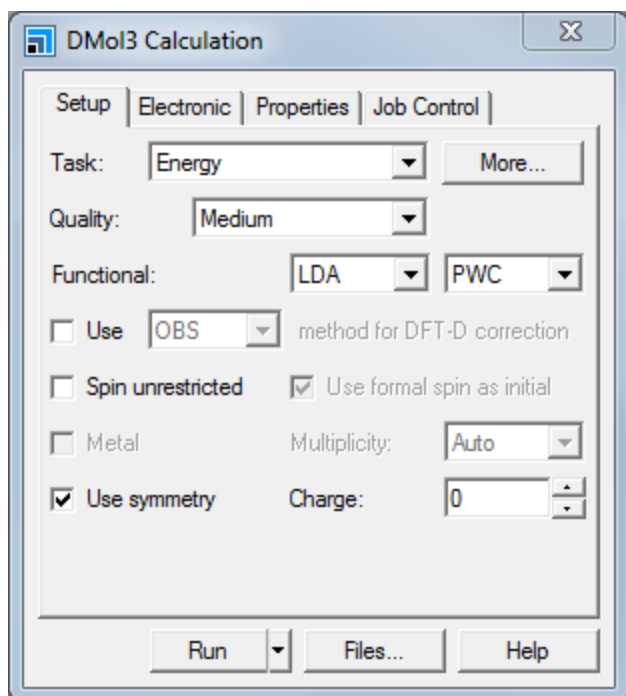
The structures of 1-butene and cyclobutane

3. To optimize the geometry and perform a vibrational analysis calculation

Prior to performing the vibrational analysis calculation, you should optimize the structures of both molecules. You will do this using the geometry optimization functionality in DMol³.

Make **1-butene.xsd** the active document. Click the **DMol3** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the DMol3 Calculation dialog.



DMol3 Calculation dialog, Setup tab

Set the **Task** to **Geometry Optimization**. Make sure that the **Quality** is set to **Medium** and change the **Functional** to **GGA** and **BLYP**.

You have just specified the basis set and the Hamiltonian to be used in this calculation. A gradient corrected functional such as BLYP is important for computing accurate thermodynamic properties.

On the **Electronic** tab, click the **More...** button to open the DMol3 Electronic Options dialog. Check the **Use smearing** checkbox on the **SCF** tab and make sure that the value of **Smearing** is set to the default, **0.005**. Close the dialog.

Smearing populates the energy levels around the Fermi level according to a thermal distribution and can help to improve SCF convergence in many cases.

On the **Properties** tab on the DMol3 Calculation dialog, check the **Frequency** checkbox.

This causes a vibrational analysis to be performed after the structure optimization has converged. The results of this analysis are used to compute enthalpy (H), entropy (S), free energy (G), and heat capacity at constant pressure (C_p) as functions of temperature. The DMol³ total energy yields the total electronic energy at 0 K. The various translational, rotational, and vibrational components are used to compute H , S , G , and C_p at finite temperatures. In this tutorial, you are mainly interested in the finite temperature corrections for the free energy.

You are now ready to run the calculations on 1-butene and cyclobutane.

Ensure that **1-butene.xsd** is the active document and click the **Run** button.

Make **cyclobutane.xsd** the active document and click the **Run** button again. Close the dialog.

The progress of the jobs during the computations is presented in the form of chart and text documents. When the jobs are complete, all of the results files are returned to the client.

The calculation for cyclobutane is much quicker than the one for 1-butene because DMol³ makes use of the D_{2D} symmetry of the molecule.

4. To calculate free energies at finite temperature from data contained in the DMol³ output document

The optimized structure for 1-butene is contained in the 1-butene DMol3 GeomOpt/1-butene.xsd file. The text output of the computation is contained in the 1-butene.outmol file. Before calculating the free energy for the isomerization reaction, you will display the calculated thermodynamic properties in a chart document.

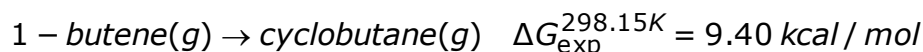
Select **File | Save Project** from the menu bar, then **Window | Close All**.

In the Project Explorer, double-click on **1-butene.xsd** in the **1-butene DMol3 GeomOpt** folder.

Select **Modules | DMol3 | Analysis** from the menu bar to open the DMol3 Analysis dialog and select **Thermodynamic properties** from the dropdown list. Ensure that **1-butene.outmol** is the **Results file** and click the **View** button and close the dialog.

The calculated thermodynamic properties are displayed in a chart document.

You will now calculate the free energy for the reaction from the data in the corresponding DMol³ output documents.



In the Project Explorer, double-click on **1-butene.outmol** in the **1-butene DMol3 GeomOpt** folder.

The output of the calculation for 1-butene is displayed in a Text Viewer.

Press **CTRL + F** and search for **Geometry optimization completed**. Write the value for the **Total Energy** displayed above the table for the last step in the **E_{total}** row for **1-butene** in the table below.

The text document should look similar to this:

```
opt==  Cycle 15  Total Energy -157.1555609  Energy change -0.0000179  Max Gradient 0.001173  Max Displacement 0.001386

                Step 15
                <-- DELOC
                <-- DELOC
                <-- DELOC
                <-- DELOC
                <-- DELOC
+-----+-----+-----+-----+-----+
| Parameter | value | tolerance | units | OK? | <-- DELOC
+-----+-----+-----+-----+-----+
| delta E   | -0.179057E-04 | 0.200000E-04 | Ha | Yes | <-- DELOC
| |F|max   | 0.117269E-02 | 0.211671E-02 | au | Yes | <-- DELOC
| |dR|max   | 0.138633E-02 | 0.944863E-02 | au | Yes | <-- DELOC
+-----+-----+-----+-----+-----+

Geometry optimization completed successfully in 15 steps.
```

Section of the DMol³.outmol document containing the total energy in Hartree for 1-butene

	1-Butene	Cyclobutane
E_{total} (Hartree)		
$G_{total}^{298.15K}$ (kcal/mol)		
G_{total} (Hartree)		
$E_{Tcorr}^{298.15K} = E_{total} + G_{total}$ (Hartree)		

Note: Since the Hartree is a large energy unit, it is important to write down all of the significant figures provided in the DMol³ output document.

Scroll to the end of the **1-butene.outmol** document.

At the end of 1-butene.outmol you will find a table containing the finite temperature corrections for the standard thermodynamic quantities (entropy, heat capacity, enthalpy, and free energy) computed from 25 to 1000 K in steps of 25 K. All these quantities include the zero-point vibrational energy (ZPVE).

Record the **G** value for 1-butene at **298.15** K in kcal/mol in the second row of the table.

The text document should look similar to this.

STANDARD THERMODYNAMIC QUANTITIES
computed from 25.00 to 1000.00 in steps of 25.00

T (K)	Entropy S (cal/mol.K)	Heat_Capacity Cp	Enthalpy H (kcal/mol)	Free_Energy G
1 25.00	42.588	8.023	65.971	64.906
2 50.00	48.362	8.838	66.180	63.762
3 75.00	52.152	9.945	66.415	62.504
4 100.00	55.165	11.037	66.677	61.161
5 125.00	57.738	12.058	66.966	59.749
6 150.00	60.024	13.047	67.280	58.276
7 175.00	62.111	14.065	67.619	56.749
8 200.00	64.060	15.155	67.984	55.172
9 225.00	65.912	16.335	68.377	53.547
10 250.00	67.698	17.604	68.801	51.877
11 275.00	69.438	18.947	69.258	50.163
12 298.15	71.021	20.237	69.712	48.537

The computed G_{total} value at 298.15 K should be about +49 kcal/mol.

Now convert G_{total} from kcal/mol to Hartree (1 Hartree = 627.51 kcal/mol).

Write down the **G** value for 1-butene at **298.15** K in Hartree in the third row of the table above.

Since the DMol³.outmol document provides the corrections for H , S , and G for finite temperature, you can simply add up the values in rows 1 and 3 of the table above to obtain the finite temperature-corrected value for G for 1-butene.

Add the values in rows 1 and 3 for 1-butene together and enter the result in row 4 of the table.

Repeat the procedure above for cyclobutane to fill the remaining cells of the table.

You can now calculate the ΔG value in kcal/mol for the isomerization of 1-butene to cyclobutane using the following formula:

$$\Delta G_{reaction}^{298.15K} = 627.51 \left[E_{Tcorr}^{298.15K}(\text{cyclobutane}) - E_{Tcorr}^{298.15K}(\text{butene}) \right]$$

The resulting computed free energy for the reaction should be about +10.75 kcal/mol, very close to the experimental value. The positive sign of the free energy indicates that this reaction will not occur spontaneously at room temperature.

Note: You may get slight variations from the values shown in this tutorial. This is mainly due to slight structural differences resulting from using the *Medium* convergence level in the DMol³ geometry optimization.

Select **File | Save Project** from the menu bar, then **Window | Close All**.

This is the end of the tutorial.

References

<http://www.wiredchemist.com/chemistry/data/entropies-organic>

Exploring the minimum energy path of chemical reactions using DMol³'s LST/QST and NEB tools

Purpose: Introduces minimum energy path calculations using DMol³ in Materials Studio.

Modules: Materials Visualizer, DMol³

Time: 

Prerequisites: [Transition-state searching using LST/QST tools](#)

Background

The calculation of a reaction path is an important part of studying reactivity. The simplest way to calculate a reaction path is to start at a saddle point and take successive steps in the direction of the negative gradient. This steepest descent approach leads to a minimum energy path (MEP). If the coordinate system is mass-weighted, this is called an intrinsic reaction coordinate (IRC).

The MEP (or IRC path) may be quite complicated and may have several minima. The highest saddle point is of most interest, as the overall reaction rate depends on the height of this reaction barrier. Following the reaction path can reveal intermediate structures and can be used to connect the reaction barrier to the correct reactant and product.

DMol³ uses the nudged elastic band (NEB) method for minimum energy path calculations. The NEB method introduces a fictitious spring force that connects neighboring points on the path to ensure continuity of the path and projection of the force so that the system converges to the MEP. The NEB method has been used widely in solid-state physics and has recently been applied to molecules as well. The advantage of the NEB algorithm is that it provides a fast qualitative examination of the MEP.

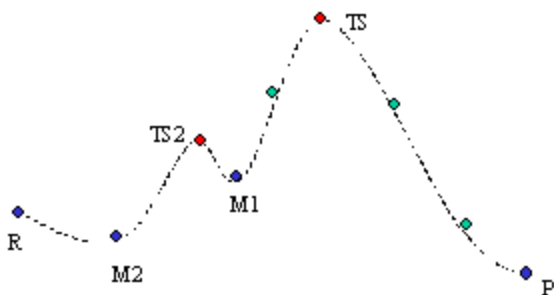


Figure 1

Consider the complex reaction pathway in [Figure 1](#). An LST/QST transition state (TS) search algorithm takes the two endpoints R and P as input and locates one of the local maxima on the reaction coordinate. Assume that in this example it locates the highest energy barrier, TS.

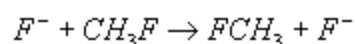
The *TS Confirmation* algorithm will take these three points as input and return a trajectory that contains at least one point in the vicinity of the new minima; in this case, M1 or M2. Points are shown in [Figure 1](#) as blue (minima) and red (maxima). In general, the path will also contain a few points that do not correspond to stationary points (green).

Note: A conventional NEB is intended to start from two end points and yield the TS and the entire reaction pathway, giving a lot of green points. In contrast, the algorithm implemented in DMol³ is intended to start at the TS and to locate the alternative minima in the direction of reactants and products. It only attempts to answer the question "Does this TS really connect the presumed reactant with the presumed product, or are there alternative minima on the reaction path?".

The optimization consists of two phases, termed 'macroiteration' and 'microiteration'. It is assumed that the points are held loosely in place by springs. Macroiterations consist of an optimization over all the images; microiterations consist of the optimization of the molecule or crystal in a direction orthogonal to the reaction pathway. The calculation is complete when both the macroiterations and microiterations have converged.

Introduction

This tutorial aims to introduce to you the NEB tool in DMol³. You will use DMol³'s LST/QST to find a transition-state structure for a simple symmetrical S_N2 reaction; fluorine exchange on methyl fluoride:



Then, you will use the *TS Confirmation* tool to map the energy path between reactants, intermediate and products.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculation](#)
- [To prepare the input trajectory document for the transition-state calculation](#)
- [To calculate the transition state using LST/QST](#)
- [To perform an NEB calculation using TS Confirmation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.


Open the **New Project** dialog and enter **LSTQST** as the project name, click the **OK** button.


The new project is created with *LSTQST* listed in the Project Explorer.

2. To prepare the structures for the calculation

In this section of the tutorial, you will sketch the reactants and products in two different 3D Atomistic documents. The first step is to open a new 3D Atomistic document and sketch the reactant, a fluoride ion, at a set distance from a methyl fluoride molecule.

Click the **New** button  on the **Standard** toolbar to open the New Document dialog. Choose **3D Atomistic** and click the **OK** button.


Sketch a single carbon atom, click the **Adjust Hydrogen** button . Change one of the hydrogen atoms to a **fluorine**.

Click the **Clean** button .

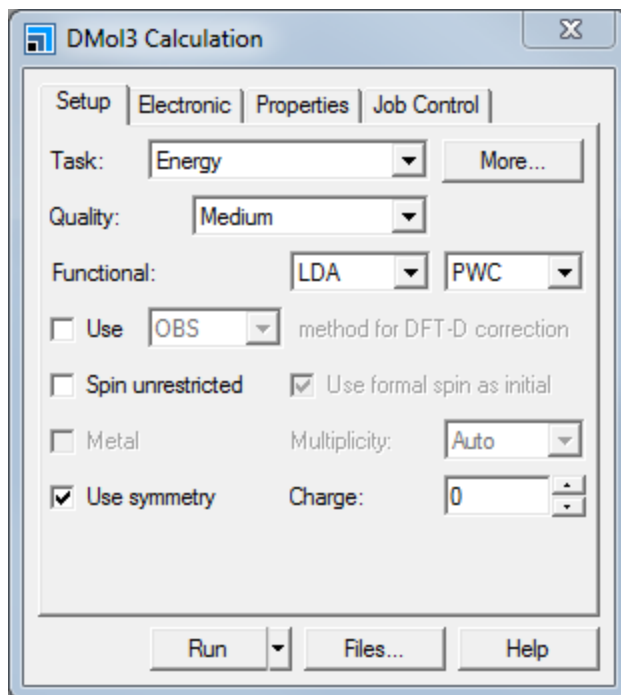
The selected hydrogen atom has been changed to fluorine and the geometry of the structure has been set to a reasonable initial configuration.

Rename the new document **methylfluoride.xsd**.

Before you continue setting up the structures, you should perform a rough geometry optimization of this molecule.

Click the **DMol3** button  on the **Modules** toolbar and choose **Calculation**, or select **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.



DMol3 Calculation dialog, Setup tab

You will perform an optimization with relatively coarse parameter settings. To achieve more accurate results, you should increase the size of the basis set.

On the **Setup** tab, change the **Task** from Energy to **Geometry Optimization** and the **Quality** from **Medium** to **Coarse**. Leave the **Functional** at the default settings of **LDA** and **PWC**. Click the **Run** button and close the dialog.

The calculation should take about 15 seconds to complete, depending on the speed of the processor in your computer server.

The progress of the calculation is updated in the form of chart and text documents. When the calculation is complete, the final optimized structure is saved in the document `methylfluoride.xsd` in a new folder called `methylfluoride DMol3 GeomOpt`. The text output of the computation is saved in the `methylfluoride.outmol` file. The results folder also contains the `methylfluoride.xtd`, a 3D Atomistic Trajectory document containing the progress of the minimization.

You will now finish setting up the inputs for the LST/QST calculation.


In the Project Explorer, select **methylfluoride.xsd** and right-click, select **Copy** from the shortcut menu.

In the Project Explorer, right-click on the project name and choose **Paste** from the shortcut menu.

You have just made a copy of the optimized methyl fluoride molecule. Before continuing to sketch, you should rename the document.


Rename the methylfluoride (2) .xsd document to SN2reactant.xsd.

You need to add a second fluorine atom at a set distance from the carbon atom.


Click the **Sketch Atom** arrow  and choose **Periodic Table...** from the dropdown list to open the Periodic Table dialog.

Select **F** and click the **OK** button. Click on the **carbon** atom of the methyl fluoride and sketch a new carbon-fluorine bond opposite to the other C-F bond. Press the **ESC** key to stop sketching.

Now, you will use the *Measure/Change* tool to position the fluorine atom so that it is approximately 3 Å from the carbon atom.

Click the **Measure/Change** arrow  and select **Distance** from the dropdown list. Select the newly created **C-F** bond, hold down the left mouse button and drag the mouse until the distance increases to approximately 3 Å.

The final step is to delete the new C-F bond.

Click the **3D Viewer Selection Mode** button . Hold down the **CTRL** key and click on the **distance monitor** and then the elongated **C-F** bond to select them. Press the **DELETE** key.

Now create the product from the reactant structure.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**. In the Project Explorer select **SN2reactant.xsd** and right-click, select **Copy** from the shortcut menu.

In the Project Explorer, right-click on the project name and choose **Paste** from the shortcut menu.

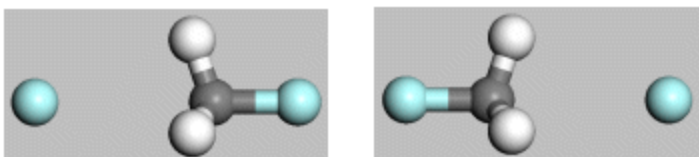
Rename the SN2reactant (2) .xsd document to SN2Product.

Select **Window | Tile Horizontally** from the menu bar. Rotate the structures so that in one 3D Viewer, the non-bonded fluorine atom is on the right, and in the other, it is on the left.

Tip: You can use the left and right arrow keys to rotate the structures about the y-axis in increments of 45 degrees.

Right-click in either of the 3D Viewers and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Atom** tab choose the **Ball and stick** option. Click in the other 3D Viewer and choose **Ball and stick** again. Close the dialog.

Your two model documents should look similar to those shown below.



SN2reactant.xsd and SN2product.xsd displayed in ball and stick style

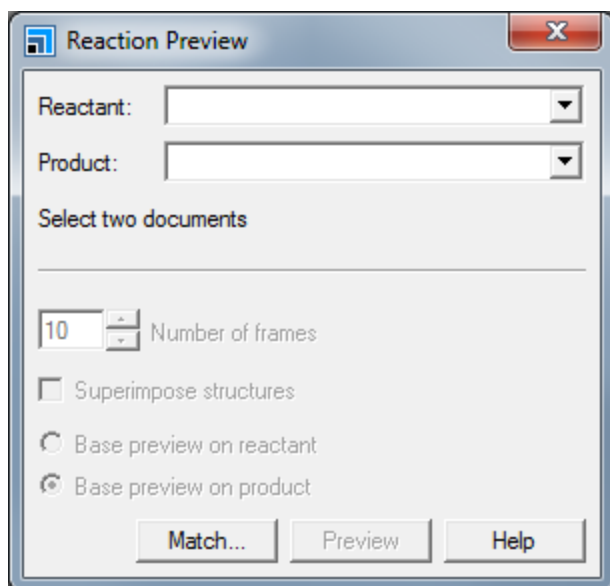
You have set up the structures you need and are now ready to create the input 3D Atomistic Trajectory document for the LST/QST calculation.

3. To prepare the input trajectory document for the transition-state calculation

For DMol³ to perform an LST/QST calculation, all the atoms in the reactant and product documents need to be paired and a trajectory document must be created. This is performed using the Reaction Preview tool.

Select **Tools | Reaction Preview** from the menu bar.

This opens the Reaction Preview dialog.



Reaction Preview dialog

Select **SN2reactant.xsd** and **SN2product.xsd** as the **Reactant** and **Product**, respectively. Click the **Match...** button.

This opens the Find Equivalent Atoms dialog, you should see that one atom is matched and 5 atoms are unmatched.

Expand the **2xF** folder in the reactant column.

The corresponding folder in the product column also opens. The reactant column should contain **5:F** and **6:F**. For the LST/QST calculation, these must map directly onto their counterparts in the product column.

Note: Depending on how you sketched the original structure, you could have either **5:F** or **4:F**. These are interchangeable throughout the rest of this tutorial.

With both 3D Atomistic documents in view, click on **5:F** in the reactant column, then click on **5:F** in the product column.

The corresponding atoms in both 3D Viewers should be selected and you should be able to see that they are not equivalent in the two documents.

Click on **6:F** in the product column.

This is the equivalent atom to **5:F** in the reactant column, so these atoms can now be matched.

Click the **Set Match** button.

The atoms are moved into the **matched atoms** folder.

Repeat this procedure for the rest of the unmatched atom pairs.

You can review the matched atoms list between reactant and product.

Expand the **6 matched atoms** node in the reactant column. Click on one of the atoms on the list in either the reactant or product column to review the pairing. Close the Find Equivalent Atoms dialog when you are satisfied.

To perform an LST/QST calculation, you need to create a trajectory path between the reactant and product as the input to the DMol³ calculation.



On the **Reaction Preview** dialog, increase the **Number of frames** to **25**. Check the **Superimpose structures** checkbox. Click the **Preview** button and close the dialog.


A new 3D Atomistic Trajectory document called SN2reactant-SN2product . xtd is displayed. You will run the DMol³ calculation on this document. You can animate the 3D Atomistic Trajectory document using the tools on the *Animation* toolbar. If this is not currently visible, you can open it from the *View* menu.

Tip: The animation looks best when viewed in *Bounce* mode.

Select **Build | Bonds** from the menu bar to open the Bond Calculation dialog. On the **Bonding Scheme** tab, check the **Monitor bonding** checkbox and close the dialog.

If the **Animation** toolbar is not visible, select **View | Toolbars | Animation** from the menu bar.

Click the **Animation Mode** arrow  and choose **Bounce**. Click the **Play** button .

When you have finished watching the animation, click the **Stop** button .

4. To calculate the transition state using LST/QST

You are now ready to set up the DMol³ LST/QST calculation.

Open the **DMol3 Calculation** dialog, on the **Setup** tab, change the **Task** from Geometry Optimization to **TS Search**. Set the **Functional** to **LDA** and **PWC**.

With the LST/QST tool, you can quickly and reliably locate transition states of a chemical reaction. This tutorial aims to demonstrate the power of the NEB method for confirming a transition state or finding additional minima on the MEP. Therefore, you will use a rough parameter set for the LST/QST calculation. Specifically, you are using LDA functionals. Due to their inherent tendency toward overbinding, LDA functionals tend to seriously underestimate reaction barriers. Sometimes, a minimum is even found where you would expect a transition state. Therefore, for a rigorous transition-state search, you would use bigger basis sets and gradient-corrected functionals. Refer to the DMol³ tutorial [Transition-state searching using LST/QST tools](#) for an overview of how to perform a more accurate reaction barrier calculation.

On the **Setup** tab of the DMol3 Calculation dialog, change the **Charge** to **-1**. On the **Electronic** tab set the **Basis set** to **DN**.

Click the **More...** button to display the DMol3 Electronic Options dialog. On the **SCF** tab, check the **Use smearing** checkbox. On the **Orbital Cutoff** tab select **Custom**. Set the **Global orbital cutoff** to **5.0 Å**. Click the **Assign** button and close the dialog.

This procedure increased the finite range cutoff of the atomic basis set. The atomic orbitals are taken to be zero beyond this distance from their atomic center. Decreasing the cutoff reduces the computation time required for a calculation, but introduces some approximations. Increasing the cutoff distance results in a more accurate calculation. In this case, the relatively weak interactions between the carbon and fluorine at the transition state are improved by using longer range cutoffs.

During the LST/QST search, you might create structures for which the self-consistent field (SCF) cycle of a DMol³ energy calculation may prove difficult to converge. By using the smearing option, you are allowing for fractional orbital occupancy, which improves the SCF convergence behavior.

On the **Properties** tab of the DMol3 Calculation dialog, check the **Frequency** checkbox.

This causes a vibrational analysis to be performed after the LST/QST calculation has finished.

You are now ready to run the calculation.

Click the **Run** button and close the dialog.

Wait until the calculation is complete.

Note: During the calculation, several different documents, including an LST/QST chart, are displayed. These report the status of the calculation. In particular, the LST/QST chart monitors the progress of the *TS Search* by showing a plot of Energy vs. Path Coordinate for LST, QST, and CG (conjugate gradient).

Select **SN2reactant-SN2product TSSearch.xcd**.

By inspecting the energy plot, you can see that the Conjugate Gradient (CG) Search has located a minimum. Although it is marked as a transition state, the structure is lower in energy than the reactants and products. Now you will find out whether this is really a transition state. At a transition state, one imaginary frequency appears in the IR spectrum. This frequency corresponds to the reaction mode and can be animated.

Double-click on **SN2reactant-SN2product.xsd** in the **SN2reactant-SN2product DMol3 TSSearch** folder in the Project Explorer. Select **Tools | Vibrational Analysis** from the menu bar to open the Vibrational Analysis dialog. On the **Analysis** tab, click the **Calculate** button.

The calculated normal modes appear in the table. There is one imaginary frequency at about -330 cm^{-1} .

Select the imaginary frequency and click the **Animation** button. Close the dialog.

A new window is opened and the corresponding reaction mode is animated. It is possible that there are other minima on the minimum energy path which the LST/QST search has missed. You will now attempt to locate these minima using the *TS Confirmation* tool.

Click the **Stop** button . Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

5. To perform an NEB calculation using TS Confirmation

The `SN2reactant-SN2product.xtd` trajectory document contains all the structures generated during the transition-state search. This is used as the input to the NEB calculation.

Make **SN2reactant-SN2product.xtd** the active document.

You are now ready to set up the NEB calculation.

Open the **DMol3 Calculation** dialog. On the **Setup** tab, change the **Task** to **TS Confirmation**. Click the **More...** button to open the DMol3 TS Confirmation dialog.

Several convergence criteria for the *TS Confirmation* calculation can be set here.

Select **Coarse** from the **Path quality** dropdown list and close the dialog.

This will speed up the calculation by calculating only 6 images.

On the **Properties** tab of the DMol3 Calculation dialog, uncheck the **Frequency** checkbox. Click the **Run** button and close the dialog.

During the calculation, several different documents and a transition state confirmation chart are displayed. These report the status of the calculation. In particular, the `SN2reactant-SN2product TSConfirmation.xcd` chart monitors the progress of the calculation by showing a plot of Energy vs. MEP Path and highlighting possible stationary points on this path.

Wait until the calculation is complete before continuing.


In the **SN2reactant-SN2product DMol3 TSConf** folder, double-click on **SN2reactant-SN2product TSConfirmation.xcd**.

The *TS Confirmation* has found two new minima (marked by asterisks in the graph) that are lower in energy than the transition state found in the *TS Search*. Now look at these minimum energy structures.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Certain chart documents are dynamically linked to the associated trajectory documents, allowing you to use the *Chart Viewer* tools to pick a point on the chart, thus displaying the appropriate frame in the trajectory document.

In the Project Explorer, double-click on **SN2reactant-SN2product.xtd** and then on **SN2reactant-SN2product TSConfirmation.xcd**. Select **Window | Tile Vertically** from the menu bar.

Click on the **Chart Viewer Selection Mode** button  and click on the minimum points in the chart.

The structure in the 3D Viewer is updated accordingly. The two minima correspond to the M1 and M2 points on the reaction pathway, see [Figure 1](#). In fact, the starting geometries with a fluorine atom 3 Å from the carbon is not the lowest energy structure; instead a state exists with the fluorine loosely bound to the CH₄.

The transition state actually connects these loosely bound structures. Ideally, they would be symmetric and exactly equal in energy. Due to the limited accuracy of the parameters used in the calculation, your results are not symmetric. You could try to produce a symmetric curve using Medium or Fine settings in DMol³.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Calculating optical properties of Coumarin

Purpose: Demonstrates how to calculate optical properties using DMol³

Modules: Materials Visualizer, DMol³

Time: 🕒 🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Coumarin and its derivatives represent a family of compounds, originally found in plants, which are optically active. Coumarin (2H-chromen-2-one) is often used as a reference standard compound for dealing with latex and liposomes.

Introduction

In this tutorial, you will calculate the optical properties of coumarin both in vacuum and in the presence of water. You will perform geometry optimization and subsequent TD-DFT calculations with and without the COSMO solvation model.

This tutorial covers:

- [Getting started](#)
- [To create and optimize the input structure](#)
- [To calculate the optical spectra of coumarin in the gas phase](#)
- [To calculate the optical spectra of coumarin in the presence of water](#)
- [To optimize geometry of an excited state](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

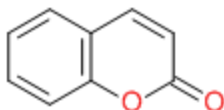
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DMol3_optical** as the project name, click the **OK** button.

The new project is created with *DMol3_optical* listed in the Project Explorer.

2. To create and optimize the input structure


You should use the sketching tools to draw the Coumarin molecule.



Open a new **3D Atomistic Document** and sketch the structure of coumarin. Use the **Adjust Hydrogen** and **Clean** tools to amend the structure.

Rename the new document **coumarin.xsd**.

For flexible molecules, you could pre-optimize the structure with a good quality forcefield such as COMPASS. However, as this molecule is very rigid, you can move on to performing the initial geometry optimization.

Click the **DMol3** button  on the Modules toolbar and choose **Calculation** to open the DMol3 Calculation dialog.

You will run a geometry optimization using the PBE functional.

On the **Setup** tab select **Geometry Optimization** from the **Task** dropdown list and set the **Functional** to **GGA PBE**.

To improve the accuracy of the calculation, you will modify the basis set. Calculation of optical properties requires the use of the 4.4 basis file.

Select the **Electronic** tab, set the **Basis set** to **DNP** and the **Basis file** to **4.4**.

You are now ready to run the initial geometry optimization.

On the DMol3 Calculation dialog, click the **Run** button.

Depending on the speed of your computer, the calculation may take several minutes to complete. When the calculation is complete, the results are returned. These include the optimized structure, `coumarin.xsd`, a trajectory containing the frames from each optimization step, and various chart and text documents containing information about the calculation.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To calculate the optical spectra of coumarin in the gas phase

In this section of the tutorial, you will perform a single point energy calculation and calculate the optical spectrum of coumarin in vacuum.

Open the optimized **coumarin.xsd**.


On the **DMol3 Calculation** dialog select the **Properties** tab. Check the **Optics** checkbox and change the **Calculate lowest states** value to **25**.

This will calculate the 25 lowest excited states, their energies, and properties such as transition intensities. Increasing the number of states in the calculation will increase the calculation time.

Note: You can also calculate linear polarizability. This requires all available excitations to be calculated and is very memory and time intensive.

Select the **Setup** tab and choose **Energy** from the **Task** dropdown list. Click the **Run** button and close the dialog.

As this is a single point energy calculation, fewer documents are returned. You will use DMol3 Analysis to calculate the optical spectrum.

Open the **coumarin DMol3 Energy\coumarin.xsd** document. Click the **DMol3** button  on the Modules toolbar and choose **Analysis** to open the DMol3 Analysis dialog.

Select the **Optics** property and click the **View spectrum** button. Close the dialog.

A chart is displayed, coumarin Optical Spectrum.xcd.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To calculate the optical spectra of coumarin in the presence of water

DMol³ enables you to include the effect of a solvent when calculating optical properties using the COSMO approach. You should optimize coumarin with COSMO switched on and then re-calculate the optical spectra. You can do this in one step.

Change focus to the original **coumarin.xsd** that you sketched. Open the **DMol3 Calculation** dialog, on the **Setup** tab change the **Task** to **Geometry Optimization**.

You can use COSMO (COnductor-like Screening MOdel) to mimic a range of solvents. In COSMO, the solute molecule forms a cavity in the dielectric continuum of given permittivity representing the solvent.

Select the **Electronic** tab and check the **Use solvation model** checkbox. Click the **More...** button to open the DMol3 Electronic Options dialog, select the **Solvent** tab.

You are going to use water as the solvent.

Ensure that **Water** is selected from the **Solvent** dropdown list and close the dialog. On the DMol3 Calculation dialog, click the **Run** button.

This calculation is likely to take several minutes to complete. When the calculation has finished, you can analyze the results to generate the optical spectrum.

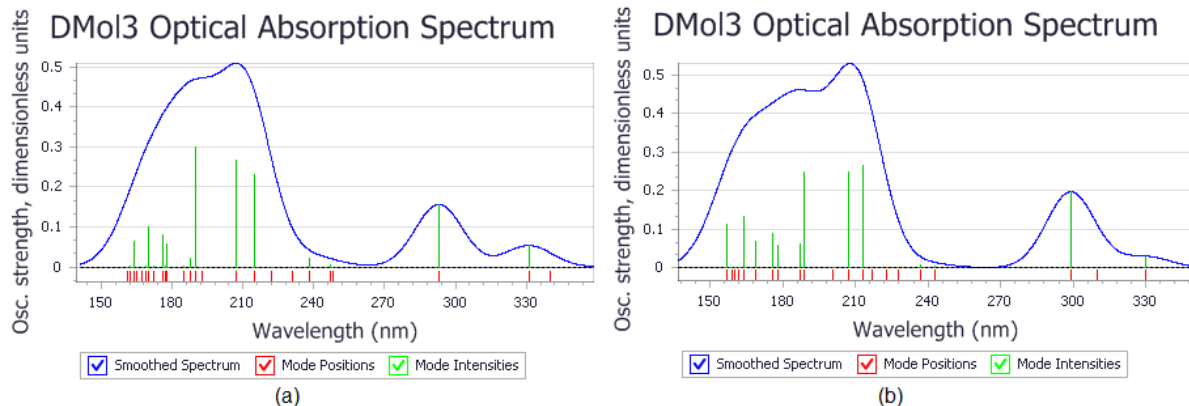
Open **coumarin DMol3 GeomOpt (2)\coumarin.xsd** and open the **DMol3 Analysis** dialog. Select the **Optics** property and click the **View spectrum** button.

You can view both spectra side-by-side so you can compare them

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Open both chart documents and select **Window | Tile Vertically**.

You should see that the spectra are slightly different with the solvent effect shifting the highest absorption band. The solvent induced shift in absorption is usually small (about 5-15 nm).



The charts show the optical spectra for (a) the molecule in vacuum and (b) the molecule in the solvent.

5. To optimize geometry of an excited state

An additional exercise that can be carried out in this tutorial is to optimize the geometry of an excited state and compare it with the geometry of the ground state. These types of calculations are significantly more time consuming than the TD-DFT evaluation of excitation energies for a fixed molecular geometry, so it is recommended that you perform them separately from the previous steps.

Excited state optimization produces not only modified geometries but also the energies that are relevant to studies of fluorescence, for example. Excitation energies reported in a TD-DFT calculation correspond to the absorption spectrum, that is the energies of absorbed photons. The final excitation energy in the DMol³ output file for an excited state geometry optimization can be interpreted as an energy of the emitted photon which can be registered in a fluorescence spectroscopy experiment. The energy difference between the last reported ground state dissociation energy and the same value for the optimized ground state geometry represents the energy to be dissipated after a fluorescence event through electron-phonon coupling.

The calculations can be performed both in the gas phase and in the presence of water; this calculation is similar to steps 3 and 4 above.

First you will calculate the emission energy in a vacuum.

Open **coumarin DMol3 GeomOpt\coumarin.xsd**.

On the **DMol3 Calculation** dialog select the **Properties** tab, ensure that the **Optics** checkbox is checked and check the **Optimize geometry for** checkbox. Keep the **Singlet** state setting and select the **1st** excitation.

Choose the **Setup** tab and select the **Energy** task.

Choose the **Electronic** tab and make sure that the **Use solvation model** checkbox is unchecked.

This will produce an optimized geometry of the lowest energy singlet excitation of the molecule in vacuum.

Click the **Run** button.

When the calculation is complete, the results folder will contain **coumarin_S1_GO** files in addition to the files generated in the previous steps of the tutorial. You can examine geometry of the excited state in

`coumarin_S1_GO.xsd` and compare it to the optimized geometry of `coumarin.xsd`. You should notice that there are significant changes in some of the bond lengths. For example, the C=O double bond weakens and it should be about 0.1 Å longer than in the ground state, while the C-O bonds in the ring structure become stronger and shorter.

Next you will calculate the emission energy in water.

Open **coumarin DMol3 GeomOpt (2)\coumarin.xsd**.

On the **DMol3 Calculation** dialog select the **Electronic** tab and check the **Use solvation model** checkbox.

Click the **Run** button.

You can also analyze the energetics of the excitation before and after the excited state optimization. The vertical absorption energy corresponds to the excitation energy at the beginning of the TDDFT optimization.

Open the **coumarin_S1_GO.outmol** output file and search for the section beginning **Done calculating TDDFT forces**.

The next three lines contain essential information about the ground and excited state energetics of this conformation.

Make a note of the value of **Excitation energy**:

This is the absorption energy.

Find the last occurrence of **Done calculating TDDFT forces** and make a note of the **Excitation energy**:

This corresponds to the emission energy of the excited state back into the ground state.

For coumarin in vacuum, you should find that the emission is about 1.57 eV lower than the absorption. When coumarin is solvated in water on the other hand, the emission is only about 0.80 eV lower than the absorption.

This is the end of the tutorial.

Kinetics of a Diels-Alder reaction

Purpose: To introduce the Reaction Kinetics task and demonstrate calculation of reaction rates.

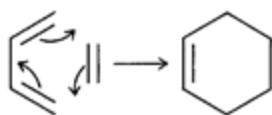
Modules: Materials Visualizer, DMol³, Forcite, COMPASS

Time: 🕒🕒🕒

Prerequisites: [Transition-state searching using LST/QST tools](#)

Background

This tutorial is based on the Diels-Alder ethene (C₂H₄) with butadiene (C₄H₆) reaction:



This reaction has a large number of derivatives, generally producing six membered rings, hence its practical utility. This reaction and its reverse (the retro Diels-Alder reaction) have been extensively studied and it has been established (from, among other things, the high stereo-specificity of the reaction) that the mechanism is that of a concerted pericyclic reaction.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculations](#)
- [To create the reaction trajectory](#)
- [To calculate the transition state](#)
- [To calculate the rate coefficient parameters](#)
- [To calculate the rate coefficient](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **kinetics** as the project name, click the **OK** button.

The new project is created with *kinetics* listed in the Project Explorer.

2. To prepare the structures for the calculations

Creating models of the reactant and products and mapping between the two models is often the key step in determining transition states and calculating rate coefficients.



Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Structures/organics** and import **benzene.msi**.

Rename the document to **ButadieneEthene.xsd**.


Open the Bond Calculation dialog and ensure that the representation is set to **Kekule**, click the **Calculate** button and close the dialog.

You will use this to create the two reacting structures of ethene and butadiene.

Select two of the **carbon-carbon single** bonds and **delete** them. Click the **Adjust Hydrogen** button


 and then the **Clean** button .

You need to arrange the two structures to align them favorably to react. You will use best fit planes to help align the structures.


Select an atom in the butadiene structure, right-click and choose **Select Fragment** from the shortcut menu. Click on the **Create Centroid** arrow  on the Sketching toolbar and select **Best Fit Plane** from the dropdown list.

Repeat this for the ethene structure.

You will use the angle between these two planes to perform the alignment.


Click on the **Measure/Change** arrow  and select **Angle** from the dropdown list. Click on the butadiene plane and then the ethene plane.


The angle between the planes is displayed, you can change some properties of the angle to improve alignment.

Change to the **Selection** tool  and select the angle monitor. In the Properties Explorer change the **AngleAxisType** property to **Through Node** and the **Angle** property to **0**.

The planes through the double bonds on each of the molecules are aligned.

Next, you will move the two structures to a distance that will favor optimization of the reaction pathway.

Click on the **Measure/Change** arrow  and select **Distance** from the dropdown list. Click on the **butadiene** plane and then **either carbon** in the ethene.

Change to the **Selection** tool  and select the distance monitor. In the Properties Explorer change the value of the **Distance** property to **5 Å**.


You will not need the planes or the angle and distance monitors, so you should delete them before proceeding.


Select the butadiene plane and press the **Delete** key.

Select the ethene plane and press the **Delete** key.

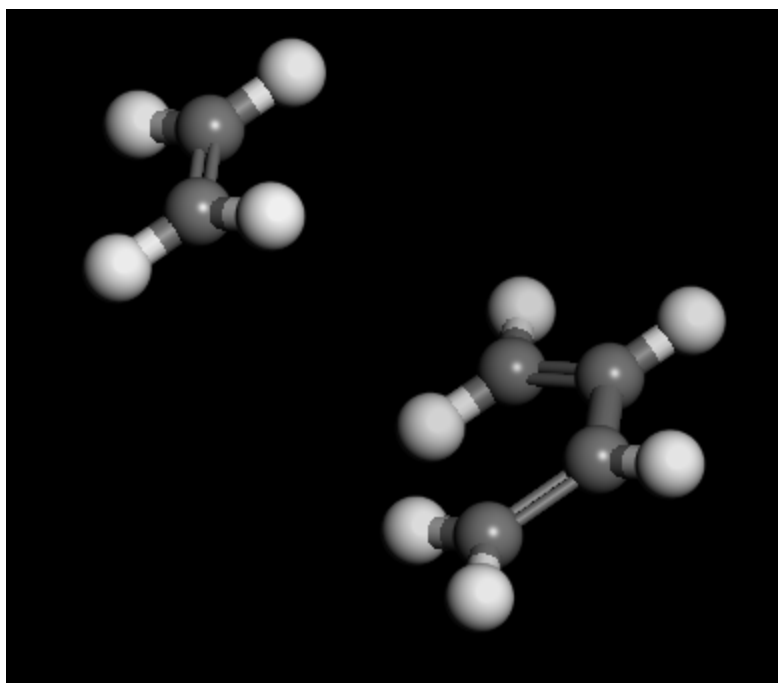
The angle and distance monitors will be automatically deleted.

Finally, you need to add a slight twist to the central single C-C bond in the butadiene molecule. The minimum energy conformation of this molecule is dictated by the diene's desire to have co-planar π -systems for maximally efficient electron delocalization, and the steric repulsion between two hydrogen atoms. This means a small twist in the molecule can reasonably be expected, but will not be found in a completely symmetric flat initial configuration.

Click on the **Measure/Change** arrow  and select **Torsion** from the dropdown list. Click on the single bond in the butadiene molecule.

Change to the **Selection** tool  and select the torsion monitor. In the Properties Explorer change the value of the **Angle** property to **5 degrees**.

You should now have the butadiene and ethane molecules in a configuration suitable for a pericyclic reaction.




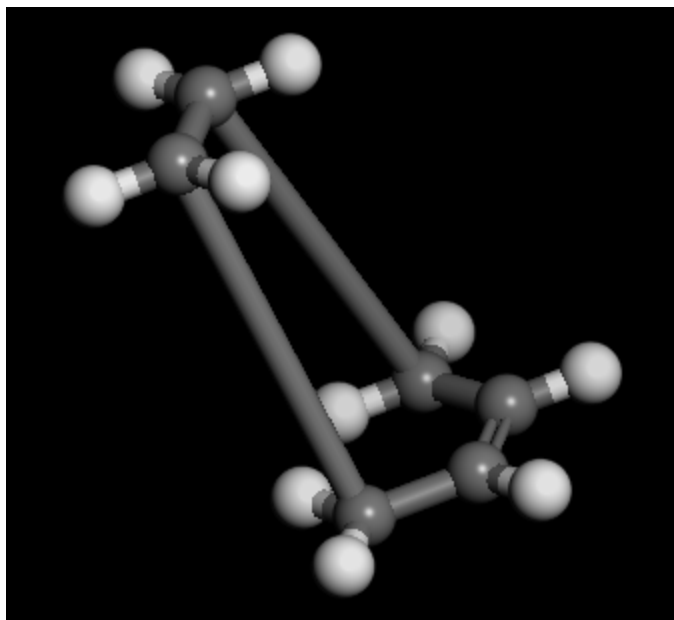
Next, you will build a model of the product structure.

In the Project Explorer make a copy of **ButadieneEthene.xsd** and rename it **Cyclohexene**.


Ensure that **Cyclohexene.xsd** is the active document. Select all **three double bonds**, in the Properties Explorer change the **BondType** to **Single**. Select the **central bond** of the **butadiene** structure and change its **BondType** to **Double**.

Tip: You might find it easier to select the bonds if you rotate the structures. Take care to rotate the whole document, not a single selected structure as this will alter the geometry and alignment.

Use the **Sketching** tool  to draw bonds between the **terminal ethene and butadiene carbons** - to form a six-membered ring.



This structure includes unreasonably long bonds, you should optimize the geometry before proceeding to model the reaction.

Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** or choose **Modules | Forcite | Calculation** from the menu bar.

Change the **Task** to **Geometry Optimization** and set the **Quality** to **Fine**. On the **Energy** tab, set the **Forcefield** to **COMPASSII**.

Click the **Run** button and close the dialog.

A new folder, named Cyclohexene Forcite GeomOpt, opens in the Project Explorer. The calculation should take less than one minute to complete and reach the stipulated convergence criteria. When completed, the Cyclohexene.xsd document in the new folder contains the optimized structure.

Select **File | Save Project** and then **Window | Close All** from the menu bar.

3. To create the reaction trajectory

For DMol³ to perform a transition-state search, all the atoms in the reactant and product documents need to be paired. This is performed using the Reaction Preview functionality on the *Tools* menu.

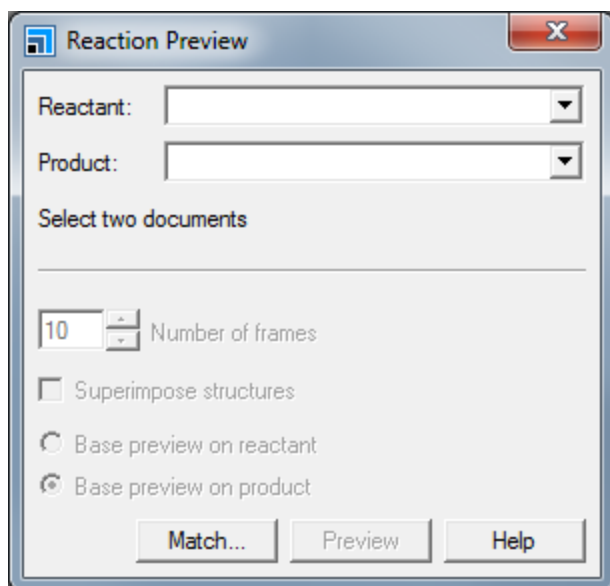
First, you should display the reactant and product structures side-by-side.

Open the **ButadieneEthene.xsd** and **Cyclohexene Forcite GeomOpt\Cyclohexene.xsd** documents. Choose **Window | Tile Vertically** to view both structures at the same time.

Now you are ready to start pairing atoms in the reactant and product structures.

Select **Tools | Reaction Preview** from the menu bar.

This opens the Reaction Preview dialog.



Reaction Preview dialog

It is easier to find the transition state starting from the cyclohexene molecule as the reactant, so the search will begin from this structure.

Select the **Cyclohexene Forcite GeomOpt\Cyclohexene.xsd** from the **Reactant** dropdown tree view and select **ButadieneEthene.xsd** as the **Product**. Click the **Match...** button to open the Find Equivalent Atoms dialog.

You should see that no atoms are matched.

For each unmatched atom in the **ButadieneEthene.xsd** list, select the equivalent atom in the **Cyclohexene.xsd** list. Begin with the hydrogen atoms at the center of the butadiene fragment, these are equivalent to the hydrogens on the cyclohexene double bond. Click the **Set Match** button. When you have set up all the matches, **close** the Find Equivalent Atoms dialog.

Tip: To make it easier to select the correctly matching atoms, change the Display Style in both documents to Ball and Stick. You can also change the Projection to Perspective in the Display Options dialog to assist in identifying equivalent atoms.

You can preview the reaction between butadiene and ethene to form cyclohexene.

On the Reaction Preview dialog, select **Base preview on reactant** and click the **Preview** button. Close the dialog.

A trajectory document is produced called **Cyclohexene-ButadieneEthene.xtd**. Animating this document gives an approximate description of the reactive collision.

4. To calculate the transition state

You are now ready to set up the DMol³ calculation to calculate the transition state.

Ensure that the **Cyclohexene-ButadieneEthene.xtd** trajectory document is in focus. Close the other documents.

Open the **DMol3 Calculation** dialog, on the **Setup** tab change the **Task** to **TS Search**. Make sure that the **Quality** is set to **Medium** and set the **Functional** to **m-GGA** and **M11-L**, check the **Spin unrestricted** checkbox.

Click the **More...** button to display the DMol3 Transition State Search dialog. Make sure the **Search protocol** is set to **Complete LST/QST** and set the **Quality** to **Medium**. Check the **Optimize reactants and products** checkbox, set the **Max. number QST steps** to **10**, and close the dialog.

On the **Electronic** tab, change the **Basis set** to **DNP+**. Click the **More...** button and check **Use smearing** on the **SCF** tab of the DMol3 Electronic Options dialog, close the dialog.

On the **Properties** tab, check the **Frequency** checkbox.

On the **Job Control** tab uncheck the **Automatic** checkbox. Type in **TS** as the **Job description**.

Click the **Run** button and close the dialog.

Note: During the calculation, several different documents and an LST/QST graph are displayed in the workspace. These report the status of the calculation. In particular, an LST/QST graph monitors the progress of the TS search by showing a plot of energy vs. path coordinate for LST, QST, and CG (conjugate gradient).

After job completion, you can view text results in the **TS.outmol** file. The **TS.xod** file contains the reactants, product, and proposed transition state.

Tip: The energy of each component of the reaction (reactant, product, and TS) in the collection document can be inspected and altered in the Properties Explorer. Select the component of interest, choose **Energy** from the **Filter** dropdown list and double-click on the **TotalEnergy** property (in kcal/mol) to open the Edit Property dialog. For example, you may wish to change this energy if you have additional information from another calculation.

5. To calculate the rate coefficient parameters

The next step is to run a Reaction Kinetics calculation to obtain the parameter required to find the rate coefficient.

Ensure that the **TS.xod** collection document is in focus. Close the other documents.

Before performing a reaction kinetics run you should ensure that your input structures are reasonable. To do this, you should perform vibrational analysis.

Select **Tools | Vibrational Analysis** from the menu bar to open the Vibrational Analysis dialog. Double-click on the **TS** structure to select it and click the **Calculate** button on the dialog.

A true transition state will only have one imaginary (negative) frequency.

In order to calculate the correct rate coefficient, the Reaction Kinetics task needs to determine the type of reaction; that is, whether it is an isomerization reaction, an association/dissociation reaction, or an exchange reaction. This is done by assigning motion groups. The Reaction Kinetics task attempts to assign motion groups to the reactive fragments; however, the motion groups on the reactant(s) and product(s) can be explicitly set using the Motion Groups dialog.

Choose **Modify | Motion Groups** from the menu bar to open the **Motion Groups** dialog. Select the **Reactant** structure in the collection document and click **Create from selection**. Repeat this for the **TS** structure. For the Product, select the **ethene** structure and create a motion group, then select the **butadiene** structure and create a motion group. Close the dialog.

You should have four motion groups assigned in total, one for the reactant and transition state, and two for the product.

Open the **DMol3 Calculation** dialog, on the **Setup** tab change the **Task** to **Reaction Kinetics**. Click the **More...** button to display the DMol3 Reaction Kinetics dialog. Check the **Optimize transition state** checkbox and close the dialog.

On the **Job Control** tab uncheck the **Automatic** checkbox. Type in **Kinetics** as the **Job description**. Click the **Run** button and close the dialog.

When this job has finished an updated `Kinetics.xod` document will be produced.

6. To calculate the rate coefficient

In this section the output `Kinetics.xod` will be analyzed to calculate the rate coefficient.

With the `Kinetics.xod` in focus, open the **DMol3 Analysis** dialog and select **Reaction kinetics**. Set the temperature range **From 200.0 K To 1000.0 K**. Uncheck the **Apply tunneling correction** checkbox and click the **Calculate** button.

A Study Table is produced, containing the parameters of the Arrhenius equation for the rate of reaction:

$$k = Ae^{-E_a/RT}$$

The calculated parameters can be compared with experimental values obtained from shock tube experiments for the dissociation reaction ([Tsang, 1965](#)), DMol³ also provides the parameters for the association reaction.

Note: Using *Fine Quality* you can obtain results which are closer to experimental values, however these calculations are likely to take significantly longer.

Parameter	Dissociation Tutorial (Medium)	Dissociation Tutorial (Fine)	Dissociation Experiment	Association Tutorial
A	$6.5 \times 10^{13} \text{ s}^{-1}$	$6.4 \times 10^{13} \text{ s}^{-1}$	$1.05 \times 10^{15} \text{ s}^{-1}$	$1.4 \times 10^{-15} \text{ cm}^3/\text{molecule/s}$
E_a/R	33000 K	33000 K	33565 K	7800 K
k(298K)	$1.2 \times 10^{-35} \text{ s}^{-1}$	$1.5 \times 10^{-34} \text{ s}^{-1}$	$1.273 \times 10^{-34} \text{ s}^{-1}$	$5.7 \times 10^{-27} \text{ cm}^3/\text{molecule/s}$

Select **File | Save Project** from the menu bar, then **Window | Close All**.

This is the end of the tutorial.

References

Tsang, W. J. *Chem. Phys.*, **42**, 1805 (1965).

Simulating electron transport with DMol³

Purpose: To introduce DMol³ calculations on transport devices

Modules: Materials Visualizer, DMol3

Time: 🕒🕒🕒

Prerequisites: Building transport devices for electron transport calculations Visualizer Tutorial

Background

The Electron Transport task in DMol³ applies the non-equilibrium Green's function (NEGF) formalism to model electron transport between two electrodes. The Electron Transport task allows you to calculate transmission functions and current voltage characteristics.

Introduction

In this tutorial you will use the DMol³ module to calculate transport properties for a lithium island connected to two hydrogen chain electrodes.

This tutorial covers:

- [Getting started](#)
- [Initial preparation](#)
- [To set up the electron transport job](#)
- [To analyze the transmission function](#)
- [To analyze the current voltage characteristics](#)
- [To analyze the charge density and potential](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

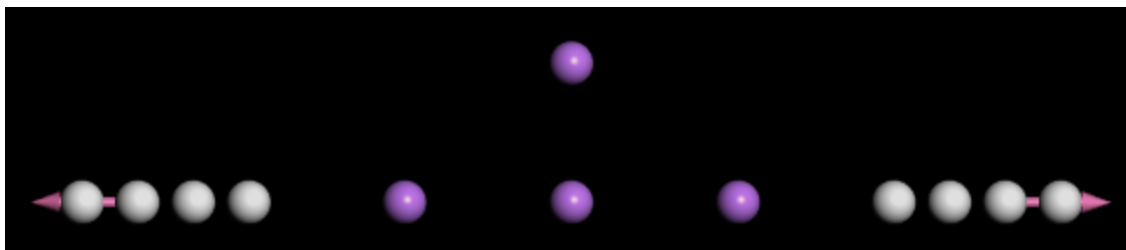
Open the **New Project** dialog and enter **DMol3 Transport** as the project name, click **OK**.

The new project is created with DMol3 Transport listed in the Project Explorer.

2. Initial preparation

The first step is to import the device structure.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Examples\Documents\3D Model\HChainLi4.xsd**, click **Open**.




Device structure

The device comprises two hydrogen chains and four lithium atoms in a central island.

3. To set up the electron transport job

You now have a device structure ready for use with the DMol³ Electron Transport task.

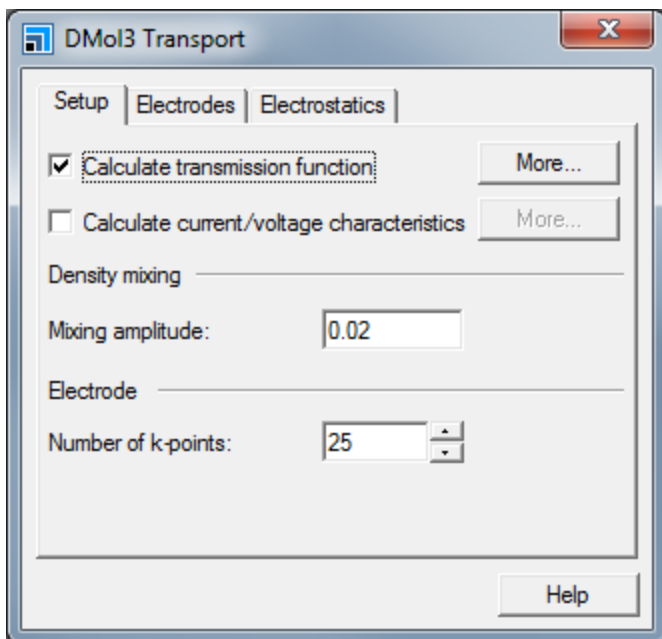
Begin by setting up a calculation for the transmission of the device.

On the **Modules** toolbar click the **DMol³ tools** button: 

Select **Calculation**. The **DMol³ Calculation** dialog is displayed.

On the **Setup** tab select **Electron Transport** in the **Task** dropdown list.

Click **More...** to open the **DMol³ Transport** dialog.



The DMol³ Transport dialog contains settings specific to the Electron Transport task.

Make sure the **Calculate transmission function** checkbox is checked.

This will request calculation of the transmission functions between the electrodes. The range and number of steps for the transmission function can be modified to fit the device. The energy range is given relative to the lowest Fermi energy for the electrodes.

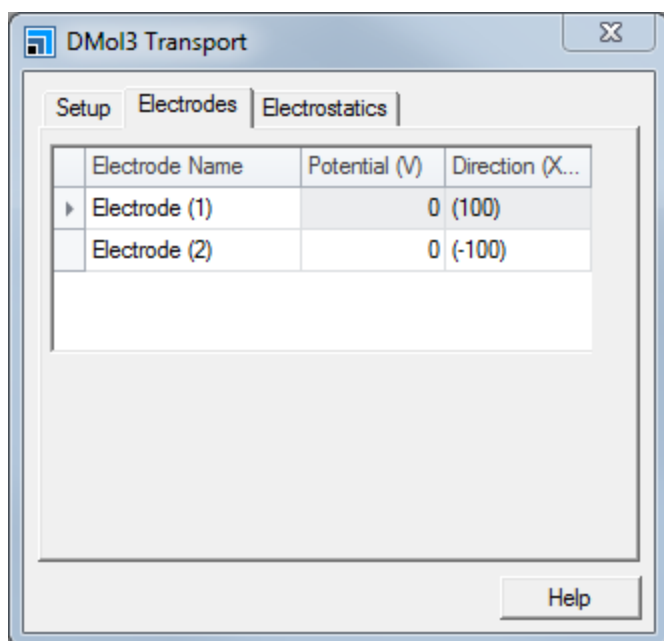
On the **Setup** tab of the DMol3 Transport dialog, click **More...** for **Calculate transmission function** to open the DMol3 Transmission dialog. Set **From** to **-2**, **To** to **3**, and the number of **Steps** to **1001**. Close the dialog.

Since a transport device is an open system it does not conserve charge during the SCF cycle and is often prone to charge fluctuations. As a result the mixing parameter used for the charge mixing should be smaller than the normal mixing parameter used in DMol³.

On the **Setup** tab of the DMol3 Transport dialog set the **Mixing amplitude** to **0.015**

As part of the calculation each electrode will be modeled as a periodic structure in order to calculate the Fermi level and other properties needed to describe the electrodes during the device calculation. You should ensure that the number of k-points used for the calculation is large enough to properly predict the Fermi level and the electronic structure of the electrodes. For this calculation the default value of **25** will be enough.

Select the **Electrodes** tab.



The Electrodes tab shows information about the hydrogen electrodes and allows you to modify settings for them. You will change the name of the electrode so that they are more easily identifiable later.

Change the name of **Electrode(1)** to **source** and **Electrode(2)** to **drain**. Close the DMol3 Transport dialog.

The names of the electrode objects are also modified in the 3D Atomistic document.

Note: If you use the Properties Explorer to change the name of electrodes, the electrode will use any settings related to the *new* name. If no settings exist the default settings will be applied. When the name is changed on the DMol3 Transport dialog the current settings will be used with the new name.

Since the convergence of the SCF cycle can be problematic for transport calculations it is prudent to increase the maximum number of SCF cycles.

On the **Electronic** tab of the DMol3 Calculation dialog click **More...** to open the DMol3 Electronic Options dialog.

On the **SCF** tab set the **Max. SCF cycles** to **500**.

You are now ready to start the transport job.

Click **Run**.

A text document named Status.txt is displayed, reporting the status of the calculation. This document is updated regularly until the calculation is complete, it can be a useful aid to indicate the progress of your calculation. The transmission calculation should only take a few minutes.

You will now set up a current calculation for the same device.

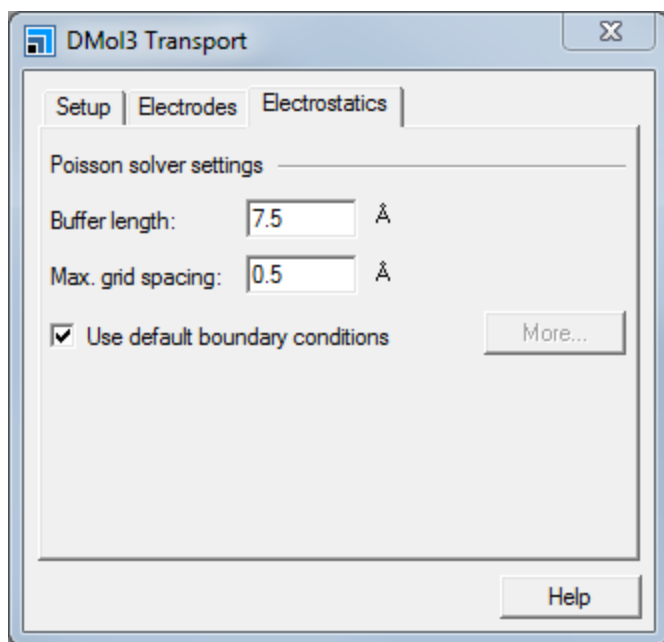
Close all of the output files and make the original **HChainLi4.xsd** the active document.

Open the DMol3 Transport dialog, on the **Setup** tab uncheck the **Calculate transmission function** checkbox and check the **Calculate current/voltage characteristics** checkbox. Click **More...** for **Calculate current/voltage characteristics** to open the DMol3 Current/Voltage dialog.

Set **Vary potential for** to **source**, set the potential range **From** to **0**, **To** to **1.5**, and the number of **Steps** to **16**. Close the dialog.

For a biased calculation the quality of the calculation can be improved by decreasing the grid spacing for the Poisson solver.

On the DMol3 Transport dialog select the **Electrostatics** tab.



On the **Electrostatics** tab of the DMol3 Transport dialog, set the **Max. grid spacing** to **0.3**

You can calculate the charge density and electrostatic potential to improve your understanding of the device.

Select the **Properties** tab of the DMol3 Calculation dialog, select the **Electron density** property, and check the **Deformation density** check box.
Select **Electrostatics** the property and click **Grid...** to open the **Dmol3 Grid Parameters** dialog. Set the **Grid resolution** to **Fine**.

You are now ready to launch the job.

Click **Run** and close the dialog.

The current calculation can take up to a few hours depending on the computational resources used.

4. To analyze the transmission function

When the transmission calculation is complete the results are returned in the HChainLi4 DMol3 Transport folder in the Project Explorer.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

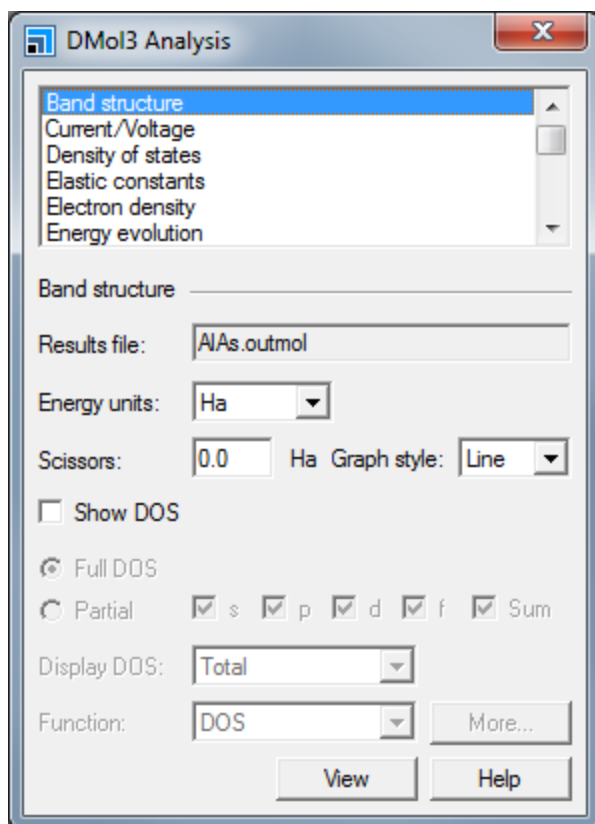
In the **HChainLi4 DMol3 Transport** folder double-click on **HChainLi4.xsd**

You will now analyze the results using the DMol3 Analysis module.

On the **Modules** toolbar click the **DMol3** button: 

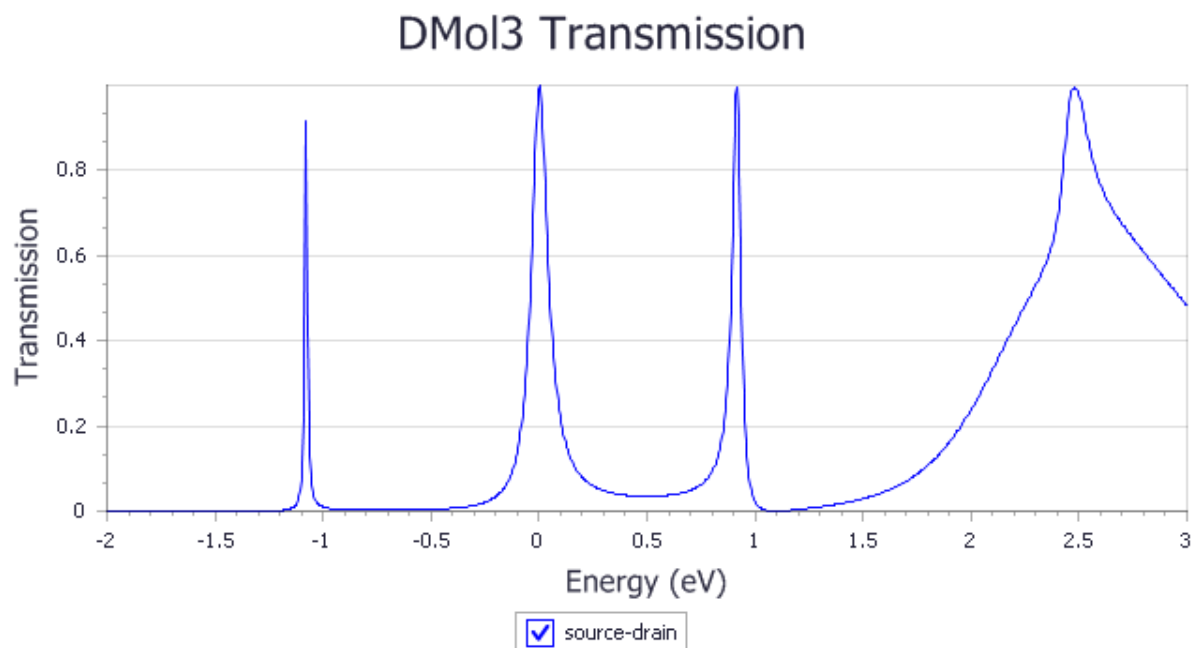
Select **Analysis** or choose **Modules | DMol3 | Analysis** from the menu bar.

This opens the DMol3 Analysis dialog.



Select **Transmission** from the list and click **View**. Close the dialog.

A plot of the transmission function is shown.



The transmission for the device will have peaks where the Li island have states. If the states are delocalized on both the island and electrode leads then the peak will be broadened by the electrodes while if the state is strongly localized on the island the peak will be sharp. The energies of the transmission function are plotted relative to the lowest chemical potential of the electrodes.

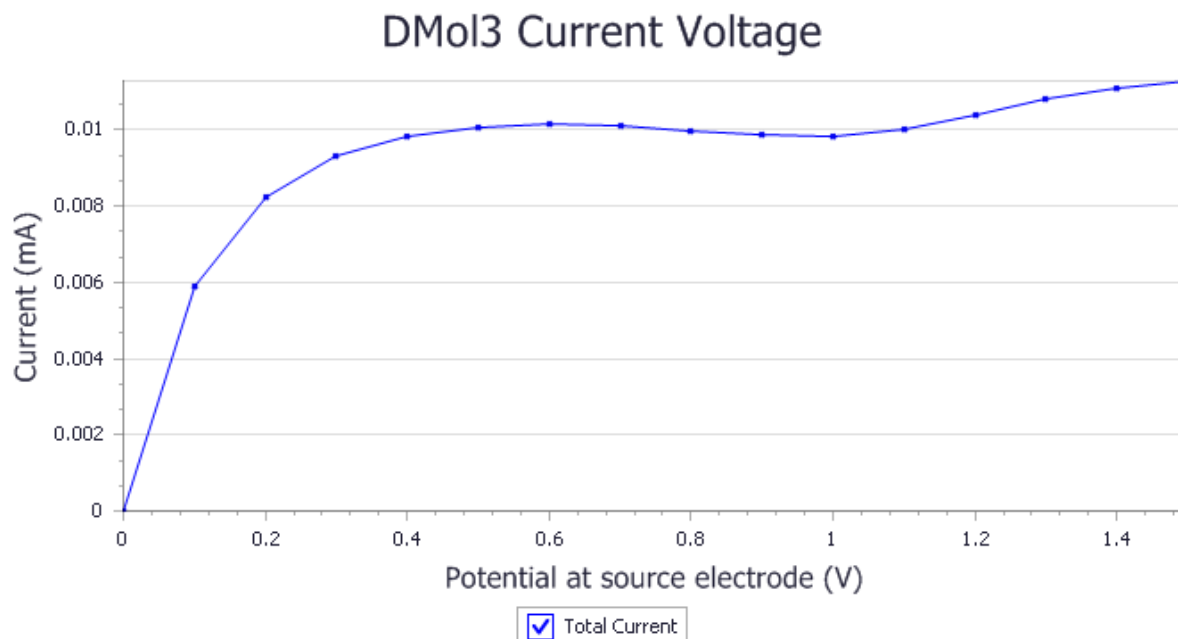
5. To analyze the current voltage characteristics

When the current calculation is complete the results are returned in the HChainLi4 DMol3 Transport (2) folder in the Project Explorer.

In the **HChainLi4 DMol3 Transport (2)** folder double-click on **HChainLi4.xsd**.

Open the **DMol3 Analysis** dialog, select **Current/Voltage** and click **View**. Close the dialog.

A plot of the current voltage characteristics is shown.



Since the device is symmetric along the transport direction we expect the current for positive and negative bias to only differ by a sign. The current is measured at the drain electrode and the voltage is varied at the source electrode. We use the convention that a positive current indicates that current is passing out of the device at the electrode where the current is measured.

To analyze the charge density and potential

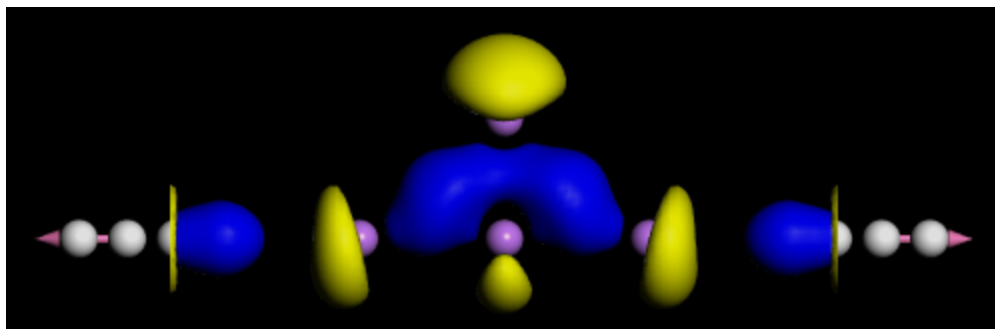
In the **HChainLi4 DMol3 Transport (2)** folder double-click **HChainLi4.xsd**.

Open the **DMol3 Analysis** dialog and select **Electron density**.

In the **Density field** dropdown list select **Deformation density** and click **Import**.

In the **HChainLi4.xsd** document open the **Display style** dialog. On the **Isosurface** tab set the **Isovalue** to **0.015** and the **Type** to **+/-**.

The **HChainLi4.xsd** document now contains an isosurface representing the deformation density for the device.



In the **HChainLi4 DMol3 Transport (2)** folder double-click on **HChainLi4.xsd**.

Open the **DMol3 Analysis** dialog and select **Potentials**.

In the **Potential field** dropdown list select **Biased electrostatic potential**. In the **Bias potential** dropdown list select **1.0 V**.


Click **Import** to import the field.

The potential field is best viewed as a slice through the device.

On the **Volume visualization** tool bar click the **Create slice** button: 

Choose **Parallel to A & B axis**, and select **Dmol3 electrostatic potential Ha*electron(-1)(1.0000 V)**.

The potential is given in atomic units and will have large values close to the atoms. To view the potential drop over the device the range of the color map needs to be changed.

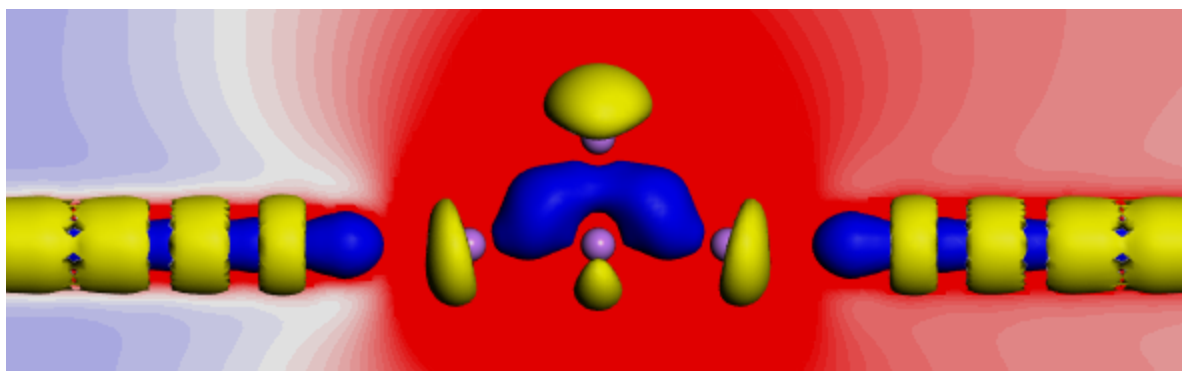
On the **Volume visualization** tool bar click the **Color maps** button: 

Set **From** to **-0.05** and **To** to **0.05**. Change the **Spectrum** to **Blue-White-Red**.

The range of the field for both charge density and electrostatic potential are set to the range of the defined device. The range can be expanded to include the extended sections of the device created during the DMol calculation.

In the **HChainLi4.xsd** document open the display style window, and on the **Field** tab set the **Display range** for **A** to **0.25** and **0.7**.

The **HChainLi4.xsd** document now shows a potential slice through the center of the device. Notice how the potential drops over the Li island section of the device.



This is the end of the tutorial.

Forcite tutorials

The following tutorials illustrate how to utilize Forcite's capabilities.

- [Geometry optimization of urea with and without symmetry constraints](#)
- [Hydrogen physisorption on a tungsten surface](#)

Some [Forcite Plus](#) tutorials are also available.

Geometry optimization of urea with and without symmetry constraints

Purpose: Illustrates the effect of symmetry when optimizing a structure using Forcite.

Modules: Materials Visualizer, Forcite, COMPASS

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Forcite in Materials Studio is a classical molecular mechanics tool, designed by BIOVIA scientists and software engineers to perform a range of tasks including fast energy calculations and geometry optimizations for single molecules as well as periodic systems. In geometry optimizations of crystal structures Forcite retains the symmetry of the systems, which is of particular importance in work relating to structure determination.

Introduction

In the determination of crystal structures it is important that both the symmetry elements are found to be correct, and that at the same time the structure is in an energy minimum. This means that an optimized structure should not change very much if a further geometry optimization is carried out without symmetry constraint.

This tutorial aims to demonstrate the use of symmetry when performing the geometry optimization of a crystal structure. For the purposes of this tutorial you will use the crystal structure of urea, a widely used chemical and pharmaceutical intermediate.

This tutorial covers:

- [Getting started](#)
- [To perform a geometry optimization of the structure and cell with symmetry](#)
- [To remove the symmetry and carry out a further geometry optimization](#)
- [To compare the results of the two runs](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **urea** as the project name, click the **OK** button.

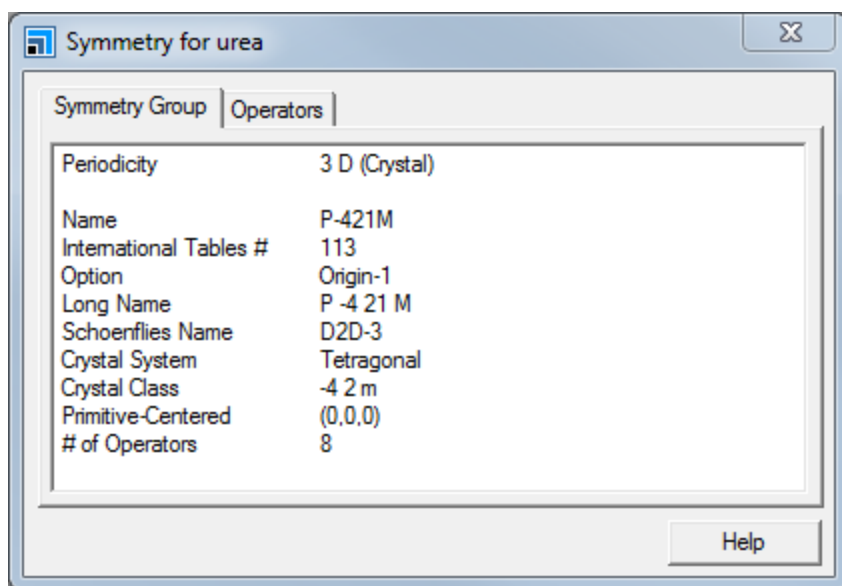
The new project is created with *urea* listed in the Project Explorer. You will load the crystal structure of the system you will be studying. In this tutorial, you will be working with *urea*.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Structures/molecular-crystals/misc** folder and double-click on **urea.msi**.

The crystal structure of *urea* is displayed in a 3D Atomistic Document called *urea.xsd*. You will check the symmetry of the structure.

Click the **Show Symmetry** button  on the **Symmetry** toolbar, or choose **Build | Symmetry | Show Symmetry** from the menu bar.

This opens the Symmetry dialog.




Symmetry dialog

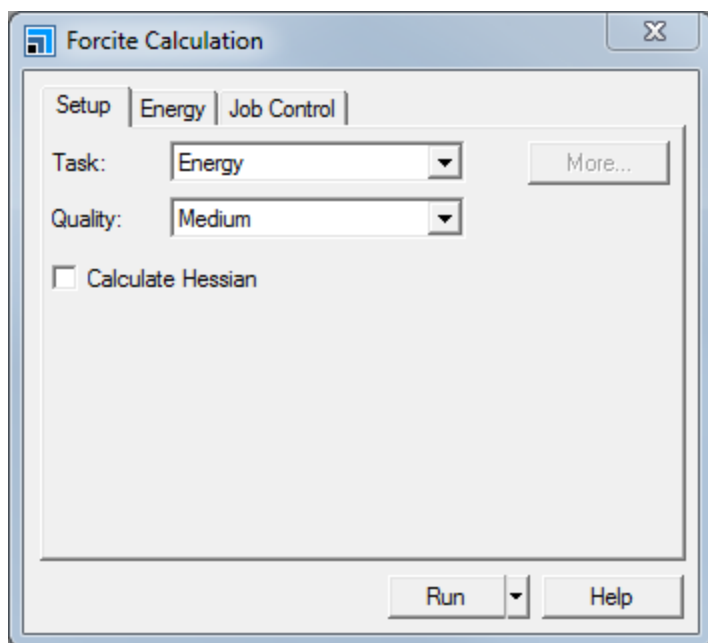
It shows that the space group is P-421M.

2. To perform a geometry optimization of the structure and cell with symmetry

The next step is to carry out a geometry optimization of *urea* using the COMPASS forcefield.

Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog.



Forcite Calculation dialog, Setup tab

Change the **Task** from Energy to **Geometry Optimization** and the **Quality** to **Fine**.

Click the **More...** button to display the Forcite Geometry Optimization dialog. Check the **Optimize cell** checkbox and close the dialog.

On the **Energy** tab choose **COMPASS** from the **Forcefield** dropdown list. Leave all the other settings unchanged.

Click the **Run** button and close the dialog.

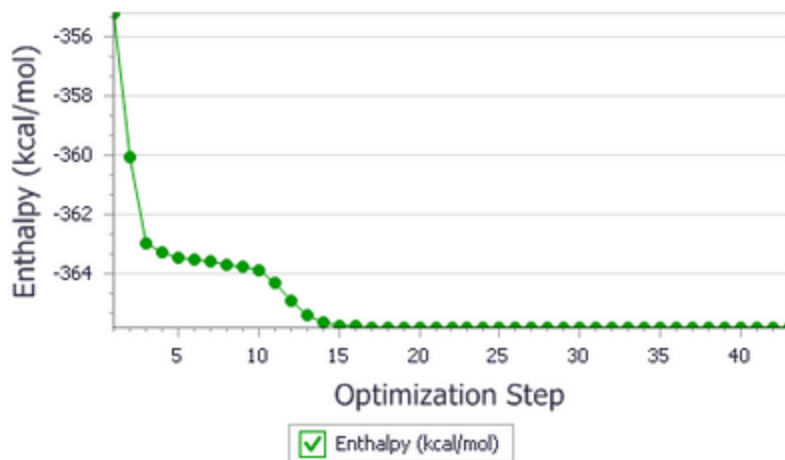
A new folder, entitled urea Forcite GeomOpt, opens in the Project Explorer. The calculation should take less than one minute to complete, that is, to reach the stipulated convergence criteria, since the library structure is already close to optimum. When completed, the urea .xsd document near the top of the new folder contains the optimized structure.

There are six other documents in the urea Forcite GeomOpt folder. The urea .txt document contains all the text information for the job, in particular the structure and energy parameter values for the initial and final structure. The Status .txt document contains the last job execution status. The urea Energy chart shows the variation of the total energy during the optimization. The urea Convergence chart shows the variation of the convergence criteria, namely Energy Change, Gradient Norm and Stress Norm as a function of the Optimization step. The simulation stopped as soon as all the required criteria were met. The urea Cell chart shows the variation of the cell parameters, and the urea Density chart shows the variation of the system density.

Open the chart document **urea Energies.xcd**.

It should look similar to the one below.

Forcite Geometry Optimization - Energy



Now you should make sure that the symmetry has not changed.

Make **urea Forcite GeomOpt/urea.xsd** the active document and open the **Symmetry** dialog.

The space group is still P-421M. Before completing this section of the tutorial you should save the project and tidy up the workspace area.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To remove the symmetry and carry out a further geometry optimization

Now repeat the same procedure without symmetry constraints. Begin by importing another copy of the urea structure.

Open the **Import Document** dialog, navigate to **Structures/molecular-crystals/misc/** and import **urea.msi**.

A second 3D Atomistic Document containing the urea structure, called urea (2).xsd, is displayed. Now remove the symmetry from the crystal structure.

Select **Build | Symmetry | Make P1** from the menu bar.

Confirm that the symmetry is now P1.

On the **Symmetry** dialog check that the Space group is **P1**. Close the dialog.

In order to reflect the changed symmetry, you should rename urea (2).xsd.

Right-click on **urea (2).xsd** in the **Project Explorer** and select **Rename** from the shortcut menu. Change the name to **urea_P1**.

The next step is to carry out a geometry optimization on urea_P1, using the same settings as before.

Open the **Forcite Calculation** dialog.

All of the previous parameters are retained and you want to run the calculation in exactly the same way as before, there is no need to make any changes to the settings.

Click the **Run** button and close the dialog.

A new folder, entitled urea_P1 Forcite GeomOpt, opens in the Project Explorer. Again, the calculation finishes very quickly. When it is complete, save the project and close all of the open windows once more.

Select **File | Save Project** on the menu bar, then **Window | Close All**.

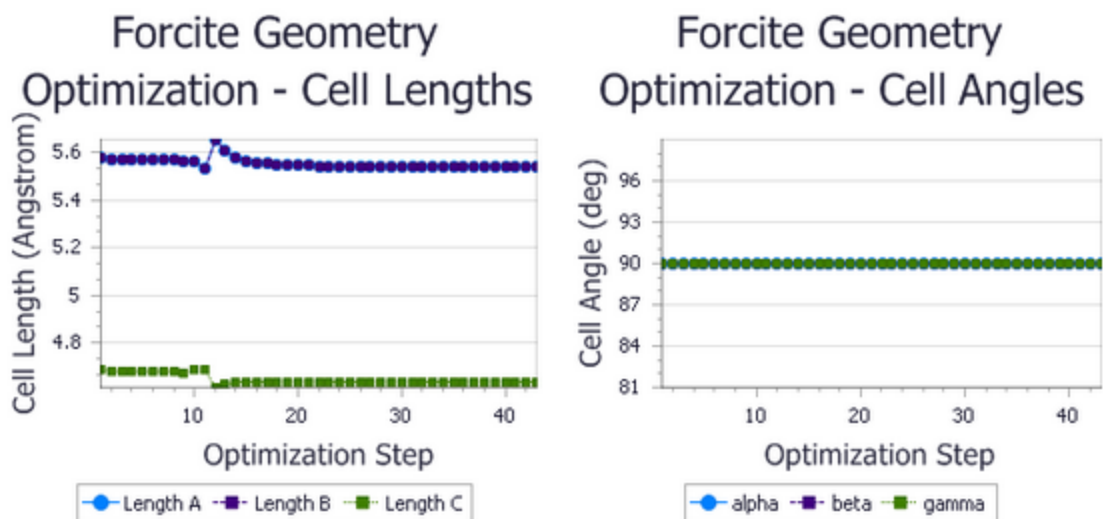
4. To compare the results of the two runs

The final step is to compare the results of the two calculations.

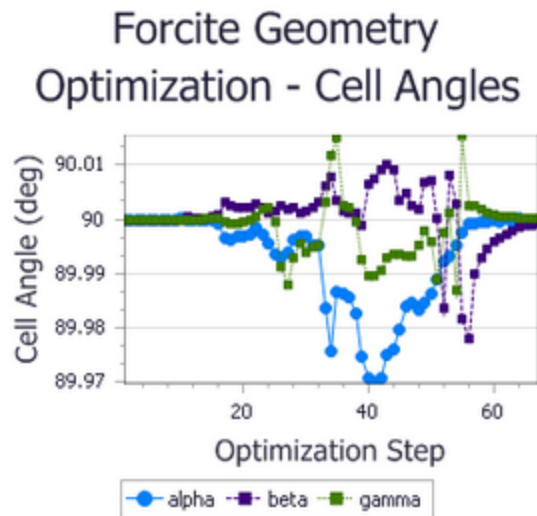
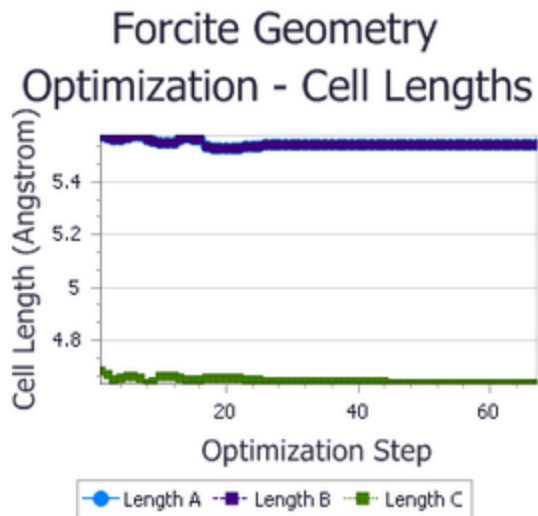
Locate and open the text output documents **urea.txt** and **urea_P1.txt** and open them. Scroll down to the final structure **Total energy**.

The values are almost identical at -365.83 kcal/mol. Now compare the two cell optimizations.

Locate and open the chart documents **urea Cell.xcd** and **urea_P1 Cell.xcd**.



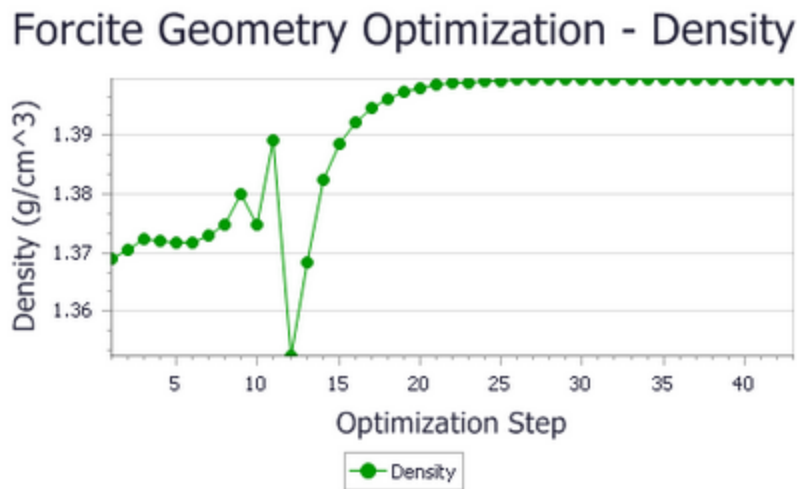
P-421M urea cell



P1 urea cell

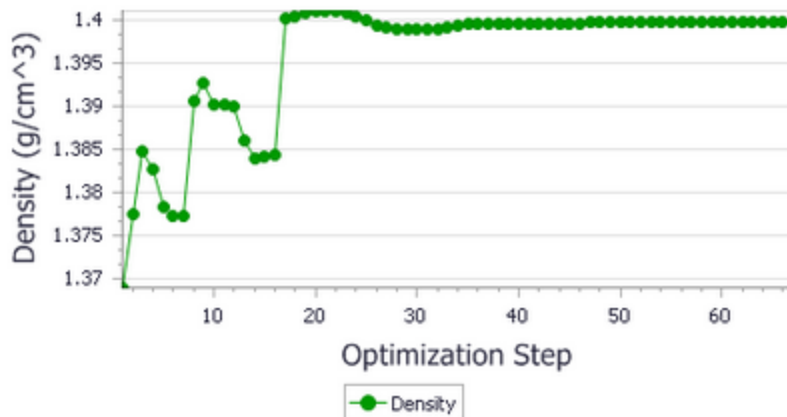
In the case of urea with full symmetry, the cell lengths have decreased slightly and the angle had remained constant at 90° in line with the symmetry constraints. In the case of the P1 structure, with no symmetry constraints, the cell angles vary during the simulation. While the exact variations are very sensitive to machine details, the angles finally converge again to 90°. So, overall the cell angles are also very similar in both cases.

Locate and open the charts **urea Density.xcd** and **urea_P1 Density.xcd**.



P-421M urea density

Forcite Geometry Optimization - Density



P1 urea density

In both cases the density of the urea cell has increased slightly as a result of the optimization. Once again, exact variations depend on machine details, but the final value will be just below 1.40 g/cm³.

You can conclude that the course the geometry optimization takes in each case is quite different but that both calculations converge to the very similar values in the end.

You have learned that symmetry elements are maintained during Forcite geometry optimization and that the presence or absence of these elements strongly affects the course of the calculation. Once a structure is close to its minimum energy conformation it may, as in this case, converge to give very similar cell parameters and energies with and without symmetry constraints.

This is the end of the tutorial.

Hydrogen physisorption on a tungsten surface

Purpose: Introduces the use of Forcite to generate an optimized structure of a molecule on a surface.

Modules: Materials Visualizer, Forcite

Time: 

Prerequisites: [Geometry optimization of urea with and without symmetry constraints](#)

Background

Forcite in Materials Studio is a classical molecular mechanics tool, designed by BIOVIA scientists and software engineers to perform a range of tasks including fast energy calculations and geometry optimizations for single molecules as well as periodic systems. It provides access to different forcefields and is easy to use for the novice as well as providing the widest range of customization options for the experienced user.

Introduction

A detailed knowledge of surface interactions and reactions plays a key role in the design of many materials and processes. An important first step in such a study is preparation of a model of molecules physisorbed to the surface with optimized geometry (that is, energy minimized). Among the different steps involved in the modeling approach are the construction of the surface from the pure crystal, the addition of the molecules near to the surface, the definition of the potentials (by the forcefield) to study the gas-solid interaction, followed by the geometry optimization calculation.

This tutorial aims to explain the different steps involved in the study of the physisorption of a gas onto a surface. The system in this tutorial is an example inspired by a case study of the adsorption of H₂ onto a Tungsten surface (see the [White \(1996\)](#) paper). In this particular case, the use of molecular mechanics can be seen as a precursor to computationally more expensive quantum mechanical methods: once the model has been optimized with Forcite, DMol³ or CASTEP can be used to study the chemisorption reaction.

This tutorial covers:

- [Getting started](#)
- [To build a metallic surface from the pure crystal](#)
- [To place the gas phase molecule on the surface](#)
- [To perform a Forcite geometry optimization](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **H2_W** as the project name, click the **OK** button.

The new project is created with *H2_W* listed in the Project Explorer. The next step is to load the crystal structure that you want to cleave, in this tutorial you will be working with pure tungsten (W).

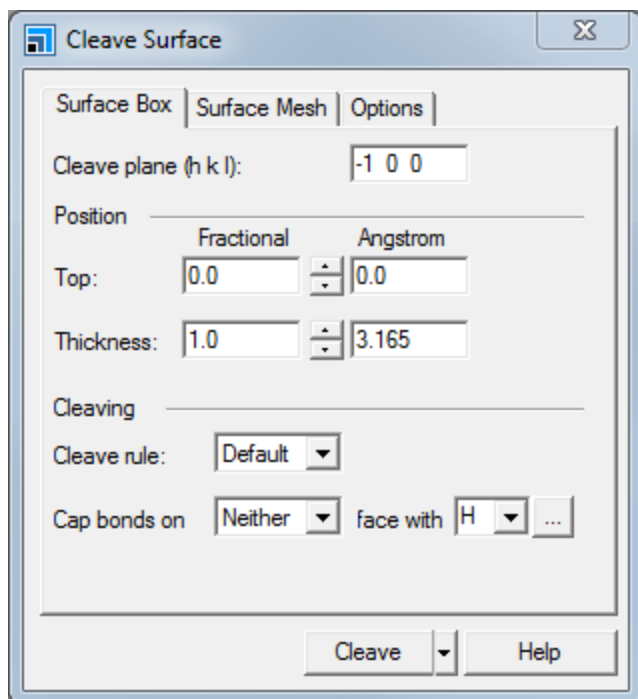
Click the **Import** button  to open the Import Document dialog. Navigate to the **Structures/metals/pure-metals** folder and double-click on **W.msi**.

The crystal structure of Tungsten is displayed in a 3D Atomistic Document called **W.xsd**.

2. To build a metallic surface from the pure crystal

Select **Build | Surfaces | Cleave Surface** from the menu bar.

This opens the Cleave Surface dialog.



Cleave Surface dialog, Surface Box tab

Blue dashed lines are displayed on the crystal indicating the plane you are cleaving. This information is also given at the top of the Surface Box tab. The default plane is $-1\ 0\ 0$, which is equivalent to the $(1\ 0\ 0)$ surface, so you do not need to change this setting.

You should change the thickness of the cell, in order to ensure that the final model includes all the significant interactions between the gas molecule and the tungsten atoms.

Increase the **Fractional Thickness** to **2.0**.

The thickness should be $6.33\ \text{\AA}$. Now that you have set up the surface parameters, you can cleave the cell.

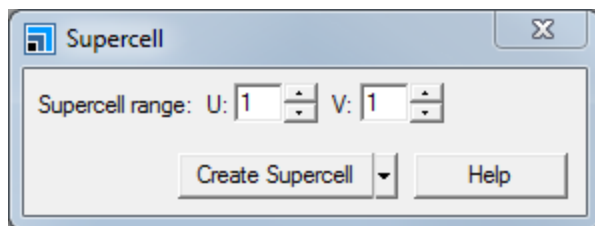
Click the **Cleave** button and close the dialog.

A new 3D Atomistic document, $W(-1\ 0\ 0).xsd$, is opened and a 2D periodic structure is displayed as a white square with the tungsten atoms.

You have now built a 2D cell out of a 3D crystal. However, before you place the gas molecules onto the surface, you need to increase the lateral extent of the surface. This is done to avoid artificial interactions between the gas molecule and its periodic images during the optimization step.

Select **Build | Symmetry | Supercell** from the menu bar.

This opens the Supercell dialog.



Supercell dialog

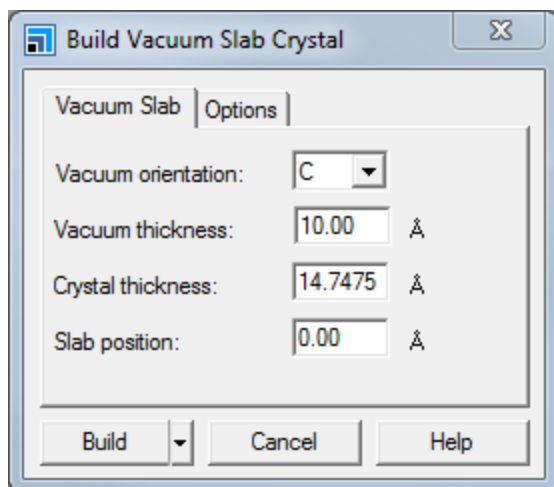
Increase the **Supercell range** for **U** and **V** to **4**. Click the **Create Supercell** button and close the dialog.

A larger surface is built, consisting of 16 of the original cells, this model has 2D periodicity. You will convert it to a 3D lattice using the *Build Vacuum Slab* functionality.

A slab is a 3D periodic cell with the surface at the bottom and a vacuum above it. This enables you to put molecules onto the surface, in the vacuum, so that the molecule does not see a periodic image of the surface above it.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar.

This opens the Build Vacuum Slab Crystal dialog.



Build Vacuum Slab Crystal dialog, Vacuum Slab tab

This dialog allows you to specify the orientation, thickness, and position of the region of vacuum.

Change the **Slab position** from 0.00 to **1.00 Å**. Increase the **Vacuum thickness** to **20.00 Å**. Click the **Build** button.

The W (-1 0 0) 3D Atomistic document updates to display a rectangular box with the surface at the bottom. The tungsten atoms are inside the cell, making it easier to visualize them.

3. To place the gas phase molecule on the surface

The next stage in this tutorial is to build a hydrogen molecule and then position it on the surface. To do this, you will sketch a hydrogen molecule in a new 3D Atomistic document, copy and paste it into the slab and dock it on the surface.

Create a new 3D Atomistic document and sketch and clean an H_2 molecule.

The next step is to copy and paste this into the document containing the slab.

Select **Edit | Copy** from the menu bar. Double-click on **W(-1 0 0).xsd** in the Project Explorer, then choose **Edit | Paste**.

Tip: You can also use the standard Windows shortcut keys CTRL + C to copy and CTRL + V to paste.

The hydrogen molecule is pasted into the cell. A second "ghost" molecule also appears, due to the periodic boundary conditions. This periodic image can easily be removed later.

You can use the Close Contacts tool to monitor how close the hydrogen is to the surface.

Select **Build | Close Contacts** from the menu bar to open the Close Contact Calculation dialog. Check the **Monitor close contacts** checkbox and close the dialog.

Now you have to select the hydrogen molecule and translate and rotate it until it is docked onto the metal surface.

Select the **hydrogen** molecule. Hold down the **SHIFT** and **ALT** keys and the **right** mouse button. Move the mouse to translate the molecule.

Tip: If you have a three button mouse or a mouse with a wheel, you can use the wheel or middle button with the SHIFT key to translate without holding down the ALT key.

As you move the hydrogen atom, a pink dashed line appears to indicate a close contact. Use these controls to position the Hydrogen molecule just above the Tungsten surface, with the pink line just showing.


You can remove the "ghost" molecule in the adjacent unit cell by changing the display style.


Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Lattice** tab select **In-Cell** from the **Style** dropdown list. On the **Atom** tab and select the **Ball and stick** option. Close the dialog.

Click anywhere in the 3D Viewer to deselect everything.

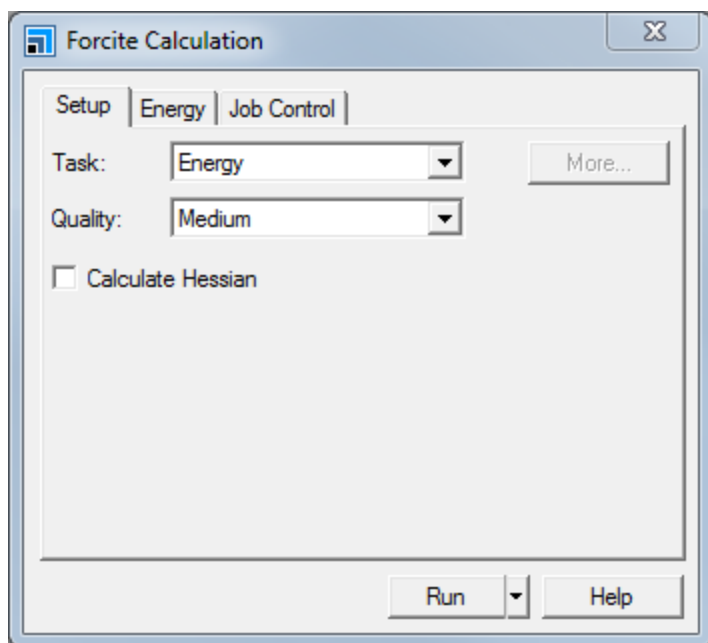
4. To perform a Forcite geometry optimization

The final step in this tutorial is to calculate the actual physisorption of the Hydrogen molecule on the Tungsten surface.

Make **W (-1 0 0).xsd** the active document. Use the **Reset View**  tool on the **3D Viewer** toolbar to place the model in the center of the window.

Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog.



Forcite Calculation dialog, Setup tab

Change the **Task** from Energy to **Geometry Optimization** and the **Quality** to **Fine**.

Click the **More...** button to display the Forcite Geometry Optimization dialog. Change the **Maximum number of iterations** to **1000** and close the dialog.

The minimization algorithm used by default is the **Smart** algorithm; it is a cascade of methods using successively Steepest descent and Conjugate gradient algorithms.

On the **Energy** tab set the **Forcefield** to **Universal**.

The final step before performing the geometry optimization is to fix the coordinates of the metallic atoms. By doing this you are assuming that the surface structure is similar to the bulk and not significantly modified by the Hydrogen atoms. For a more accurate and detailed study, it may be necessary to relax the surface of the crystal before performing the geometry optimization.

Hold down the **ALT** key and double-click on **any Tungsten atom**. All of the Tungsten atoms are now highlighted.

Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. On the **Atoms** tab check the **Fix Cartesian Position** check box and close the dialog.

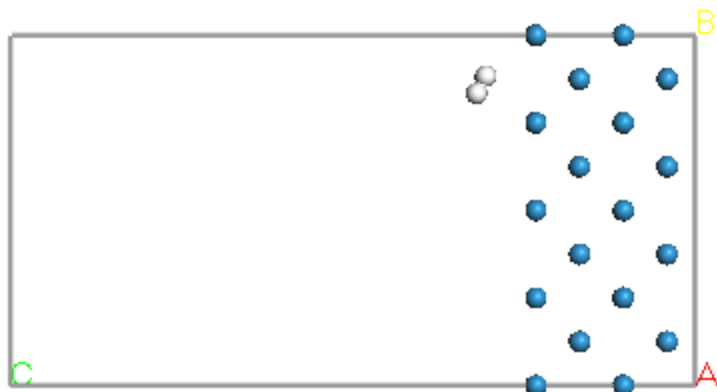
Click anywhere in the **3D Viewer** to deselect all the atoms.

You are now ready to run the simulation.

Click the **Run** button on the Forcite Calculation dialog.

A new folder, entitled W (-1 0 0) Forcite GeomOpt, opens in the Project Explorer. The calculation should take less than one minute to complete, and reach the stipulated convergence criteria. When completed,

the $W(-1\ 0\ 0)$.xsd document near the top of the new folder contains the optimized structure which should look similar to the one shown below.



There are four other documents in the $W(-1\ 0\ 0)$ Forcite GeomOpt folder. The $W(-1\ 0\ 0)$.txt document contains all the text information for the job, in particular the structure and energy parameter values for the initial and final structure. The Status.txt document contains the last job execution status. The $W(-1\ 0\ 0)$ Energy chart shows the variation of the total energy during the optimization. The $W(-1\ 0\ 0)$ Convergence chart shows the variation of the convergence criteria, namely Energy Change and Gradient Norm as a function of the Optimization step. The simulation stopped as soon as all the required criteria were met.

You have now prepared a structure which would be well suited for further simulations, such as the dissociation reaction, using the DMol³ or CASTEP modules.

This is the end of the tutorial.

References

White, J.A.; Bird, D.M.; Payne, M.C. *Phys. Rev. B*, **53**, 1997 (1996), <http://dx.doi.org/10.1103/PhysRevB.53.1667>.

Forcite Plus tutorials

The following tutorials illustrate how to utilize the Forcite Plus capabilities.

- [Finding low energy configurations of a molecule on a surface](#)
- [Using Materials Studio to edit a forcefield](#)
- [Calculating the diffusivity of a gas in a polymer](#)
- [Polymer interactions with a metal oxide surface](#)
- [Calculating the miscibility of two polymers](#)
- [Running a confined shear simulation](#)
- [Calculating the solvation free energy of propionic acid in *n*-octanol](#)

Some [Forcite](#) tutorials are also available.

Finding low energy configurations of a molecule on a surface

Purpose: Demonstrates the use of molecular dynamics and geometry optimization in looking for low energy minima.

Modules: Materials Visualizer, Forcite Plus, QSAR, COMPASS

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial and [Geometry optimization of urea with and without symmetry constraints](#)

Background

The potential energy surface of a small molecule can be very complex, with many local energy minima and one global energy minimum. There are several methods that can be used to determine the global minimum including Monte-Carlo algorithms and different forms of molecular dynamics. One common molecular dynamics method, called quench molecular dynamics, performs a standard molecular dynamics calculation with an additional geometry optimization step, in which a geometry optimization is performed on every frame in the trajectory file. Effectively, molecular dynamics is used to sample many different low energy configurations.

Introduction

In this tutorial, you will use Forcite Plus to perform molecular dynamics on a system comprising a small organic molecule, o-chlorophenol, and a metal-oxide surface, titanium dioxide. You will cleave the titanium dioxide surface from the rutile form of the TiO_2 crystal structure. You will place the molecule on the surface, optimize and then run quench molecular dynamics. You will use a study table to look for the lowest energy conformation and finally, you will use the study table to calculate the binding energy.

This tutorial covers:

- [Getting started](#)
- [To sketch and optimize chlorophenol](#)
- [To build and optimize the TiO₂ surface](#)
- [To equilibrate the molecule on the surface](#)
- [To sample configurations using quench dynamics](#)
- [To calculate the binding energy](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

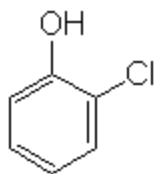
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Cl_phenol** as the project name, click the **OK** button.

The new project is created with *Cl_phenol* listed in the Project Explorer.

2. To sketch and optimize chlorophenol


You are going to sketch the molecule ortho-chlorophenol.



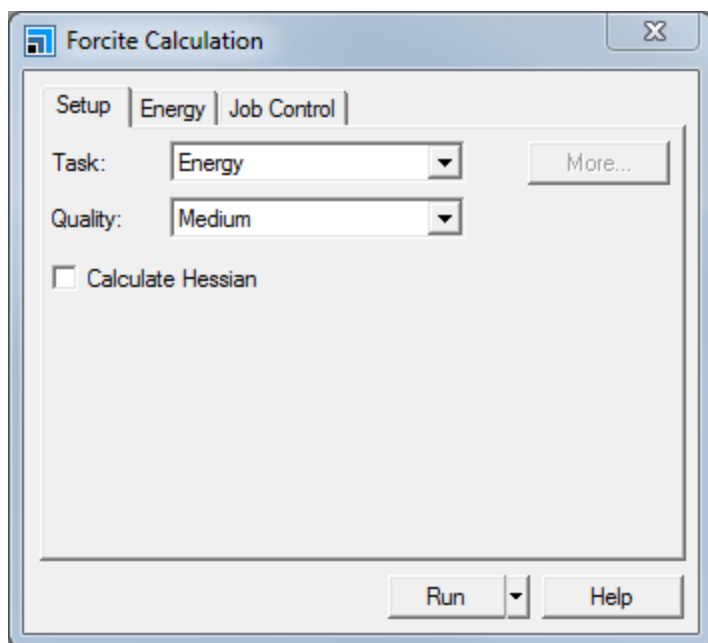
Create a new **3D Atomistic Document**. Sketch a molecule of ortho-chlorophenol, make sure that you use the **Adjust Hydrogen** and **Clean** tools.

In the Project Explorer, rename the 3D Atomistic Document **chlorophenol.xsd**.

The molecule you have sketched will not have an accurate geometry so you should optimize the geometry using a classical simulations tool. Classical simulations tools require a forcefield which describes the forces between atoms in terms of a sum of functions in the distances, angles, and so on, between atoms of various types. For this tutorial, you will use the Forcite classical simulations engine and the COMPASS forcefield.

Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** from the dropdown list, or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog.



Forcite Calculation dialog, Setup tab

On this dialog, you can choose what type of calculation to perform, the *Quality* controls different settings depending on the task chosen. On the *Energy* tab, you can select the forcefield, charging method, and customize the treatment of non-bond terms.

Change the **Task** to **Geometry Optimization**. On the **Energy** tab change the **Forcefield** to **COMPASS**.

COMPASS is a well validated forcefield with its own charges. Hence, when you chose COMPASS, the *Charges* selection automatically changes to [Forcefield assigned](#). The non-bond settings default to [Atom based](#). This setting is suitable for small molecules but when you introduce the TiO_2 surface in later, you will change these to [Ewald](#).

Click the **Run** button.

A job is launched and displayed in the Job Explorer. A new folder called chlorophenol Forcite GeomOpt is created in the Project Explorer. When the job completes, you are notified and the results folder contains 6 files.

- chlorophenol.xsd - contains the optimized geometry of the initial structure
- chlorophenol - Calculation - an xml state file containing the settings for the job. Clicking on this file opens the Forcite Calculation dialog with the settings specified in the calculation.
- chlorophenol Convergence.xcd - plots the evolution of the energy change and gradient normal change.
- chlorophenol Energies.xcd - plots the evolution of the enthalpy. The dramatic drop indicates an initial bad geometry that was refined.
- Status.txt - contains the live update status.
- chlorophenol.txt - a text version of the initial settings, and a breakdown of energies for the initial and final structure

3. To build and optimize the TiO_2 surface

Materials Studio has an extensive structure library containing many common metal oxides. Three forms of titanium dioxide exist and you will be working with the rutile form.

In the Project Explorer, right-click on the root project icon and select **Import...** from the shortcut menu to open the Import Document dialog. Navigate to **Structures\metal-oxides** and import **TiO2_rutile.msi**.

Before cleaving the surface, you should optimize the geometry of the crystal structure.

On the **Setup** tab on the Forcite Calculation dialog click the **More...** button to open the Forcite Geometry Optimization dialog. Check the **Optimize cell** checkbox and close the dialog.

As this is a 3D periodic structure, you can choose to either optimize the cell and atomic positions or just the atomic positions. In this case, you will optimize the cell and atomic positions.

In the Properties Explorer, change the **Filter** to **Lattice 3D**.

The rutile form of titanium dioxide belongs to the P42/MNM space group. Forcite will optimize the structure within the symmetry constraints.

Click the **Run** button and close the Forcite Calculation dialog.

Again, a new folder, **TiO2_rutile Forcite GeomOpt**, is created. When the calculation is complete, the same set of documents that were displayed in the chlorophenol folder are displayed here. In addition, since this is a periodic structure, Forcite also reports the change in cell parameters and density.

Note: The **TiO2_rutile.txt** output file reports that there are missing parameters for some energy contributors. These will not affect the outcome of the tutorial but can be avoided by manually applying forcefield types and then deleting all the bonds in the structure. This procedure is employed in **step 2** of the [Polymer interactions with a metal oxide surface](#) tutorial.

Now you have optimized the structure, you are going to cleave the crystal to show the active 110 surface.

Tip: If you do not know the active surface, you can use the Morphology module to find it.

Select **File | Save Project** from the menu bar, followed by **Window | Close All** from the menu bar.

Open the optimized **TiO2_rutile.xsd** document. Choose **Build | Surfaces | Cleave Surface** to open the Cleave Surface dialog. Change the **Cleave plane** to **1 1 0** and press the **TAB** key.

In **TiO2_rutile.xsd**, a blue box is displayed with the cleave plane displayed as a solid blue line and the depth displayed by dotted lines.

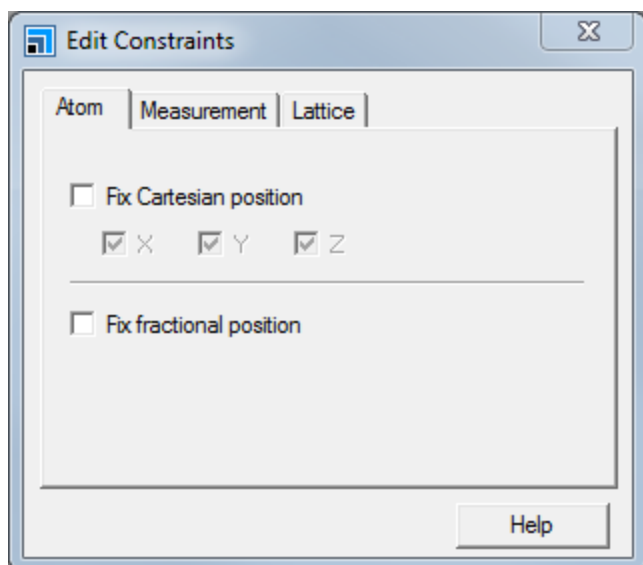
Use the spinners to increase the **Fractional Top** to **0.399** and the **Fractional Thickness** to **3.0**. Click the **Cleave** button and close the dialog.

A new 3D Atomistic Document, **TiO2_rutile(1 1 0).xsd** opens. The surface, denoted by a solid white rectangle, should contain a mixture of titanium and oxygen atoms.

You are now going to optimize the surface. As you have already optimized the bulk crystal structure, you can constrain the geometry of the bottom layers as these represent the bulk structure.

Click on the **3D Viewer Selection Mode** tool. Orient your structure with the surface at the top of the screen. Select the bottom mixed Ti and O layer and the partial O layers immediately above and beneath it. Choose **Modify | Constraints** from the menu bar.

This opens the Edit Constraints dialog.

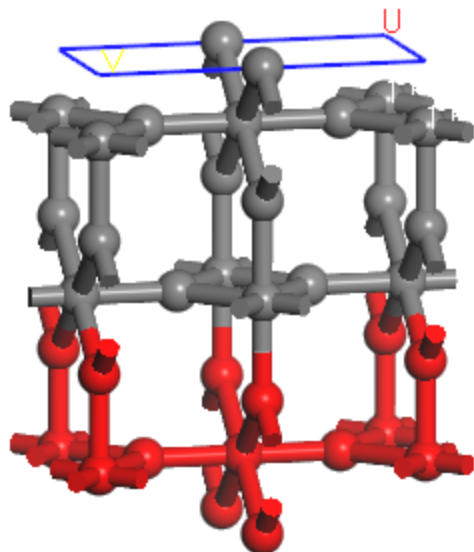


Edit Constraints dialog, Atom tab

Check the **Fix Cartesian position** checkbox and close the dialog.

Click in the 3D Viewer to deselect everything. Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. In the **Coloring** section on the **Atom** tab, change the **Color by** setting to **Constraint**.

Your structure should look similar to the one below, with the constrained atoms colored red and the unconstrained atoms colored gray.




TiO₂ surface in Stick display style.

On the Display Style dialog, change the **Color by** setting back to **Element** and close the dialog.

You are now ready to optimize the surface.

Open the Forcite Calculation dialog and click the **Run** button.

Once again, the results are returned to a new folder. The final step in this section is to determine how large to make the surface. The surface must be large enough to accommodate the organic molecule whilst minimizing interactions with ghost molecules. Therefore, you should begin by using a distance monitor to calculate the length of chlorophenol.

Open the optimized **chlorophenol.xsd**. Click the **Measure/Change** arrow  and select **Distance**. Select the **Cl** atom and the opposite **H** atom.

A distance monitor is displayed and the value distance should be of the order of 5.6 Å. Assuming that a 2 Å region around each molecule is sufficient to minimize intermolecular interactions, you would need a unit cell of the order of $5.6 + 2 \times 2$ or about 9.6 Å. Now you need to determine how many copies of the current surface you must generate to achieve this.

Make the optimized rutile surface active. In the Properties Explorer, change the **Filter** to **Lattice 2D**.

The cell parameters should be of the order of 3.0 and 6.3 Å for U and V respectively. Therefore, a supercell of 3×2 should be enough to accommodate the organic molecule.

Choose **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Change **U** to **3** and **V** to **2**. Click the **Create Supercell** button and close the dialog.

You have now created your surface. Before continuing, you should save the project.

Choose **File | Save Project** from the menu bar.

4. To equilibrate the molecule on the surface

The next stage is to place the molecule on the surface and optimize the structure. You will do this by creating a new document in the root project folder and using that for the calculations.

With the enlarged optimized surface active, choose **File | Save As...** from the menu bar to open the Save As dialog. Navigate to the root project folder, change the **File name** to **ChloroTiO2_110** and click the **Save** button.

This saves a copy of the surface in the root project folder. You now need to paste the organic molecule onto the surface.

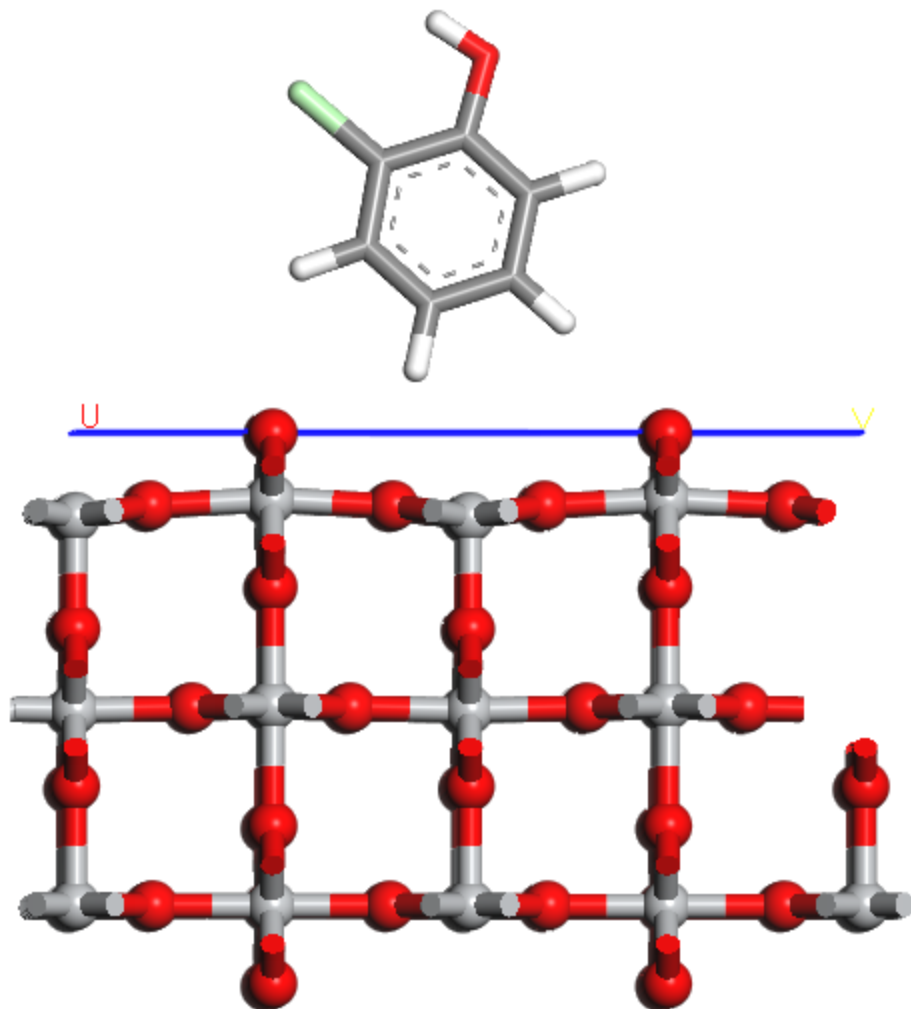
Select the optimized **chlorophenol.xsd**. Choose the **3D Viewer Selection Mode** tool and select the distance monitor. Press the **DELETE** key. Press **CTRL + C** and change focus back to **ChloroTiO2_110.xsd**. Press the **CTRL + V** keys.

The chlorophenol is pasted into the document containing the surface. Now the molecule must be oriented so that it lies perpendicular to the surface.

Hold down the **SHIFT** and **ALT** keys, right-click and position the chlorophenol so that it is hovering over the surface.

Tip: If you are using a mouse with a wheel or a middle button, you can translate the fragment by holding down the **SHIFT** key and the middle mouse button or wheel.

The initial starting structure should look similar to the image below.



Chlorophenol hovering over the TiO_2 surface in Stick display style.

Note: You must take care to ensure that the chlorophenol molecule does not penetrate the surface. Use the CPK display style to verify this before attempting to optimize the system.

This structure should now be optimized.

Click the **Run** button on the Forcite Calculation dialog.

A new results folder opens and the optimized structure is returned to it. The molecule should orient itself approximately flat on the surface.

This is one energy minimum for the structure however it is only a guess at the minimum energy adsorption site. To calculate the global energy minimum, you could try around 20 different starting configurations to make sure you have covered as much of phase space as possible.

Alternatively, you could use a quench molecular dynamics approach to sample many different configurations. Before continuing, you should save the project and close all the documents.

Choose **File | Save Project** followed by **Window | Close All** from the menu bar.

5. To sample configurations using quench dynamics

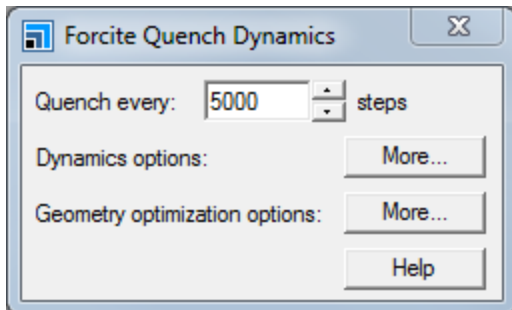
When using molecular dynamics to sample the different interactions of the molecule with the surface, you will constrain the surface atoms.

Re-open the optimized **ChloroTiO2_110.xsd**. Use the **3D Viewer Selection Mode** tool to select all the atoms in the TiO_2 surface. Open the **Edit Constraints** dialog, uncheck and re-check the **Fix Cartesian position** checkbox. Close the dialog.

You are now ready to run a molecular dynamics simulation.

On the Forcite Calculation dialog, change the **Task** to **Quench** and click the **More...** button.

This opens the Forcite Quench Dynamics dialog.

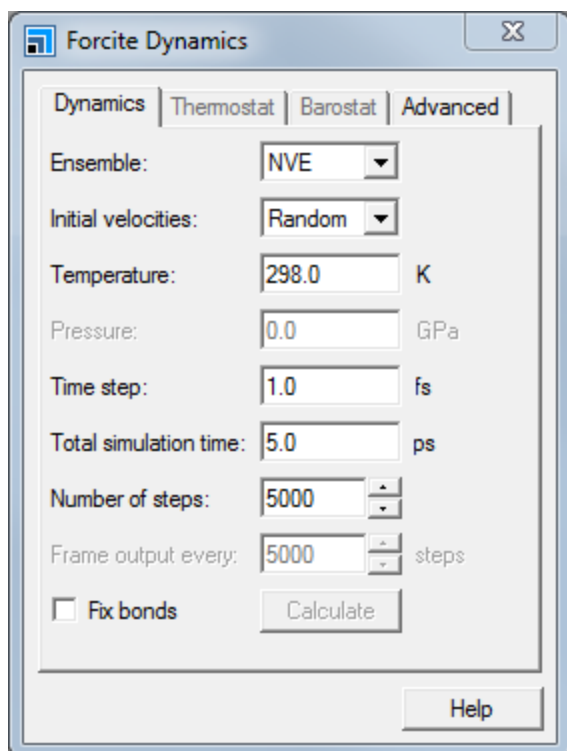


Forcite Quench Dynamics dialog

This gives you access to the basic quenching options. However, you will need to open the Dynamics options to set the temperature and so on.

Click the **More...** button for **Dynamics options**.

This opens the Forcite Dynamics dialog.



Forcite Dynamics dialog, Dynamics tab

Note: The Frame output every X steps option is grayed out as this is set by the Quench every X steps on the Forcite Quench Dynamics dialog.

Set the **Temperature** to **350 K**.

This temperature represents a trade-off between a system with too much kinetic energy, where the molecule desorbs from the surface, and a system with not enough kinetic energy for the molecule to move around the surface. You may need to perform several calculations at different temperatures to determine the correct temperature. For this tutorial, 350 K is a good temperature.

You will use the default number of 5000 steps to run the dynamics at 350K which will give you 5ps of simulation time. Currently, a quench, or geometry optimization, is performed every 5000 steps. For this simulation, it would only perform one quench. Therefore, you should change the quench value to every 250 steps.

Close the Forcite Dynamics dialog. On the Forcite Quench Dynamics dialog, change the **Quench every** to **250** steps and close the dialog. On the Forcite Calculation dialog, click the **Run** button and close the dialog.


Another new folder, Ch1oroTiO2_110 Forcite Quench will appear in the Project Explorer, containing the usual updated results files plus these:

- ChloroTi02_110.xsd - The input structure
- ChloroTi02_110 Quench Energy.xcd - Chart containing the energies of the quenched structures
- ChloroTi02_110 Quench.std - Study table containing the results of the quench dynamics including a breakdown of the energies.
- ChloroTi02_110 Quench.xtd - Trajectory document containing the quenched structures
- ChloroTi02_110.xtd - Trajectory document containing the original, non-quenched, structures
- ChloroTi02_110.txt -Text document containing initial settings and a summary of the results.



First, you should look at the initial, non-quenched trajectory.

In the Project Explorer, double-click to open **ChloroTiO2_110.xtd**.

The .xtd document is the trajectory containing the frames from the dynamics run. You can animate the trajectory using the animation toolbar.

Choose **View | Toolbars | Animation** to display the **Animation** toolbar, click the **Play** button .

The trajectory document plays and you can visualize the movement of the chlorophenol molecule on the surface. You may notice that the chlorophenol molecule appears to move away from the surface. This is an artifact of the 2D periodic boundary conditions. You can change the visualization to remove this artifact.

Click the **Stop** button . Click the **Animation Mode** arrow  and select **Options** from the dropdown list to open the Animation Options dialog. Check the **Recalculate atom visibility every frame** checkbox and close the dialog. Click the **Play** button.

The chlorophenol molecule moves around on the surface.

Click the **Stop** button to stop the animation.

Next you can examine the quenched trajectory.

Change focus to **ChloroTiO2_110 Quench.xtd** and click the **Play** button.

There are several low energy confirmations but which of these is the lowest energy? You can either consult the Forcite text output document or use the study table.

Stop the animation and change focus to the **ChloroTiO2_110 Quench.std** study table document.

The trajectory is viewed in the study table with the first column containing the structures, then the remaining columns containing trajectory and energy breakdowns. The total energy is in column D, labeled as Hamiltonian.

Select column **D, Hamiltonian**. Click the **Quick Plot** button .

The total energy is plotted against the row number.

Click the **Chart Viewer Selection Mode** tool. With the study table visible, click on a point in the chart.

Selecting a point in the chart highlights the corresponding row in the study table. You can use this method to identify the low energy conformations. Alternatively, you can use the Sort tool on the study table.

Make the study table active and select the **Hamiltonian** column again. Click the **Sort Ascending** button .

The rows are ordered with the lowest energy first. You can visualize the frames by double-clicking on the structures in column A.

Double-click to open the lowest energy frame in column A.

You can also use a 3D Atomistic Collection Document to overlay all the structures to see if there is a preferential binding site on the surface.

Make the study table document active. Select the structure column A, move your mouse over any cell in this column, right-click and select **Extract To Collection** from the shortcut menu. Click the **OK** button on the warning dialog.

The default view allows you to visualize placement of all the molecules.

Open the **Display Style** dialog, on the **Lattice** tab change the **Style** to **In-Cell**.

The molecules are all overlaid on the 2D surface allowing you to see if there is a preferred orientation or adsorption site. You should see there is effectively one binding mode.

6. To calculate the binding energy

You can calculate the binding energy between the molecule and surface using the following equation:

$$\text{Binding Energy} = E_{\text{total}} - (E_{\text{chlorophenol}} + E_{\text{TiO}_2\text{Surface}})$$

Therefore, you must begin by performing single point energy calculations for the chlorophenol and TiO_2 surface separately. You can automate this task to a degree by using the study table.

In the study table, select columns G, Bond energy to V, Temperature using the **SHIFT** key. Right-click on any heading cell and select **Delete** from the shortcut menu. Select the **Frame number** column and click the **Sort Ascending** button. Move the study table to the project root.


This clears the rest of the study table and sorts it so that when you insert the trajectories, the frames will match up with the correct numerical data. Now you must insert two more copies of the optimized trajectory and delete the surface and cell that you do not need.

Click on a cell in column B. In the Project Explorer, right-click on the **ChloroTiO2_110 Quench.xtd** document and select **Insert Into**. Repeat this to insert the trajectory into column C.

Two new columns are created containing the trajectory document. You will edit the frames in column B so that they only contain chlorophenol and the frames in column C so that they only contain the surface.

Right-click on the heading cell for column B and select **Properties**. In the Column Properties dialog, change the **Description** to **Chlorophenol** and click the **OK** button. Change the description for column C to **TiO2 surface**.

You should now open the first frame in column B and remove the surface.


Double-click on the first cell in column **B**. Choose the **3D Viewer Selection Mode** tool and select all the atoms in the surface. Press the **DELETE** key. Click the **Commit Edit To Study Table** button . Close the **Detail View**. Using a similar procedure, remove the chlorophenol from column **C**.

Tip: You can hold down the SHIFT key to force selection mode even if other tools are selected.


You have created two cells with the isolated structure in. You could repeat this procedure for the other cells in the study table so that you can calculate an average energy. However, for this case, you should just do this for the first three rows.

Repeat the above procedure to change the structures in rows **2** and **3** so that column **B** only contains chlorophenol and column **C** only contains the TiO_2 surface.

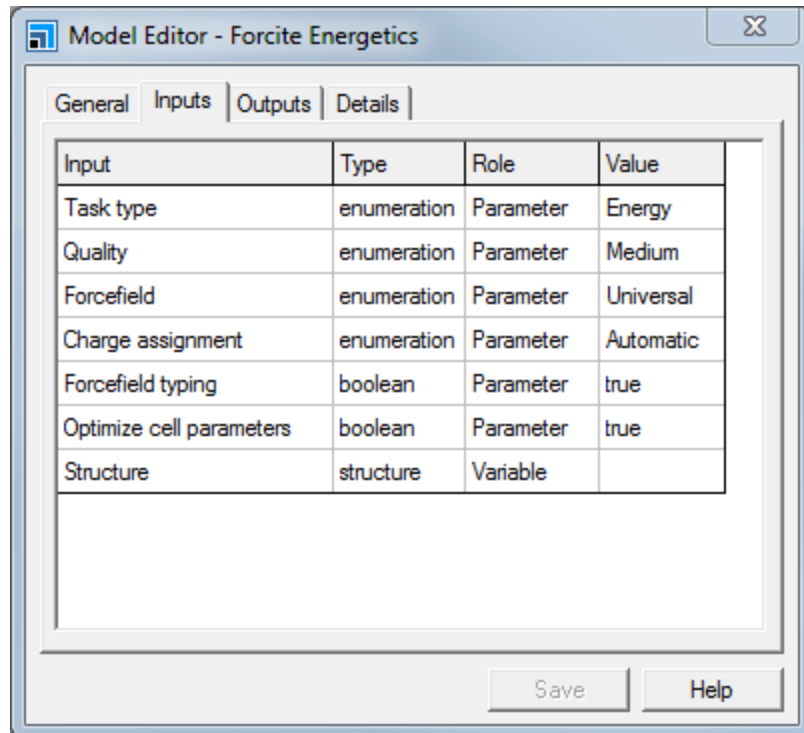
You should also filter the frames so that you only calculate the binding energies for rows 1-3.

Select rows **1-3** and click the **Filter** button .

The selected frames are filtered onto a new tab in the study table document. This allows you to work on the selection only.

Select column **B** and click the **Models** button . Scroll down and double-click to edit the Forcite Energetics **Total energy** model.

The Model Editor dialog is displayed



Model Editor - Forcite Energetics dialog, Inputs tab

On the Model Editor - Forcite Energetics dialog, select the **Inputs** tab. Change the **Forcefield** value to **COMPASS** and click the **Save** button. Close the Model Editor - Forcite Energetics dialog.

On the Models dialog, click the **Run** button.


A new column is displayed in the study table. When the job completes, the red text in this column will change to blue values. When this occurs, you can launch the second job.

In the study table, select column **C**. On the Models dialog, click the **Run** button and close the dialog.

Another new column is displayed and the energy of the surface is calculated.

Note: As the atoms in the surface are constrained, the energy of the forces between them remain constant throughout the simulation. Since these constant forces will not affect the overall motion of the sorbate, they are excluded from the calculation and so they are not reported. Hence, in the case of the constrained TiO_2 surface, the energy reported is zero.

Now that you have calculated the individual energies, you should define a function that calculates the binding energy.

Scroll to the right of the study table. Click the **Define Function** button . In the **Expression** box, enter **H-(I+J)**. In the **Name** box enter **Binding Energy** and click the **OK** button.

Finally, if you wish to get the mean, and other statistics about your binding energy, you can use the Univariate Analysis dialog.

Select column **K**, **Binding Energy**, and choose **Statistics | Initial Analysis | Univariate Analysis** from the menu bar.

A grid document opens which reports the various statistics about your data including the mean binding energy.

Using the quench molecular dynamics method above you have found the preferred binding site for this structure and surface and calculated the binding energy. You could now functionalize this organic molecule further and look to see if there are different interactions or you could change the surface. You may also wish to try a longer run to sample more configurations.

This is the end of the tutorial.

Using Materials Studio to edit a forcefield

Purpose: Illustrates a workflow for editing forcefield parameters in Dreiding to improve the fit between calculated and experimental crystal structure data.

Modules: Materials Visualizer, Conformers, and Forcite Plus. DMol³ is optional.

Time: 🕒🕒🕒

Prerequisites: [Using Conformers to probe geometry-energy relationships](#)

Background

The forcefield is the core of a classical simulation calculation as it embodies how each type of atom in the structure interacts with the atoms around it. For each atom in the system, a forcefield type is assigned which describes the local environment of the atom. A forcefield contains a variety of information describing properties such as equilibrium bond lengths and electrostatic interactions between pairs of forcefield types. Typically, forcefields attempt to be either general, to cover many systems, or parameterized, for a specific problem. A general forcefield, such as Dreiding, has many parameters for atoms in different environments. However, for specific cases, it will never perform as well as a forcefield that has been parameterized for that case alone. Therefore, it can be useful to be able to edit a forcefield for use with systems for which it has not been parameterized.

This can occur in many scenarios: you might want to parameterize a forcefield to mimic a sorption isotherm for a molecule in a zeolite framework, you might have experimental crystal data that you want to use to increase the accuracy of a Polymorph prediction calculation or you may want to alter a forcefield to better describe the density of a polymer. In all these cases, you need to edit the underlying forcefield and observe the effect of those changes.

Editing forcefields is a complex task as many of the interactions are coupled, either explicitly or implicitly. For example, the energy profile on rotating a torsion angle does not just depend on the torsion term but also the non-bond energies. Therefore, getting the correct parameters can take considerable time and involve many different calculations. The best approach is to make small systematic changes and see the effect on the system. As with all forms of parameterization, there will also be a trade-off between obtaining the result and overfitting.

Introduction

In this tutorial, you will modify a single torsion angle of a small molecule to improve the match between the optimized model and the crystal structure. Initially, you will optimize the crystal structure of an explosive material, triaminotrinitrobenzene (TATB), using the Dreiding forcefield. You will then modify the Dreiding forcefield to improve the match between the crystal structure and the forcefield optimized model structure. You will use a combination of the Conformers module to probe torsion-energy relationships, DMol³ to provide ab initio data, and Forcite to optimize the crystal structure.

This tutorial covers:

- [Getting started](#)
- [To optimize the crystal structure](#)
- [To examine the torsion angle](#)
- [To work with the non-bond terms](#)
- [To modify the van der Waals terms](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ff_edit** as the project name, click the **OK** button.

The new project is created with *ff_edit* listed in the Project Explorer. The next step is to load the crystal structure that you want to work with - the explosive TATNBZ.

Open the **Import Document** dialog and navigate to **Examples\Documents\3D Model** and double-click on **TATNBZ.xsd**. Rename the structure **TATNBZ_crystal.xsd**.


2. To optimize the crystal structure

You will perform all the editing work on the isolated molecule before applying the modified forcefield to the crystal structure to verify your changes. You should make a copy of the isolated molecule.

In the **Project Explorer**, right-click on the project root and select **New | 3D Atomistic** from the shortcut menu.

In **TATNBZ_crystal.xsd**, click on an atom in one of the molecules, right-click and choose **Select Fragment**. Press the **CTRL + C** keys. Change to the new atomistic document and press **CTRL + V**. In the **Project Explorer**, rename the new atomistic document to **TATNBZ_molecule.xsd**.

If you examine the crystal structure you should see that the nitro groups are in the plane of the benzene ring. You will now optimize the structure with the standard Dreiding forcefield using Forcite.

Ensure that **TATNBZ_crystal.xsd** is the active document. Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** from the dropdown list to open the Forcite Calculation dialog.

Change the **Task** to **Geometry Optimization**. On the **Energy** tab, change the **Forcefield** to **Dreiding** and change the **Charges** to **Charge using Gasteiger**.

You could use a more complex charging method such as applying ESP charges using DMol³, but the Gasteiger charges will be suitable for development of a customized forcefield.

Click the **Run** button. When the job completes, open the optimized **TATNBZ_crystal.xsd**.

You should see that the nitro groups are no longer in plane with the benzene ring. The off-plane nature of the nitro groups of the optimized structure can affect the way these molecules pack together in a crystal, so obtaining a planar nitro group is important.

There is a single torsion between the nitro group and the benzene ring which will control the planarity of the group. Modifying the parameters that control this torsion this will be the focus of this tutorial.

3. To examine the torsion angle

Now that you have identified the torsion angle that you want to change, you can begin to look in more detail at the energy profile for that torsion angle. A Conformers calculation will give you the energy


profile by calculating single point energies as the torsion is rotated through 360°.

Right-click in **TATNBZ_molecule.xsd** and select **Label** from the shortcut menu to open the Label dialog. Ensure the **Object type** is set to **Atom** and choose **Name** from the **Properties** list. Click the **Apply** button.

Use the **Measure/Change** tool to define a torsion on the nitro group for the atom sequence **O5-N5-C5-C4**.

On the **Label** dialog, click the **Remove** button and close the dialog.


You will use the Conformers module to systematically rotate the torsion and calculate the energy at each point.

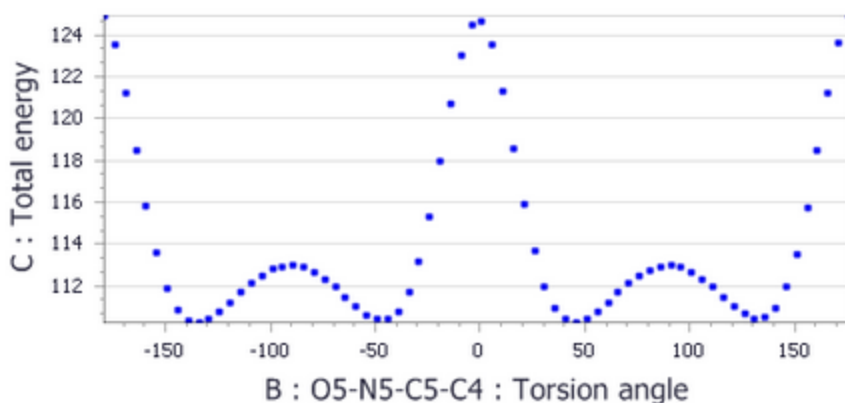
Click the **Conformers** button  on the **Modules** toolbar and select **Calculation** from the dropdown list to open the Conformers Calculation dialog. Click the **Torsions...** button to open the Conformers Torsions dialog.

Change the **# Steps** to **72** and close the dialog.

On the **Energy** tab, change the **Forcefield** to **Dreiding** and select **Charge using Gasteiger** from the **Charges** dropdown list. Click the **Run** button and close the dialog.

When the calculation completes, you can plot the torsion-energy to see the energy profile.

Select columns **B** and **C** in the study table and click the **Quick Plot** button . Rename the chart document **Dreiding_Original.xcd**.




Torsion-Energy plot for the nitro-benzene torsion angle calculated by Dreiding

You can see from the torsion-energy plot that there are large maxima at 0° and 180° giving a barrier to rotation of about 14 kcal mol⁻¹. From examining the crystal structure, you would expect there to be energy minima at 0° and 180° not maxima as shown by the torsion-energy plot.

You could also compare this potential energy surface with that predicted by DMol³. As you already have a study table containing the conformers, you can use the DMol³ Model to calculate the energy for each conformer.

Note: As this calculation requires accurate energies, you will use fine settings and this calculation is likely to take more than one hour. A study table with the calculated results has been provided in the `Examples\StudyTables` folder. If you wish to use this instead, please skip the next two steps.

In the study table, select column **A**. Click the **Models** button  to open the Models dialog. Locate the **DMol³ Molecular Energy** model and double-click to edit it.


For this calculation, you need accurate energies. So you should use a good functional and a fine convergence level.

On the **Inputs** tab of the **Model Editor - DMol3 Molecular** dialog, change the **Functional** to **BLYP** and the **Quality level** to **Fine**. Click the **Save** button and close the dialog. Click the **Run** button on the Models dialog.

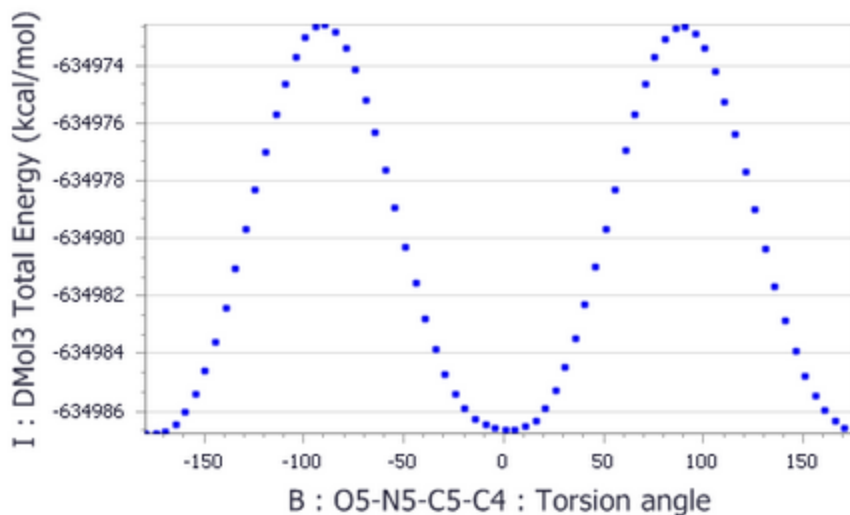
The Fine quality level not only changes the SCF convergence criteria but other settings such as the basis set. This calculation will take some time to complete and you are recommended to run it remotely or overnight. You must wait for the calculation to complete before moving to the next step or import the example study table.

Open the study table, or import the example study table from `Examples\StudyTables\TATNBZ_conformers.std`.

You will see that the Total Energy (DMol3 Molecular) is in Hartree so you need to convert this to kcal mol⁻¹ (1 Hartree = 627.51 kcal mol⁻¹). Assuming that the Total Energy column is in column D, you need to define a function of D×627.51. Once converted, you should plot the energies as you did for the original conformers plot.

Click the **Define Function** button  to open the Define Function dialog. In the **Expression** text area, type **D*627.51**. Enter **DMol3 Total Energy (kcal/mol)** as the **Name** and click the **OK** button. Select the column containing the torsions, and the newly created column and click the **Quick Plot** button.


Note: The absolute energies will be very high as they are not optimized with DMol³. However, you are only interested in the relative barrier height, not the absolute energies.



Dihedral-energy plot of the DMol³ single point energies

From the chart, you should see that the barrier height is approximately 14 kcal mol⁻¹. Later in the tutorial, you will try to get the same approximate barrier height from the forcefield calculations.

Now that you have the energy profile predicted by Conformers and DMol³, you can compare this with the torsional term in Dreiding. The Forcefield Manager is used to create an editable copy of a standard forcefield.

Click the **Forcite** button  on the **Modules** toolbar and select **Forcefield Manager** from the dropdown list. In the **Standard Forcefields** section, select **Dreiding**. Click the >> button. Close the dialog.

A copy of the Dreiding forcefield is made in the project and the `Dreiding.off` forcefield is opened for you to edit. The forcefield document consists of four tabs:

Summary - contains summary text describing the forcefield.

Types - contains the forcefield types and properties associated with them.

Interactions - contains the main interactions such as valence and non-bond terms.

Equivalences - contains the definitions of the equivalences for the interactions.

Before editing the forcefield, you can change the name of the forcefield document.

In the **Project Explorer**, change the name of the forcefield document to **Dreiding_new.off**.

You are now ready to explore the forcefield document.

In **Dreiding_new.off**, select the **Types** tab.

This contains the forcefield types available in Dreiding, a description of the type, element, and van der Waals parameters for each forcefield type. The display of other properties can be switched on using the checkboxes on the Forcefield Type Properties dialog, for example hybridization, charge, and hydrogen bond.

There are many forcefield types describing the different local environments for each element, with some elements having more than one forcefield type. Scrolling through all of these would be tedious so you can filter those displayed by their forcefield type. Filter boxes are displayed in yellow in the forcefield document.

In the yellow **Type Filter** box, type **C_*** and press the **ENTER** key.

Only the atom types associated with the carbon atoms are now displayed in the Types dialog.

Change the **Type Filter** back to *****.

You can also filter by the forcefield types present in a 3D Model document.

Check **Filter by selection in** and select **TATNBZ_molecule.xsd** from the dropdown list.

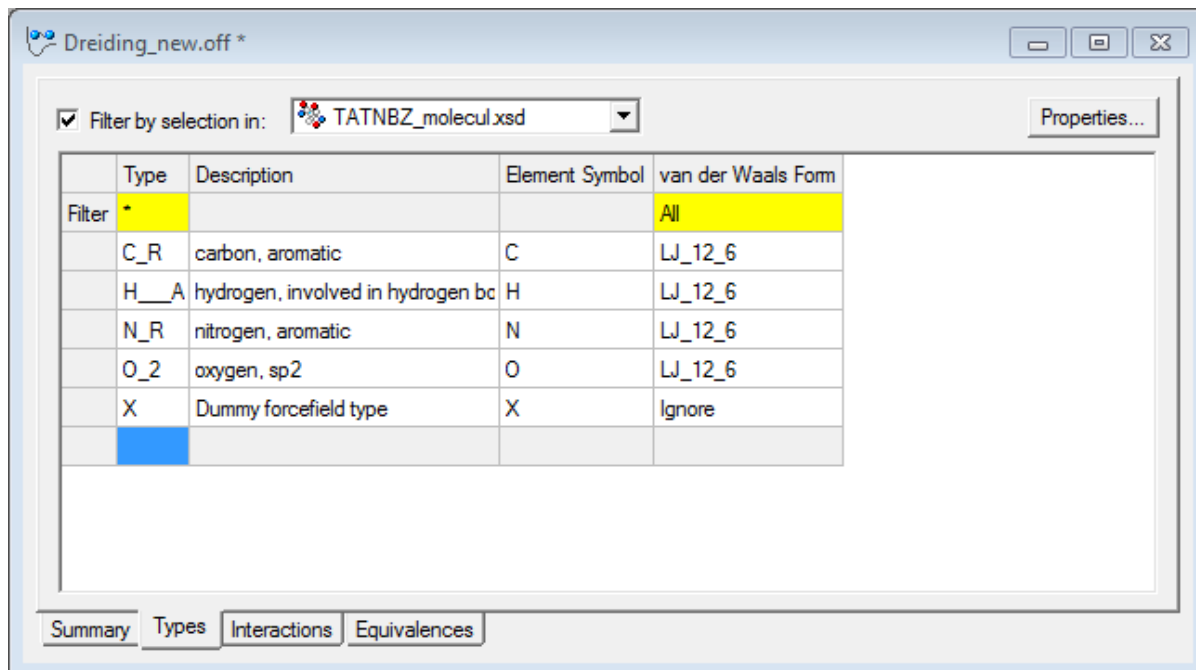
You will see a warning dialog. This is because there are no forcefield types assigned to the atoms in the molecule. You can assign forcefield types using the Forcite Calculation dialog.

Open the **Forcite Calculation** dialog. On the **Energy** tab, click the **More...** button associated with **Forcefield** to open the Forcite Preparation Options dialog. Uncheck **Calculate automatically** for *Forcefield types* and change focus to **TATNBZ_molecule.xsd**. Click the **Calculate** button. Check **Calculate automatically** again. **Close** both Forcite dialogs.

This calculates the forcefield types on the atoms in TATNBZ_molecule. You need to refresh the forcefield types in the forcefield document.

Change focus back to **Dreiding_new.off**. Reselect **TATNBZ_molecule.xsd**.

You should now see the four forcefield types that represent the atoms in the document and a dummy forcefield type.



Dreiding_new forcefield document showing forcefield type information

You are interested in the torsion angle between the aromatic carbon, C_R and aromatic nitrogen, N_R.

Change to the **Interactions** tab. Change the **Show interaction** to **Torsion**.

There are six different combinations of the torsion terms. You can change the *Functional Form* filter to view the different options.

Click the **Functional Form** filter and select **Dihedral**.

The value of the parameters used in the Dihedral functional form describing the torsion are displayed. The parameters are all documented in the online help.

Select one of the displayed rows and press the **F1** key.

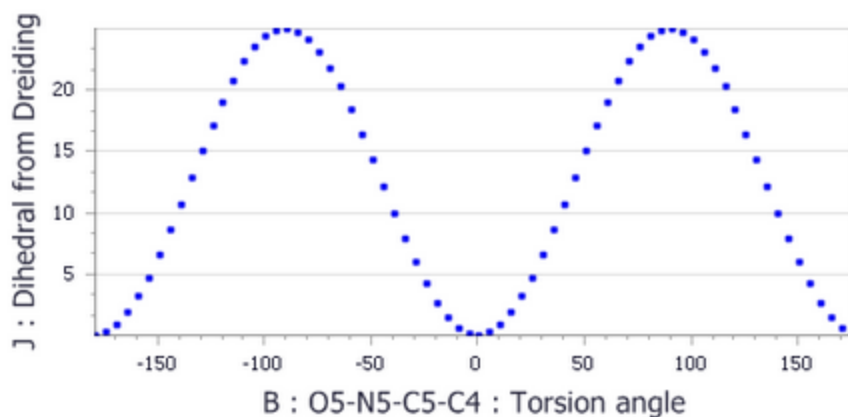
The help is displayed showing the different functional forms. The functional form for the Dihedral Torsion is:

$$E = \frac{1}{2} \sum_j \{B_j(1 - d_j \cos[n_j \phi])\}$$

You can use the Conformers study table that you generated earlier to plot the variation of the pure torsional term and compare the functional form for the whole energy expression derived from Conformers and DMol³. For the forcefield interaction, you will replace B_j in the above equation with 25, d with 1 and n_j with 2. You will use the value of the angle from column B_j in the study table, converted to radians.

Change focus to **TATNBZ_conformers.std** and open the **Define Function** dialog. In the **Expression** text area, type **(25*(1-1*cos(2*B*0.0174532925)))/2**. Set the **Name** to **Dihedral from Dreiding** and click the **OK** button. Select columns **B** and **J** and click the **Quick Plot** button.

The chart generated should match the one below, showing minima and maxima that correspond to the DMol³ plot but with a higher energy barrier than expected.



Dihedral-energy plot using the pure dihedral contribution from the forcefield editor for X C_R N_R X torsion.

From the above plot, you can see that the dihedral torsion looks reasonable. This suggests that the problem must lie somewhere else. In the next section, you will look at exploring the non-bonded terms to see how they affect torsion energy.

4. To work with the non-bond terms

From the previous calculations, you observed that the energy contribution for the pure dihedral differed significantly from that of the observed energy change on rotation of the torsion. You can use the forcefield editor to switch off contributions from the different types of interaction in a system to see the effect they have. As you are only changing a terminal torsion angle, the contributions that change, apart from the energy of the torsion itself, are the non-bond energies. Therefore, you will switch off the non-bond energies to see what effect they have on the torsion-energy plot.

As it is likely that the oxygen atom of the nitro group is strongly hydrogen bonded to the adjacent amine, it makes sense to disable the hydrogen bond term first.

Change to **Dreiding_new.off**. On the **Interactions** tab, click the **More...** button.

This opens the Forcefield Preferences dialog where you can set general preferences for the forcefield.

Uncheck the **Hydrogen Bond** checkbox in the Interactions list.

Tip: You do not need to save the forcefield document before you use it with modules such as Conformers or Forcite. You are advised to save it if you are making lots of changes.

You now need to run another Conformers calculation with the new forcefield to see the effect of switching off the hydrogen bond interactions.

Open **TATNBZ_molecule.xsd** in the project root. Open the **Conformers Calculation** dialog and select the **Energy** tab. Select **Browse...** from the **Forcefield** dropdown list to open the **Choose Forcefield** dialog. Select **Dreiding_new.off** and ensure that **Charges** is set to **Charge using Gasteiger**.

In the *Forcefield* box, you will now see `\Dreiding_new`. The back slash indicates that the forcefield has been selected from the project and is not a standard forcefield.

Note: This forcefield will be transferred to the server when the calculation is run and will be returned in the new job results folder.

On the **Conformers Calculation** dialog, click the **Run** button.

When the job has completed, open **TATNBZ_molecule.std** and generate a plot of columns **B** and **C**. Compare this with **Dreiding_Original.xcd**.

You should see that disabling the Hydrogen Bond interaction has little effect on the torsion-energy plot. Next, try disabling the electrostatic interactions.

Change to **Dreiding_new.off**. On the **Forcefield Preferences** dialog, uncheck the **Electrostatic** checkbox in the Interactions list. Change the focus back to **TATNBZ_molecule.xsd** in the project root. Open the **Conformers Calculation** dialog, and change to the **Energy** tab.

Your edited version of Dreiding is still the chosen forcefield so you can just run the calculation.

Run the Conformers calculation. When the job has completed, plot the torsion and energy and compare with **Dreiding_Original.xcd**.

You should see that the low energy maxima have decreased in height compared with having electrostatics switched on. You should also see that the overall energy has increased by a few kcal mol⁻¹.

Finally, you should switch off the van der Waals interactions to see the effect.

Change to **Dreiding_new.off** and uncheck the **van der Waals** checkbox in the Interactions list on the Forcefield Preferences dialog. **Run** the Conformers calculation on **TATNBZ_molecule.xsd**. In the output study table, plot the torsion and energy and compare with **Dreiding_Original.xcd**.

When you switch off the van der Waals terms, you should see a major effect on the energy torsion-energy plot. The profile should closely resemble the plot you generated from the Dihedral interaction. This shows that the van der Waals terms are playing a major part in the energy profile of this torsion angle. Modifying the van der Waals terms will be the focus of the next section.

Change to **Dreiding_new.off**. Check the **van der Waals**, **Hydrogen Bond**, and **Electrostatic** checkboxes in the Interaction list and close the **Forcefield Preferences** dialog.

The change on removing the van der Waals potential is related to the close distance between the oxygen atoms on the nitro groups and the hydrogen atoms on the amine groups. By modifying the van der Waals term to have a shorter equilibrium distance, and so less repulsive at shorter distances, you should see that the Conformers plot begins to match more closely that predicted by DMol³.

Change focus to **TATNBZ_molecule.xsd** in the project root. Use the **Measure/Change** tool to add a **Distance** monitor between an oxygen atom and the adjacent hydrogen atom.

The distance should be about 1.8 Å. You will use this information when modifying the van der Waals terms in the next section.

5. To modify the van der Waals terms

The van der Waals terms in Dreiding are generated automatically based on combinations of parameters for each forcefield type. As the parameters are stored on each forcefield type, they are displayed in the forcefield document on the Types tab. You can also add your own specific custom van der Waals terms for pairs of atoms and these will be used instead of automatically calculated terms.

On **Dreiding_new.off**, change to the **Types** tab. Click the yellow filter box for **van der Waals Form** and select **LJ_12_6**.

Note: You will notice that you can either choose to show the functional form or to *Ignore* the interaction. If you choose *Ignore*, the interaction is not calculated in the energy expression. Choosing *Ignore* for the *van der Waals* forcefield type would ignore all van der Waals interactions that contain that type. Although this may seem drastic for this example, ignore can be useful if you want to switch off individual interactions.

You can set either a functional form or choose to ignore the van der Waals parameters. Dreiding uses a simple Lennard-Jones 12-6 form for calculating the van der Waals parameters where D0 is the well-depth and R0 is the equilibrium distance.

Note down the values of D0 and R0 for both H__A and O_2.

You should see that the well depth for H__A is very shallow compared with that of O_2. The combination of parameters is usually calculated using an arithmetic mean. However, as the well depth for hydrogen is very small, in this case a geometric combination of the well depth parameter gives a better representation of the van der Waals interaction.

The geometric mean is calculated as the square root of the product of well-depths and is equal to 0.0031 for H__A and O_2.

Change to the **Interactions** tab. Change the **Show interaction** to **van der Waals**. Change the **Functional Form** to **LJ_12_6**.

You will note that there are no specific van der Waals terms defined for Dreiding. To introduce a specific van der Waals term the forcefield type sequence must be specified first.

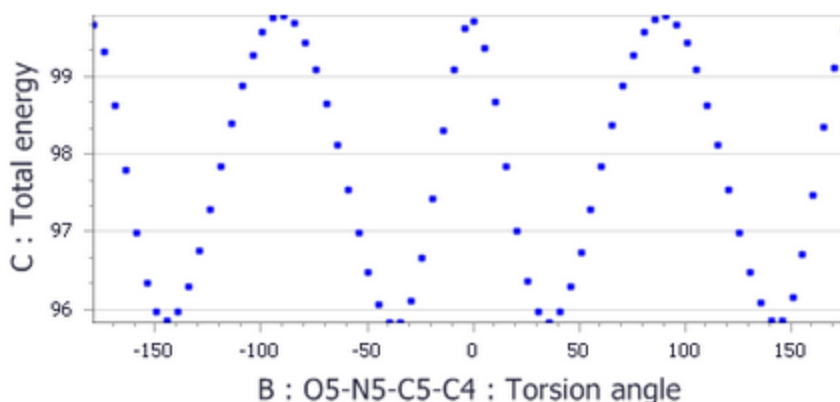
Click in the **Fi** box for the first empty row and choose **H__A** from the dropdown list. Click in the **Fj** box and choose **O_2** from the dropdown list. Click in the **Functional Form** box and choose **LJ_12_6**. Set the value of **D0** to **0.0031**.

For this test, you should leave the **R0** calculated using the arithmetic mean. This gives a value of 3.29.

Set the value of **R0** to **3.29**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd** in the project root. Generate the torsion-energy plot.

You should see that the height of the minima has changed by about $0.5 \text{ kcal mol}^{-1}$ but has not had a large overall effect on the plot. The other way to change the functional form is to decrease the value of the equilibrium distance. Previously, you calculated the distance from an oxygen to hydrogen atom in the molecule. This was about 1.8 \AA compared with a **R0** of 3.29 \AA . This suggests that the repulsive part of the van der Waals potential is making a significant contribution to the torsional potential. To rectify this you should decrease the value of **R0**. Although it is tempting to set the equilibrium value to that of the distance measured, this could overfit the interaction which may lead to changes in the overall structure. In reality, choosing the right number can involve some guesswork but it is better to start higher and decrease, running multiple Conformers calculations. For the purposes of this tutorial, an **R0** of 2.7 \AA is used.

On **Dreiding_new.off**, change the value of **R0** to **2.7**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.



Dihedral-energy plot for the adjusted van der Waals parameters from the forcefield editor for X_C_R_N_R_X torsion.

The plot shows that changing the equilibrium position has a significant effect on the energy profile of the torsion angle with the maximum at 0 and 180 degrees decreased substantially in energy. However, the overall energy barriers are now significantly lower than those predicted in the DMol³ calculations previously. To compensate for this, you should increase the torsion energy barrier.

On **Dreiding_new.off**, change the **Show Interaction** to **Torsion** and the **Functional Form** filter to **Dihedral**. Change the **X N_R C_R X** value of **B** to **50**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.

You see that the new torsion-energy plot is now similar to that predicted by the ab-initio calculations with torsion barriers of a similar magnitude and in the same locations. There are still two low energy minima either side of 0 and 180 degrees and these will cause distortion of the structure. However, changing the values of the H__A O_2 van der Waals interaction will no longer have much effect.

This suggests that the small repulsion terms must be caused by another atom interacting with the oxygen on the nitro group.

Change focus to **TATNBZ_molecule.xsd** in the project root. Add a **Distance** monitor between an oxygen atom and the nearest nitrogen on an amine group.

The distance should be around 2.5 Å. As with the oxygen-hydrogen interaction, this is smaller than the equilibrium distance in the forcefield. The distance means the van der Waals repulsions will be large and this could be causing the small maxima in the potential energy surface.

Change focus back to **Dreiding_new.off**. Change to the **Types** tab and note down the **D0** and **R0** values for **N_R** and **O_2**.

As with the hydrogen and oxygen van der Waals terms, you will calculate the new D0 term using a geometric mean and set the R0 to 2.7 Å.

Change to the **Interactions** tab and show only **van der Waals** interactions. Click the yellow filter box for **Functional Form** and select **LJ_12_6**. Click in the empty **Fi** box and choose **N_R**. Click in the empty **Fj** box and choose **O_2**. Click in the **Functional Form** box and choose **LJ_12_6**. Set the value of **D0** to **0.086** and the value of **R0** to **2.7**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.

There should be no extra minima present and the shape of the chart should look similar to that of the DMol³ generated plot previously with slightly flatter minima. However, as you have changed the functional form of the van der Waals parameters for oxygen and nitrogen, the energy barrier for the dihedral is now too high. From the DMol³ calculation, you want this to be approximately 14 kcal mol⁻¹.

Change focus back to **Dreiding_new.off**. On the **Interactions** tab, select the **Torsion** interaction. On the **Functional Form**, select **Dihedral**. Change the value of **B** for **X N_R C_R X** to **35**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.

This should give an energy barrier of about 14 kcal mol⁻¹. You could continue to tweak the parameters to improve the forcefield further but this should be good enough to test with the crystal structure.

Open the original **TATNBZ_crystal.xsd**. Open the **Forcite Calculation** dialog. Change to the **Energy** tab and choose **\Dreiding_new.off** as the forcefield. Click the **Run** button.

When the calculation completes, you should see that the nitro groups are nearly aligned in the plane of the benzene rings as they are in the crystal structure.

From here, you could run a Polymorph Prediction calculation with the new forcefield.

This is the end of this tutorial.

Calculating the diffusivity of a gas in a polymer

Purpose: Introduces the use of forcefield methods to calculate the diffusion coefficient of a gas in a dense material.

Modules: Materials Visualizer, Forcite Plus, Amorphous Cell, COMPASS

Time: 🕒 🕒

Prerequisites: Using the polymer builder Visualizer Tutorial

Background

The diffusivity of a gas in an organic solvent, polymer, or zeolite can be calculated by running a molecular dynamics simulation and determining the mean square displacement of the gas in the material. This allows you to calculate the self-diffusivity coefficient of the gas and gives an insight into the overall diffusivity. As you are performing a molecular dynamics calculation, you can analyze the effect of temperature, pressure, density, and the size and structure of the penetrant on diffusion.

Introduction

In this tutorial, you will calculate the diffusivity of methane in poly(*cis*-1,4-butadiene) (PBD) by constructing an amorphous cell containing methane and PBD. After you have constructed the cell, you will perform a molecular dynamics simulation and calculate the mean square displacement of the methane molecule. Although the tutorial will only demonstrate a short calculation, you will become familiar with the methodology involved. The tutorial is based on a paper published by Meunier ([2005](#)), which examined the diffusion of gases in diene polymers.

This tutorial covers:

- [Getting started](#)
- [To set up the initial structures](#)
- [To build an amorphous cell](#)
- [To relax the cell](#)
- [To run and analyze molecular dynamics](#)
- [To calculate the diffusion coefficient](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **gas_polymer** as the project name, click the **OK** button.

The new project is created with *gas_polymer* listed in the Project Explorer.

2. To set up the initial structures

The first stage is to build and optimize a methane molecule and the PBD polymer so that you can construct your amorphous cell. To make it easier to select the methane molecules later, use a different display style.

Use the **Homopolymer** building tools to create a **20** repeat unit polymer of **c_butadiene** from the **dienes** library.

Create a new **3D Atomistic Document** and sketch a methane molecule. Change the **Display style** for atoms to **CPK**. **Rename** the new document **methane**.

In this tutorial you will use charge groups in the calculation of the electrostatic and van der Waals interactions. Charge groups are small atomic fragments that have a net charge of zero. This means that the electrostatic interactions between two groups can be evaluated with a straightforward distance-based cutoff, avoiding the computationally more expensive Ewald method.

Since charge groups are defined on the repeat units, they are automatically available for the polymer. You can verify this by coloring the atoms by charge group.

Make **Polyc_butadiene.xsd** the active document. Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Change the **Color by** option to **Charge Group**. When verified, change the **Color by** option back to **Element** and close the dialog.

Note: Since you will use forcefield assigned charges later, it is assumed that these charges also add up to zero for each group. If not, the calculation will fail and charge groups must be recalculated.

Charge groups are not present on sketched molecules, so you must first calculate the charge group for the methane molecule and configure Forcite to use charge groups instead of the default summation methods for non-bond calculations.

Make **methane.xsd** the active document.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog. On the **Energy** tab select **COMPASS** from the **Forcefield** dropdown list. Set both the **Electrostatic** and **van der Waals** summation methods to **Group based**.

Click the **More...** button for **Forcefield** to open the Forcite Preparation Options dialog. Uncheck the **Calculate automatically** checkbox for **Forcefield types**, then click the **Calculate** button. Ensure that the **Charges** are set to **Forcefield assigned** and click the charges **Calculate** button.

Click the **More...** button for **Charge groups** to open the Forcite Charge Groups dialog and click the **Calculate** button.

On the **Forcite Preparation Options** dialog check the **Calculate automatically** checkbox and close the dialog.

Before building the amorphous cell, you will optimize the geometry of both molecules.

On the **Setup** tab of the Forcite Calculation dialog, select **Geometry Optimization** from the **Task** dropdown list. Change the **Max. iterations** to **1000**.

Now optimize the methane molecule.

Make **methane.xsd** the active document and click the **Run** button on the Forcite calculation dialog.

A new folder, methane Forcite GeomOpt, is created in the Project Explorer. When the calculation is complete, the minimized structure is stored in the new folder. Continue the minimization with the polymer.

Make **Polyc_butadiene.xsd** the active document and click the **Run** button. Close the Forcite Calculation dialog.

The same process is repeated and the minimized structure is returned to Polyc_butadiene Forcite GeomOpt\Polyc_butadiene.xsd.


Note: The torsion degrees of freedom in the polymer will be modified by Amorphous Cell. These will be optimized later, after the cell is constructed.

Before proceeding with the amorphous cell construction, clear the workspace.

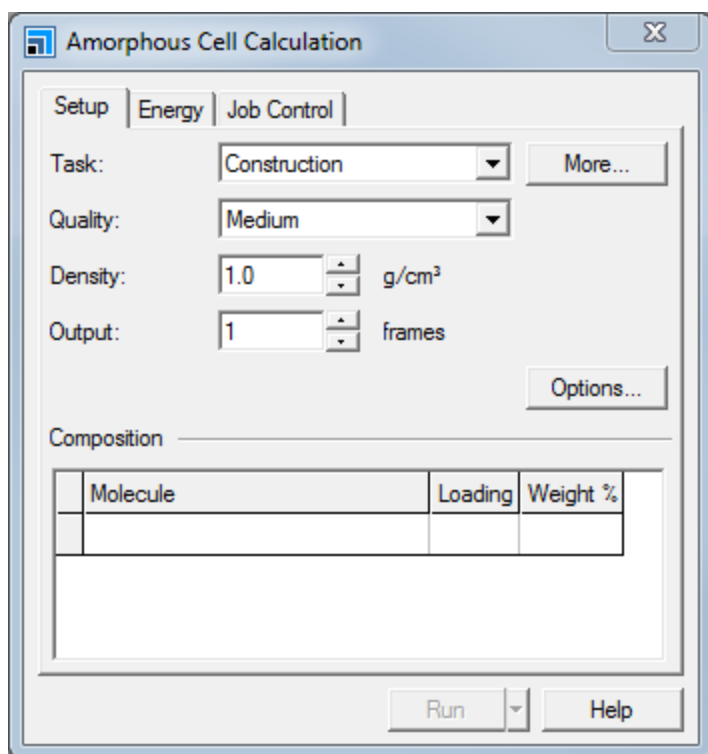
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To build an amorphous cell

Once you have prepared the two structures, you can build multiple copies of them in a cell using the Amorphous Cell module.

Click the **Amorphous Cell** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the Amorphous Cell Calculation dialog.



Amorphous Cell Calculation dialog, Setup tab

The first step is to define the composition in terms of number of molecules of each component. You want the cell to contain four molecules of methane and ten of PBD at a density of 0.95 g/cm^3 .

Set the **Density** to **0.95 g/cm³**.

In the **Molecule** column of the Composition grid select the document **methane Forcite GeomOpt\methane.xsd** containing the optimized structure of methane. In the **Loading** column enter **4**.

In the next row select **Polyc_butadiene Forcite GeomOpt\Polyc_butadiene.xsd** and a loading of **10**.

The estimated extensions of the cell are displayed at the bottom of the dialog, based on the loadings and the density. In this case a cube with cell lengths of about 27 Å will be constructed. Orthorhombic and tetragonal lattice types are also available, but are not used in the tutorial.

Amorphous Cell can optimize the structure as part of the construction. In this case you will optimize and equilibrate separately using Forcite and not use this feature.

Click the **Options...** button to open the Amorphous Cell Options dialog. Uncheck the **Optimize geometry** checkbox. Close the dialog.

Now select the same forcefield as used in Forcite.

On the **Energy** tab of the Amorphous Cell Calculation dialog select **COMPASS** from the **Forcefield** dropdown list.

The default job description in Amorphous Cell corresponds to the name of the first component, in this case **methane**, which is used as seedname in all output documents. In this tutorial you will change the default to **cell**.

On the **Job Control** tab uncheck the **Automatic** checkbox and enter **cell** into the text field. Click on the **gas_polymer** tree root in the Project Explorer and click the **Run** button. Close the dialog.

A new folder, **cell AC Construct**, is created and displayed in the Project Explorer. When the calculation is complete, a trajectory document, **cell.xtd**, is produced containing the amorphous cell.

Note: If you construct multiple frames, they are all stored in the **.xtd** document. They can be viewed and accessed using the Animation toolbar.

Double-click on **cell.xtd**.

The document contains a periodic cell with ten PBD oligomers and four methane molecules.

In the following steps it is most convenient to work with the model in a structure document (**.xsd**) rather than a trajectory document (**.xtd**). so you should make a copy of the structure in a new 3D Atomistic document.

Right-click in the trajectory document and select **Copy** to copy everything.

Select **File | New...** from the menu bar and choose **3D Atomistic** document and click the **OK** button. Right-click in the new document and select **Paste** to paste the copied structure. **Rename** the new document to **cell**.

Before performing the relaxation, clear the work area.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

4. To relax the cell

When you generate an amorphous cell, the molecules may not be equally distributed throughout the cell, creating areas of low density. To correct this, you must perform a short energy minimization to optimize the cell. After the minimization, you should run a short molecular dynamics simulation to equilibrate the cell. This procedure of minimization and molecular dynamics is known as relaxing the structure and should be carried out whenever you construct an amorphous cell.

To perform the geometry optimization, you must first configure Forcite to use charge groups for 3D periodic structures.

Re-open the newly created structure document **cell.xsd**. Open the **Forcite Calculation** dialog and select the **Energy** tab. Change both **Electrostatic** and **van der Waals** summation methods to **Group Based**.

Note: Forcite has separate settings for nonperiodic and periodic structures. The dialog always shows the settings corresponding to the periodicity of the active document, defaulting to nonperiodic.

Now you are ready to minimize the total energy of the cell.

On the Forcite calculation dialog, click the **Run** button.

When the job is complete, the final structure is stored in the folder `cell Forcite GeomOpt`. You will continue relaxing the structure by running molecular dynamics on it with a periodically changing temperature, also known as annealing the system. For the purpose of this tutorial you will just run one anneal cycle.

On the **Setup** tab of the Forcite Calculation dialog, select **Anneal** from the **Task** dropdown list and click the **More...** button to open the Forcite Anneal Dynamics dialog.

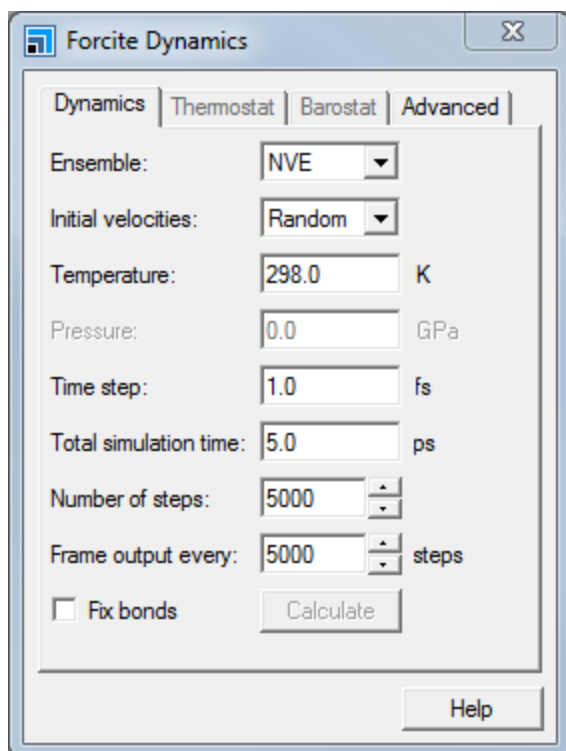
Set the number of **Annealing cycles** to **1**, the **Initial temperature** to **300 K**, and the **Mid-cycle temperature** to **500 K**. Close the dialog.

Now perform an anneal calculation on the optimized structure.

Make **cell.xsd** in the `cell Forcite GeomOpt` subfolder the active document. Click the **Run** button on the Forcite Calculation dialog.

The anneal task produces various output documents. The final structure after the last change of temperature is contained in the structure document `cell.xsd` in the folder `cell Forcite Anneal`. You will proceed by running a short molecular dynamics simulation on this structure, now at constant temperature.

Make **cell.xsd** in the `cell Forcite Anneal` subfolder the active document. On the **Setup** tab of the Forcite Calculation dialog, select **Dynamics** from the **Task** dropdown list and click the **More...** button to open the Forcite Dynamics dialog.



Forcite Dynamics dialog, Dynamics tab

There are different types of molecular dynamics simulations available, classified by the ensemble names, [NVE](#), [NVT](#), [NPT](#), and [NPH](#). The letters refer to:

N = constant number of molecules

V = constant volume

E = constant energy

T = constant temperature

P = constant pressure

H = constant enthalpy

Note: The NPT ensemble should be used if the density (and hence the volume) chosen at construction needs adjusting to the outside pressure (usually atmospheric pressure); if the system has been built at a reasonable density, NVT can be used and the pressure should average to 1 atm or 0.0001 GPa.

You constructed the cell at a density of 0.95 g/cm^3 . Since this is also the average density of this system at 300 K and 1 atm, with the selected forcefield, it is not necessary to relax the density further using NPT. Instead you can proceed using [NVT](#) dynamics.

Select **NVT** from the **Ensemble** dropdown list and change the **Temperature** to **300**.

For the purpose of this tutorial you will reduce the number of steps to [2000](#). For such a short run the [Velocity Scale](#) thermostat is more suitable than the default.

Change the **Number of steps** to **2000**. On the **Thermostat** tab select **Velocity Scale** as the thermostat. Click the **Run** button on the Forcite Calculation dialog.

Note: In a realistic simulation, you would probably need to run at least 50000 steps (50 ps) to equilibrate the cell correctly. You can monitor the equilibration progress by looking up the energies in the live update chart, which should be constant apart from small fluctuations.

When the simulation completes a number of documents are returned. The final structure is contained in the structure document `cell.xsd` in the folder `cell Forcite Dynamics`.

Now clean up your workspace area again.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

5. To run and analyze molecular dynamics

When you equilibrated the system, you were only interested in the final structure. However, to calculate the mean square displacement of the methane molecules in the cell, you need to have many frames so that you can analyze where the methane molecules are moving. You will run another molecular dynamics simulation and generate a trajectory document which you can analyze using the Forcite Analysis tool.

To avoid too many subfolders, first move the working document to the top of the folder tree.

In the Project Explorer, double-click on `cell.xsd` in the `cell Forcite Dynamics` folder. In the Project Explorer **drag** this file to the top of the `gas_polymer` folder tree.

Previously, you ran dynamics at constant temperature (NVT), however for the production run, you will continue the simulation at constant energy (NVE). This is because some thermostats can interfere with the dynamics of the system, and potentially affect the diffusion coefficient that you will calculate later on. In order to collect enough data for the analysis, you should increase the number of steps and reduce the frame output interval. For the purpose of this tutorial you will just perform 5000 steps.



On the Dynamics tab of the Forcite Dynamics dialog select **NVE** from the **Ensemble** dropdown list. Change the **Number of steps** to **5000** and the **Frame output every** to **250**. Close the Forcite Dynamics dialog.

On the Forcite Calculation dialog click the **Run** button and close the dialog.

Tip: For a real production run you should increase the number of steps so that the simulation time is at least 50 ps.

As the calculation progresses, two chart documents are updated. One plots the total energy and various components with time and the other plots the temperature. As this is an NVE ensemble calculation, the total energy should be constant. There will be exchange of kinetic and potential energy, but provided the equilibration was long enough, there should be no net exchange. Likewise in an equilibrated system, the temperature will fluctuate around an average value of 300 K without systematic change.

When the calculation finishes, a trajectory `cell.xtd` containing 21 frames is returned on which the analysis will be performed.

Make `cell.xtd` the active document. Click the **Play** button  on the **Animation** toolbar. When you have finished watching the animation, click the **Stop** button .

To calculate the mean square displacement of the methane molecules, you need to distinguish them from the polymer molecules. This can be achieved by defining them as a set.


To select all the methane molecules hold down the **CTRL** key and **double-click** on each molecule in turn.

Tip: To automatically select all molecules of a kind you can use the Find Patterns tool.

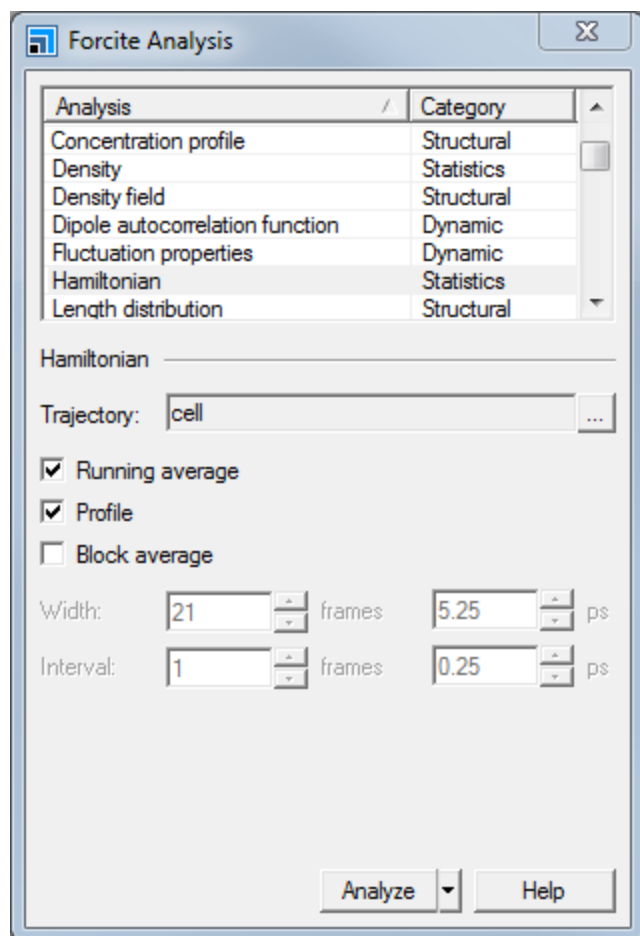
Now you can use the Edit Sets tool to create a set of the selected atoms.

Select **Edit | Edit Sets** from the menu bar to open the Edit Sets dialog. Click the **New...** button, enter the name **methane**, and click the **OK** button. Close the Edit Sets dialog. Click anywhere in the trajectory document to undo the selection.

Now that you have defined the methane molecules as a set, you can analyze their movement.

Click the **Forcite** button  on the **Modules** toolbar and select **Analysis** from the dropdown list.

This opens the Forcite Analysis dialog.



Forcite Analysis dialog

There are many different types of analysis that you can perform with Forcite and they are split into three categories; *Structural*, *Statistics*, and *Dynamic*. Mean square displacement is in the *Dynamic* section.

Select **Mean square displacement** from the list. Select **methane** from the **Sets** dropdown list and set the **Length** to **21**.

Click the **Analyze** button and close the dialog.

Note: Since the statistical accuracy of the MSD data decreases with the length of the time interval, by default the MSD is not calculated beyond half the number of frames.

The Forcite Analysis tool calculates the mean square displacement and generates a chart document, `cell Forcite MSD.xcd`, which contains a plot of the mean square displacement (MSD) of the methane molecules with time. A study table, `cell Forcite MSD.std`, is also produced. The value of the MSD for a given time reported in the chart is the average over all time intervals of that length and over all atoms in the set.

6. To calculate the diffusion coefficient

The mean square displacement typically has two regions. At short times the gas molecule collides inside a small pocket of free volume. Since the molecule is confined it does not diffuse on this time scale and the MSD levels off to a constant. On a longer time scale the molecule jumps out of the confined area to another pocket of free volume. The resulting motion of repeated jumps is diffusion, characterized by a mean square displacement that is linear in time. In practice, the statistics decreases with the time interval, often resulting in large fluctuations at the end.

The increase of MSD with time is related to the diffusion coefficient D :

$$D = \frac{1}{6N_{\alpha}} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_{\alpha}} \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$$

where N_{α} is the number of diffusive atoms in the system. The MSD in Forcite is already averaged over all atoms in the methane molecules.

To determine the diffusion coefficient you need to fit a straight line, $y = a*x+b$, to the data in the diffusive regime and abstract the slope a . The units of a are $\text{\AA}^2/\text{ps}$. According to the above definition, D then follows as:

$$D = a/6$$

You can perform the fit using any external spreadsheet or charting package. Here you will use the Plot Graph tool in Materials Studio. First delete the rows corresponding to the initial, non-linear, part of the graph, and the final, noisy, part.

In the study table `cell Forcite MSD.std` select the first few rows. Right-click in the row-header column and select **Delete**. Repeat this for the last few rows.

Now perform a linear regression on the remaining data.

Select columns **A** and **B** in `cell Forcite MSD.std`. On the **Tools** menu, select **Plot Graph** to open the Plot Graph dialog. Ensure that **Graph type** is set to **Scatter (2-D)** and check the **Show best fit line** checkbox. Click the **Plot** button.

A chart document is returned with a best fit line. The linear coefficient a can be read off the legend. Divide this value by 6 to obtain the diffusion coefficient in $\text{\AA}^2/\text{ps}$. To convert to the more commonly used unit cm^2/s , the resulting value must be divided by 1e4 .

Calculated values for the diffusion of methane in PBD have been reported in the range between $2.25 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ([Meunier, 2005](#)). This was obtained using ten chains of PBD polymer chains with 30 repeat units and four molecules of methane in an amorphous cell. The cell was equilibrated using a temperature cycle annealing method. Several cycles of NPT dynamics were performed with heating and cooling between 400 and 250 K (in 25 K steps), over 5 - 10 ps. Following equilibration NVT dynamics at simulation temperatures of 250 to 400 K in 25 K increments were performed over 3 ns. Using mean square displacement analysis the diffusion coefficient was obtained as a function of temperature.

Your calculated value may be very different to the reported values, since the run length was very short with limited statistics in the diffusive region.

This is the end of the tutorial.

References

M. Meunier "Diffusion coefficients of small gas molecules in amorphous cis-1,4-polybutadiene estimate by molecular dynamics simulations", *J. Chem. Phys.*, **123**, 134906 (2005).

Polymer interactions with a metal oxide surface

Purpose: Introduces concepts associated with the calculation of interactions between a polymer and a metal oxide surface. These include the construction of the amorphous polymer and metal oxide surface and the molecular dynamics simulations required to calculate the interaction energy.

Modules: Materials Visualizer, Amorphous Cell, Forcite Plus, COMPASS

Time: 🕒 🕒

Prerequisites: Using the layer builder, Using the polymer builder Visualizer Tutorials

Background

Interactions at polymer surfaces and interfaces are critical to products including adhesives, coatings, contact lenses, composites, prosthetic devices, films, lubricants, paints, and printing inks. Properties of interest to researchers include the structure of the interface or interphase, how it differs from the bulk, surface tension, wetting, and the chemistry/mechanics of adhesion.

Introduction

This tutorial shows how to build a metal oxide surface with 2D periodic boundary conditions and to calculate the interaction energy of a polymer with that surface.

This tutorial covers:

- [Getting started](#)
- [To cleave and relax the surface](#)
- [To increase the surface area and change the periodicity](#)
- [To build the polymer](#)
- [To add the polymer to the surface using the layer builder](#)
- [To optimize the layer and run molecular dynamics](#)
- [To calculate the interaction energy](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.


1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **polymer_metal** as the project name, click the **OK** button.

The new project is created with *polymer_metal* listed in the Project Explorer.

The first step is to import and cleave the 00-1 plane of alumina, Al_2O_3 .

Click the **Import** button on the toolbar . Navigate to **Structures\metal-oxides** and double-click on **Al2O3.msi**.

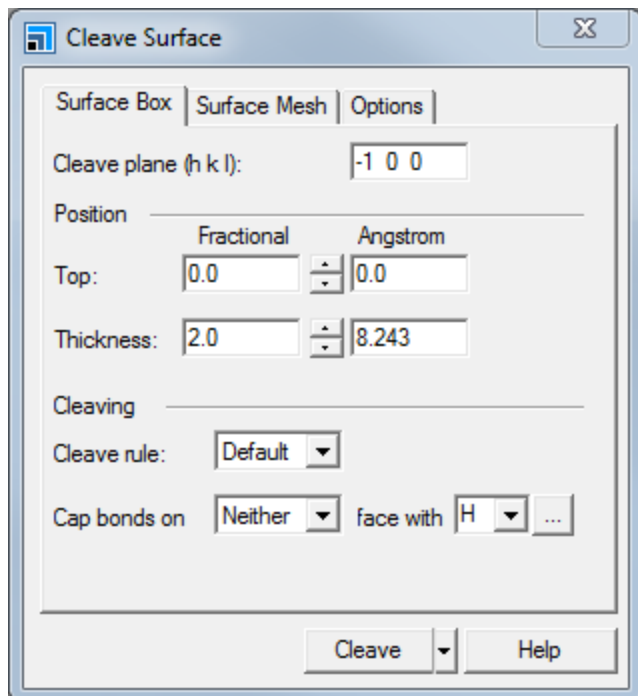
A 3D Viewer containing the crystal cell of alumina is displayed.

2. To cleave and relax the surface

You will cleave the crystal to provide a surface for the calculations later.

Select **Build | Surfaces | Cleave Surface** from the menu bar.

This opens the Cleave Surface dialog.



Cleave Surface dialog, Surface Box tab

Now you can set the Cleave Plane and the Thickness.

Change the **Cleave plane (h k l)** from -1 0 0 to **0 0 -1**. Press the **TAB** key.

As the non-bond cutoff distances in the forcefield settings are 9.5 Å, the thickness of your surface must be more than 9.5 Å. For the 0 0 -1 plane it is approximately 13 Å.

Click the **Cleave** button and close the dialog.

A new model document named **Al2O3 (0 0 -1) .xsd** is displayed, containing the cleaved surface.

Right-click in the new document and select **Lattice Parameters** from the shortcut menu to open the Lattice Parameters dialog.

The lengths of the U and V dimensions of the surface are 4.759.

Later, you will need to increase the surface area but first you will relax the surface.

Close the Lattice Parameters dialog.

To relax the surface, you have to minimize the energy of it using molecular mechanics. Although the surface is ionic in nature, the typing of the model by the COMPASS forcefield requires bonds to exist between the aluminum and oxygen atoms. However, for calculations to proceed correctly, these bonds must be removed after the typing is complete.

Click the **Forcite** button  on the **Modules** toolbar and select **Calculation**.

This opens the Forcite Calculation dialog.

On the **Setup** tab select **Geometry Optimization** from the **Task** dropdown list.

On the **Energy** tab select **COMPASS** from the **Forcefield** dropdown list and click the **More...** button to open the Forcite Preparation Options dialog.


Usually, when a Forcite calculation is performed, the atom types are calculated automatically before each calculation. However, you do not want this to happen as bonds are present between the oxygen and aluminum atoms which are not parameterized as the structure is ionic. Therefore, you need to pre-assign the forcefield types and prevent them being recalculated during the simulation.

Uncheck the **Calculate automatically** checkbox and click the **Calculate** button and close the Forcite Preparation Options dialog.

This assigns a forcefield type to each atom, these can be displayed by labeling the atoms.

On the **Energy** tab select **Forcefield assigned** from the **Charges** dropdown list.

Only the top few layers of atoms in the surface will interact with the polymer and the rest of the atoms can be considered to be part of the bulk and therefore have little effect. This means that you can constrain the bulk atoms so that they are not minimized.

Rotate the model so that the surface is at the top. Click the **Selection** button  on the 3D Viewer toolbar. Select all the atoms apart from the two rows next to the surface by dragging a bounding box around the other atoms.

The structure should look similar to the image below.



Bulk atoms to be constrained

Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. Check the **Fix Cartesian position** checkbox and close the dialog.

Click in the 3D Viewer to deselect the atoms.

The final step before relaxing your surface is to remove the bonds between the aluminum and oxygen atoms.

Hold down the **ALT** key and double-click on any bond. Press the **DELETE** key.

You are now ready to relax the surface.

On the **Forcite Calculation** dialog, click the **Run** button and close the dialog.

A new folder, entitled Al₂O₃ (0 0 -1) Forcite GeomOpt, opens in the Project Explorer. The calculation should take less than one minute to complete. When completed, the minimized structure is in the Al₂O₃ (0 0 -1) .xsd document at the top of the new folder.

3. To increase the surface area and change the periodicity

The current surface area is very small and it should be increased. You can do this by making a supercell.

Ensure that the optimized **Al₂O₃ (0 0 -1).xsd** in the Al₂O₃ (0 0 -1) Forcite GeomOpt folder is the active document.

Select **Build | Symmetry | Supercell** from the menu bar to open the **Supercell** dialog. Increase the **Supercell range** to **3** for both **U** and **V**. Click the **Create Supercell** button and close the dialog.

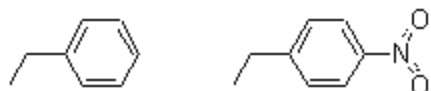
The enlarged surface is displayed. You can use the Build Vacuum Slab Crystal dialog to change the periodicity from 2D to 3D.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. Change the **Vacuum thickness** to **0.0** and click the **Build** button.

A warning dialog is displayed. Click the **Yes** button.

4. To build the polymer


The polymer that you are going to simulate is poly-p-nitrostyrene. This is not a pre-built monomer but you can build it by editing a current monomer, styrene.



Structures of styrene and p-nitrostyrene

In the **Project Explorer**, right-click on the project root and select **Import...** from the shortcut menu. Navigate back to **Structures\repeat-units\vinyls\styrene.msi** and click the **Open** button.

To change the styrene monomer to p-nitrostyrene, you should add a nitro group para to the ethyl group on the phenyl ring. You can sketch the nitro group using the 3D Sketching tools or alternatively add it from the Fragment Browser.

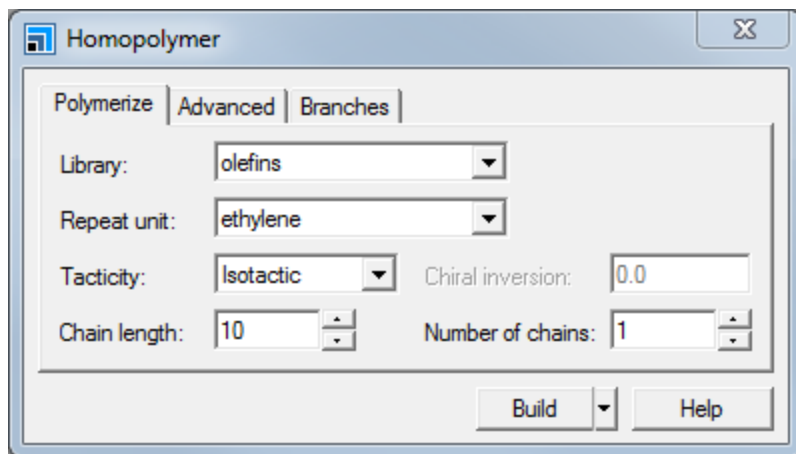
Click the **Sketch Fragment** arrow  on the **Sketch** toolbar and select **Fragment Browser**. Expand the **Functional Groups** node and select **Nitro**. Click once on the para hydrogen of the phenyl ring. Close the Fragment Browser dialog.

You should change the name of the monomer before you continue.

In the **Project Explorer**, right-click on **styrene.xsd** and select **Rename** from the shortcut menu. Change the name to **p-nitrostyrene**. Open the **Properties Explorer** and change the **Filter** to **Repeat Unit**. Change the **Name** to **p-nitrostyrene**.

You can use this monomer to build a homopolymer by using the polymer building tools.


Select **Build | Build Polymers | Homopolymer** from the menu bar to open the Homopolymer dialog.



Homopolymer dialog, Polymerize tab

Change the **Library** to **Current project** and the **Repeat unit** to **p-nitrostyrene**. Change the **Tacticity** to **Atactic** and the **Chain length** to **8**. Click the **Build** button and close the dialog.

You have generated your ideal polymer, entitled **Polyp-nitrostyrene.xsd**, though the adopted conformation is not very realistic. Amorphous Cell can be used to obtain realistic polymer conformations, this generates chains containing sequences of backbone dihedrals typical of those found in actual melts or in ideal solutions.

Click the **Amorphous Cell** button  on the **Modules** toolbar and select **Calculation**.

This opens the Amorphous Cell Calculation dialog. You need to define what you want in your amorphous cell, in this case it is one copy of your polymer.

Choose **Confined Layer** from the **Task** dropdown list and select the **Polyp-nitrostyrene.xsd** from the **Molecule** dropdown list in the **Composition** grid.

Note: In a real simulation, you would generate many different chains in order to average over configurational space.

Before building the cell, you need to specify the target density and the cell parameters for your confined layer.

Change to the **Al2O3(0 0 -1).xsd** document containing the slab, right-click and select **Lattice Parameters**. Note down the **a** and **b** parameters and close the dialog.

These should be of the order of 14-15 Å and you should therefore specify that the **a** and **b** lattice parameters for the polymer are the same as the **U** and **V** parameters for the surface.

On the **Amorphous Cell Calculation** dialog click the **More...** button to open the Amorphous Cell Confined Layer dialog. Select **Orthorhombic** from the **Lattice type** dropdown list and set the values of both **a** and **b** to the lattice parameters you wrote down and close the dialog.

On the **Setup** tab of the Amorphous Cell Calculation dialog set the **Density** to **0.8**. On the **Energy** tab set the **Forcefield** to **COMPASS**. Click on the **polymer_metal** tree root in the Project Explorer and click the **Run** button. Close the dialog.

A new folder is created in the Project called Polyp-nitrostyrene AC Layer. The job should complete in a few minutes and the amorphous structure is in the Polyp-nitrostyrene.xtd trajectory document.

Note: If you create more than one configuration, the other configurations are contained in the trajectory document and can be accessed from the Animation toolbar.

5. To add the polymer to the surface using the layer builder

Now that you have a minimized surface and polymer, you will use the Layer builder to place the polymer over the surface.

Select **Build | Build Layers** from the menu bar to open the Build Layers dialog. For **Layer 1**, select the optimized surface (Al2O3 (0 0 -1).xsd in the Al2O3 (0 0 -1) Forcite GeomOpt folder) and for **Layer 2** select the polymer you have just confined in a cell and minimized (Polyp-nitrostyrene.xtd).

When you build the layered structure, the polymer will be able to see both sides of the surface due to periodic boundary conditions. Therefore, you should add a large vacuum above the polymer so that it only sees one side of the surface.

On the **Layer Details** tab. Increase the **Vacuum** for **Layer 2** to **30.0**.

On the **Matching** tab select the lattice parameters for **Layer 1**. Click the **Build** button, on the warning dialog click the **Yes** button. Close the Build Layers dialog.

A new document, entitled Layer .xsd, is displayed and this contains the surface, polymer and vacuum. All further calculations will be performed using this structure as the starting point.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

6. To optimize the layer and run molecular dynamics

In the Project Explorer double-click on **Layer.xsd**.

A molecular dynamics simulation is needed to equilibrate the system. Ideally, this would consist of a minimum of 30 ps of molecular dynamics to allow the system to fully equilibrate but, due to time constraints, you will only run 0.5 ps. As the surface was minimized in an earlier step, you can constrain the entire surface.

Select all the surface atoms. Open the **Edit Constraints** dialog and uncheck then **check** the **Fix Cartesian position** checkbox. Close the dialog and click in the 3D Viewer to deselect the atoms.

You should ensure that all the aluminum oxide atoms are constrained.

Right-click and select **Display Style** from the shortcut menu, on the **Atom** tab of the Display Style dialog select **Constraint** from the **Color by** dropdown list. All the Al_2O_3 atoms should be red. If some are not you should repeat the previous step. Change the **Color by** option back to **Element**. **Close** the dialog.

The geometry of the polymer layer with respect to the metal oxide surface should be optimized before continuing.

Open the **Forcite Calculation** dialog and set the **Task** to **Geometry Optimization**. Click the **More...** button to open the Forcite **Geometry Optimization** dialog and set the **Max. iterations** to **5000**, close the dialog. Click the **Run** button.

The generated optimized structure is now ready for the dynamic simulation. Molecular dynamics is one of the simulation types available in the Forcite module.

On the **Forcite Calculation** dialog set the **Task** to **Dynamics**. Click the **More...** button to open the Forcite Dynamics dialog and set the **Number of steps** to **500**, close the dialog.

Click the **Run** button and close the Forcite Calculation dialog.

This calculation could take several minutes to run. As the calculation runs, charts containing temperature and energies are updated. The text document `Status.txt` indicates the CPU time and the number of steps completed so far. When the calculation is complete, the final structure is present in the `.xsd` document.

7. To calculate the interaction energy

You can calculate the interaction energy by using the following equation.

$$E_{\text{Interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{polymer}})$$

E_{total} is the energy of the surface and the polymer, E_{surface} is the energy of the surface without the polymer and E_{polymer} is the energy of the polymer without the surface. These calculations are all single point energies and should not be undertaken whilst constraints are defined in the model as this will result in a failed calculation.

Open the final structure from the dynamics calculation, **Layer.xsd**. Select all the atoms and open the **Edit Constraints** dialog, uncheck the **Fix Cartesian position** checkbox and close the dialog.

You have to calculate single point energies for the total system, the polymer and the surface.

Open the **Forcite Calculation** dialog. Set the **Task** to **Energy** and click the **Run** button. When the job is complete, scroll down the output text document and note the **Total energy**.

This is E_{total} . To get the value for E_{polymer} , you need to calculate the single point energy of the polymer in the 3D lattice but without contributions from the surface. To do this, you should save the system as a different document so that you can remove the surface.

Change the focus back to your **Layer.xsd** document. Select **File | Save As...** from the menu bar, enter **polymer_only.xsd** and click the **Save** button. Change focus to **polymer_only.xsd** and select and delete all of the metal oxide atoms.

Now you need to perform a single point energy calculation on the polymer.

On the **Forcite Calculation** dialog, click the **Run** button. When the job is complete, scroll down the output text document and note the **Total energy**.

This is E_{polymer} . Finally, you need to calculate the energy of the surface.

Make **Layer.xsd** the active document and save it as **surface_only.xsd**. In **surface_only.xsd** select and delete the polymer.

Open the **Edit Constraints** dialog and check that there are no constraints on the metal-oxide atoms, close the dialog.

On the **Forcite Calculation** dialog, click the **Run** button. When the job is complete, scroll down the output text document and note the **Total energy**.

This is E_{surface} . You can now use the above equation to calculate the interaction energy of the polymer and the surface. You should obtain a negative number, indicating that the polymer is binding to the surface.

This methodology gives basic instructions on how to calculate the energy of interaction between a polymer and a metal-oxide surface. However, if you were to perform an in-depth study of this type of interaction, you would be advised to use Materials Studio's scripting interface to vary structures and calculate the interaction energy for each variation.

This is the end of the tutorial.

Calculating the miscibility of two polymers

Purpose: To demonstrate the use of the amorphous cell and molecular dynamics tool for calculation of polymer properties.

Modules: Materials Visualizer, Amorphous Cell, Forcite Plus

Time: 🕒 🕒

Prerequisites: Using the polymer builder

Background

Among the more common uses for atomistic simulation tools in polymer science is the prediction of polymer miscibility. Blends of polymers are desirable since they are easier to produce than novel polymers and circumvent legislative problems. Frequently a pair (or more) of polymers with desirable properties are blended in the hope that the resultant mixture will have improved characteristics. Materials Studio can be utilized to determine the solubility parameters, cohesive energy density and Flory-Huggins interaction parameter of any number of polymers.

Introduction

In this tutorial, you will use the polymer building tools to construct two polymers. You will then use Amorphous Cell and Forcite to create a cell containing an amorphous blend of the two polymers. Finally, you will run a molecular dynamics simulation and analyze this to obtain the cohesive energy density.

This tutorial covers:

- [Getting started](#)
- [To build two syndiotactic homopolymers](#)
- [To optimize the geometries](#)
- [To use Amorphous Cell to construct an amorphous blend](#)
- [To run molecular dynamics on the cell](#)
- [To calculate the cohesive energy density](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

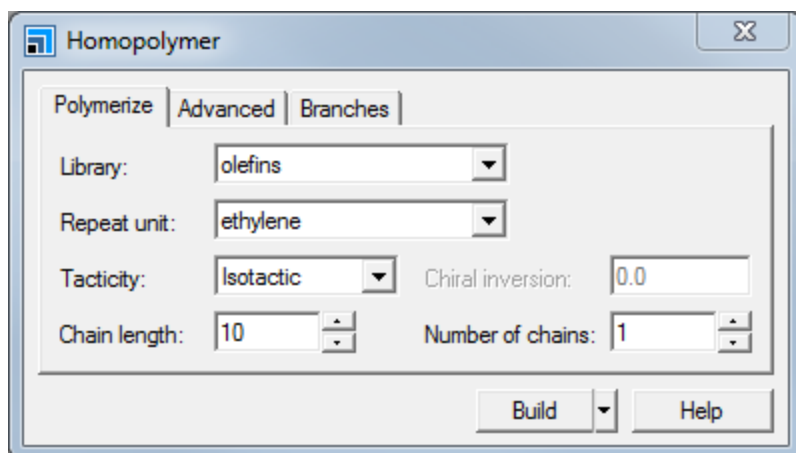
Open the **New Project** dialog and enter **miscibility** as the project name, click the **OK** button.

The new project is created with *miscibility* listed in the Project Explorer.

2. To build two syndiotactic homopolymers

The first stage in this tutorial is to use the polymer builder to build polystyrene and polypropylene.

Select **Build | Build Polymers | Homopolymer** from the menu bar to open the Homopolymer dialog.



Homopolymer dialog, Polymerize tab

You need to build an 18 repeat unit polypropylene polymer.

Select **propylene** from the **Repeat unit** dropdown list and change the **Chain length** to **18**. Select **Syndiotactic** from the **Tacticity** dropdown list and click the **Build** button.


A 3D Atomistic Document called Polypropylene.xsd is displayed. Now repeat this procedure for polystyrene.

Select **vinyls** from the **Library** dropdown list and set the **Repeat unit** to **styrene**. Leave the other options as they are, click the **Build** button and close the dialog.

A second 3D Atomistic Document, called Polystyrene.xsd, is displayed.

3. To optimize the geometries

When the polymers are constructed, there is no geometry optimization performed. Therefore, before you build your amorphous blend, you should perform an initial geometry optimization.

Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog which allows you to perform a geometry optimization calculation.

The default maximum number of iterations is 500 but you do not need to perform this number as you only want to get a starting geometry. Therefore, you should perform 200 iterations.

Change the **Task** to **Geometry Optimization**, click the **More...** button to open the Forcite Geometry Optimization dialog. Change the **Max. iterations** to **200** and close the dialog.

Click the **Run** button.

If the Job Explorer is not already open, it will be displayed. This provides basic information about the job as it progresses. A new folder is also displayed, named Polystyrene Forcite GeomOpt, and this is where the results from the calculation will be returned.

A status text document and two chart documents are displayed, these allow you to monitor the progress of your job.

When the job finishes, the minimized structure is entitled `Polystyrene.xsd` and is located in the `Polystyrene Forcite GeomOpt` folder. A text document, `Polystyrene.txt`, is also produced. This contains all the energy information about the calculation.

When the job has finished, you can minimize the energy of the other polymer.


In the **Project Explorer**, double-click on **Polypropylene.xsd**. On the **Forcite Calculation** dialog, click the **Run** button.

When the job is complete, you should save the project and then close all the windows.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To use Amorphous Cell to construct an amorphous blend

Once you have built your polymers, you need to combine them in an amorphous cell.

Click the **Amorphous Cell** button  on the **Modules** toolbar and choose **Calculation** from the dropdown list or choose **Modules | Amorphous Cell | Calculation** from the menu bar.

This opens the Amorphous Cell Calculation dialog.

Initially, you need to define the polymers that are going to be added to your cell.

In the **Composition** grid select the optimized **Polystyrene.xsd** for the first row in the **Molecule** column and the optimized **Polypropylene.xsd** for the second row. Set the target **Density** to **0.9 g/cm³**.

As you change the target density, the cell parameters are automatically adjusted.

Click on the **miscibility** tree root in the Project Explorer. Click the **Run** button and close the dialog.

After a few seconds, a new folder `Polystyrene AC Construct` is displayed in the Project Explorer. As before, a summary of the job status is displayed in the Job Explorer.

The Job Explorer indicates any jobs that are running that are associated with this project. It shows useful information such as the server and job identification number. You can also use this explorer to stop the job if you need to.

There are no live updates from this calculation, so you should wait for the calculation to complete before continuing. This could take a short time.

5. To run molecular dynamics on the cell

Unless you request otherwise, Amorphous Cell performs a geometry optimization on a newly created cell. This is required because the molecules may not be equally distributed throughout the cell, creating pockets of vacuum. After a cell has been built, you should run a short molecular dynamics simulation to equilibrate the system. This procedure of minimization and molecular dynamics is known as relaxing the structure and should be carried out whenever you construct an amorphous cell.

Once the cell has been well equilibrated, you can perform the production run to generate conformations which you will use in the cohesive energy density calculation.

In this case, you will perform a short equilibration run and a short production run.

Note: As long as your system is equilibrated, a longer production run will give a more accurate result.

Open the **Forcite Calculation** dialog and change the **Task** to **Dynamics**.

Click the **More...** button to open the Forcite Dynamics dialog.

On the **Dynamics** tab change the **Ensemble** to **NVT**. On the **Thermostat** and change the **Thermostat** to **Velocity Scale**.

Ensure that the trajectory document generated by the Amorphous Cell Construction job is active. Click the **Run** button.

The equilibration run is performed using the NVT ensemble to ensure that the system is at the correct temperature.

On the **Dynamics** tab of the **Forcite Dynamics** change the **Ensemble** to **NVE**. Make sure that the **Frame output every** is **500** and close the dialog.

This means that the trajectory document will contain 11 frames.

Ensure that the trajectory document generated by the previous Forcite Dynamics job is active. Check the **Restart** checkbox and click the **Run** button.

When the calculation is finished, you should save the project.

Choose **File | Save Project** from the menu bar.

6. To calculate the cohesive energy density

Once you have an equilibrated trajectory document, you can calculate the cohesive energy density using the Forcite Cohesive Energy Density task.

On the **Forcite Calculation** dialog change the **Task** to **Cohesive Energy Density**.

You can either choose to apply the analysis to a single frame of the current document or you can choose a logical trajectory document. The logical trajectory option allows you to add together multiple dynamics runs on the same structure and analyze all of them. In this case, you will define a logical trajectory containing all the frames of the single dynamics run you have completed.

Open **Polystyrene.xtd** output trajectory from the Forcite Dynamics calculation.

Leave the **Frame filter** set to **ALL** and click the **More...** button to open the Forcite Cohesive Energy Density dialog. Check the **Include structure in study table** checkbox and close the dialog.

The study table containing the results of the calculation will include the structures for each frame analyzed.

Click the **Run** button and close the dialog.

The cohesive energy density calculation uses the client-server architecture and the results are returned to the Polystyrene Forcite CED folder. Several documents are returned, including a trajectory, study table, and status and summary text documents.

In the text document **Polystyrene.txt**, scroll down to find the line "--- Cohesive energy density & solubility parameters ---".

The text document contains the average cohesive energy density in J/m³.

The cohesive energy density is used in determining the miscibility of polymers. The energy of mixing, per unit volume, is related to the cohesive energy densities of the blend and the pure components as follows:

$$\frac{\Delta E_{mix}}{V} = \phi_A \left(\frac{E_{coh}}{V} \right)_A + \phi_B \left(\frac{E_{coh}}{V} \right)_B - \left(\frac{E_{coh}}{V} \right)_{AB}$$

where ϕ_A and ϕ_B are the volume fractions of A and B in the mixed system. The first two terms can be calculated in the same way as above by using only one polymer component.

Typically the energy of mixing of polymer blends is positive, indicating that energy is required to mix. This is often expressed in terms of the dimensionless Flory-Huggins parameter χ ,

$$\chi = \frac{1}{\phi_A \phi_B} \left(\frac{\Delta E_{mix}}{k_B T} \right)$$

Where the energy of mixing is expressed with respect to the volume unit used in Flory-Huggins theory. A common approximation to the Flory-Huggins parameter is to write:

$$\chi = \frac{v}{k_B T} (\delta_A - \delta_B)^2$$

where v is the reference volume used for χ , and δ is the solubility parameter:

$$\delta = \sqrt{\frac{E_{coh}}{V}}$$

The results generated by this tutorial allow you evaluate all of these properties.

This is the end of the tutorial.

Running a confined shear simulation

Purpose: Introduces the use of Forcite to calculate confined shear.

Modules: Materials Visualizer, Amorphous Cell, Forcite Plus, COMPASS

Time: 🕒🕒🕒

Prerequisites: Using the polymer builder, [Finding low energy configurations of a molecule on a surface](#)

Background

The confined shear task in Forcite performs a simulation of shear flow of a fluid confined between semi-rigid walls or surfaces. The fluid can either be a liquid or an oligomer. The surfaces would normally be an inorganic oxide or metal - although practically any chemically reasonable type of confining surface material can, in principle, be used.

This is achieved by imposing a user-defined velocity on the walls. The two walls are sheared with an equal but opposite velocity and they are held in a fixed position relative to one another by harmonic springs.

Introduction

This tutorial shows you how to perform a confined shear simulation on a layered structure. It starts with building and defining the different layers using a combination of tools, such as Amorphous Cell and the Layer Builder. Once you have your layered structure, you will then use the confined shear task to run the simulation.

This tutorial covers:

- [Getting started](#)
- [To setup the Fe layer](#)
- [To build a tridecane molecule](#)
- [To construct the layered system](#)
- [To equilibrate the layered system](#)
- [To run the confined shear simulation and analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ConfinedShear** as the project name, click the **OK** button.

The new project is created with *ConfinedShear* listed in the Project Explorer.

2. To setup the Fe layer

The first stage is to import the metal from the structure library.

Click the **Import** button  on the toolbar to display the Import Document dialog. Ensure that **3D Atomistic Files** is selected from the file types dropdown list for the **File name**. Navigate to and select the file **Structures\metals\pure-metals\Fe.msi** and click the **Open** button.

The next stage is to build a supercell out of your existing cell.



Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase the **Supercell range** to **7 7 3** and click the **Create Supercell** button. Close the dialog.

3. To build a tridecane molecule

To build a tridecane molecule, first build a dodecane molecule using the Polymer Builder.

Select **Build | Build Polymers | Homopolymer** from the menu bar to open the Homopolymer dialog. On the **Polymerize** tab, change the **Chain length** to **6**. Ensure that the **Repeat unit** is defined as **ethylene**, in the **olefins Library**. Click the **Build** button and close the dialog.

The dodecane molecule is displayed in a new 3D Viewer. You will modify the structure to add an extra methyl group at one end of the chain.

Choose the **Selection** tool  on the toolbar and select a terminal hydrogen at one end of the chain. Click the **Modify Element** arrow  and select **Carbon** from the dropdown list. Click anywhere in the 3D Viewer to deselect the atom.


Click the **Adjust Hydrogen** button  and then the **Clean** button .

Before continuing, you should rename the new molecule to tridecane

Use the **Project Explorer** to rename Polyethylene.xsd to **tridecane.xsd**.

4. To construct the layered system

In this section, you will build an amorphous cell containing the tridecane and then place this between two layers of iron using the Layer Builder.

Click the **Amorphous Cell** button  on the **Modules** toolbar and choose **Calculation**.

This opens the Amorphous Cell Calculation dialog.

Select **Confined Layer** from the **Task** dropdown list.

You should define the number of tridecane molecules to load and the density of the cell, for this tutorial, this is 0.7 g cm^{-3} .

Select **tridecane.xsd** from the **Molecule** list and set the **Loading** to **25**. Set the **Density** to **0.7 g/cm³**.

Click the **More...** button to open the Amorphous Cell Confined Layer dialog and select **Orthorhombic** from the **Lattice type** dropdown list.

The cell parameters define the size of the lattice. As you want to make a layered structure, you need to change the *a* and *b* parameters so that they are the same as those of the metal layer.

Double-click on **Fe.xsd** in the Project Explorer to make it the active document. Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu. Enter the **a** and **b** values displayed in the Lattice Parameters dialog in the **Lengths (Å)** section on the Amorphous Cell Confined Layer dialog. **Close** the Lattice Parameters and Amorphous Cell Confined Layer dialogs.

The default mode of the Amorphous Cell algorithm is to use the bonds between the backbone atoms as rotatable bonds. When you build a polymer, the backbone atoms are defined automatically as a path between the head and tail atoms. In this case, you have edited the structure and added an extra methyl group which does not have backbone atoms defined. Amorphous Cell can automatically find all flexible torsions which, in this case, would include the newly added torsion.

On the Amorphous Cell Calculation dialog, click the **Options...** button to open the Amorphous Cell Options dialog. Check the **Include non-backbone torsions** checkbox and close the dialog.

Before launching the job, you should define the energy settings and specify a new job description.

On the **Energy** tab of the Amorphous Cell Calculation dialog, select **COMPASS** from the **Forcefield** dropdown list and **Group based** from the **Electrostatic** dropdown list for the summation method.

Click the **More...** button for **Forcefield** to open the Amorphous Preparation Options dialog. Verify that **Calculate automatically** is checked for **Charge groups**. Close the dialog.

Amorphous Cell will automatically calculate charge groups after the charges have been assigned. The default calculation method is *Divide-and-conquer*, which will, recursively, divide the molecule into charge neutral groups.

Click the **Run** button and close the dialog.

When the job is complete, a document called `tridecane.xtd` is returned to the `tridecane AC` Layer folder in the project.

Once you have built the amorphous cell, you can add this to your layered structure.

Select **Build | Build Layers** from the menu bar to open the Build Layers dialog. On the **Define Layers** tab, set **Layer1** to **Fe.xsd**, **Layer2** to **tridecane.xtd**, and **Layer3** to **Fe.xsd**.

This will build a trilayer structure with the tridecane sandwiched between two iron layers.

Select the **Layer Details** tab on the Build Layers dialog.

This allows you to specify whether or not to add vacuums to either end of the layered structure.

Select the **Options** tab, check the **Configure for confined shear use** checkbox. Change back to the **Layer Details** tab and then the **Define Layers** tab.

For the confined shear simulation to work, the layers must have specific names, seen on the *Define Layers* tab. Also, a 20 Å vacuum is added to the structure so that the non-bond interactions from the bottom wall do not influence the top wall.

Click the **Build** button and close the dialog.

After a few seconds, a new 3D Atomistic document, called Layer .xsd, opens containing your layered structure.

In the Project Explorer, drag and drop this into the root of the project. Make **Layer.xsd** the active document and press the **UP** arrow key twice to rotate the view.

You should now be able to see the layered structure.

5. To equilibrate the layered structure

Before performing the shear, you should first run a short geometry optimization and a long NVT dynamics to equilibrate the tridecane wax. As you only want to equilibrate the wax atoms, you should constrain the iron atoms.

In the 3D view, hold down the **ALT** key and double-click one of the Fe atoms. Select **Modify | Constraints** from the menu bar to open the Edit Constraints. Check the **Fix Cartesian position** checkbox and close the dialog.

Now you have constrained the position of the Fe atoms, you can relax the tridecane.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog.

On the **Setup** tab, change the **Task** to **Geometry Optimization**.

On the **Energy** tab and set the **Forcefield** to **COMPASS**. Change the **Electrostatic** and **van der Waals** summation methods to **Group based**.

Click the **More...** button for **Forcefield** to open the Forcite Preparation Options dialog. Ensure that the **Calculate automatically** checkbox is checked in the **Charge groups** section and close the dialog.

The charge groups for tridecane were already calculated by Amorphous Cell. Forcite will complete the charge groups assignment on the structure by adding one to each Fe atom.

Click the **Run** button.

The initial relaxation of the structure should have removed any bad contacts generated from the Amorphous Cell building and layer building process. You should also run a molecular dynamics calculation to provide further equilibration. In this case, you will use a simulated annealing calculation which runs a set of short molecular dynamics calculations at different temperatures.

On the Forcite Calculation dialog select the **Setup** tab. Change the **Task** to **Anneal** and click the **More...** button to open the Forcite Anneal Dynamics dialog.

On this dialog, you can set the parameters for the temperature cycle. For the purposes of this tutorial, you will leave the default values but for a real calculation, you should be looking at performing at least 50,000 steps of equilibration dynamics.

Close the Forcite Anneal Dynamics dialog and click the **Run** button on the Forcite Calculation dialog.

The calculation should take a few minutes to run. When it is complete, you should have three structure documents:

- Layer.xsd - contains the structure from the final frame of the annealing calculation
- Layer_Anneal1.xtd - trajectory document with the lowest energy frame from each anneal cycle
- Layer.xtd - trajectory with all frames from the cycle

You will use Layer.xsd as the input to the confined shear calculations.

Select **File | Save Project** followed by **Window | Close All** from the menu bar. Re-open the annealed Layer.xsd.

6. To run the confined shear simulation and analyze the results

Before performing the confined shear run you should remove the constraints on the Fe atoms.

Select all the atoms in **Layer Forcite Anneal\Layer.xsd** and open the Edit Constraints dialog. On the **Atom** tab uncheck the **Fix Cartesian position** checkbox and close the dialog.

Now you can set up the confined shear simulation.

On the **Setup** tab of the Forcite Calculation dialog select **Confined Shear** from the **Task** dropdown list. Click the **More...** button to open the Forcite Confined Shear dialog.

Ensure that the **Wall velocity** is set to **0.05 Å/ps** and click the **More...** button to open the Forcite Dynamics dialog.

Change the **Number of steps** to **5000** and the **Frame output every** to **250**. Close the Forcite Confined Shear and Forcite Dynamics dialogs.

Note: If you run this tutorial with a simulation time of 250 ps, you will see the shearing of the polymer. This would run overnight on a standard PC.

You are now ready to run your simulation.

Click the **Run** button and close the dialog.

The confined shear job starts and a new folder, Layer Forcite ConfShear, opens.

When the calculation completes, the following documents are returned:

- Layer.xsd - structure document containing the final output structure
- Layer_Temperature.xcd - chart document showing change in temperature with time
- Layer_Wall_Stress.xcd - chart document showing change in stress along the walls with time
- Layer_Energies.xcd - chart document showing change in energy with time
- Layer.txt - summary of the calculation settings and results
- Status.txt - contains the live update status
- Layer.xtd - trajectory document containing frames snapshotting the progress of the shearing

You will analyze the changes in velocity in the z direction through the cell. This corresponds to the (0 0 1) h k l direction.

Double-click on **Layer.xtd** in the Layer Forcite ConfShear folder.

Select **Modules | Forcite | Analysis** from the menu bar to open the Forcite Analysis dialog. Choose **Velocity profile** from the list and select **FLUID** from the **Sets** dropdown list. Make sure that the **Flow direction** is set to **A** and click the **Analyze** button.

A chart document and study table document containing the velocity profile information are opened.

This chart document contains the FLUID (tridecane) component of the velocity profiled across the z direction. The chart is zero between 0 and 9.9 Å and over 36.2 Å, as these regions correspond to the walls of metal atoms (where there is no polymer). The polymer region lies between 9.9 and 36.2 Å, in this region the plot is noisy. A fully-equilibrated and well-averaged simulation run would show the velocity changing from a negative value at the bottom wall to a positive at the top wall.

A temperature profile can also give information about localized heating in the system.

On the Forcite Analysis dialog, choose **Temperature profile** and select **FLUID** from the **Sets** dropdown list. Check the **Specified direction (h k l)** checkbox and set the direction to **0 0 1**. Click the **Analyze** button.

A chart for the temperature profile across the cell is generated. In this example, you should see that the temperature is fairly constant with localized heating where chains are pulling across each other causing friction.

You also can calculate the concentration profile of the tridecane atoms to see how they vary across the cell.

On the Forcite Analysis dialog select **Concentration profile** from the list. Select **FLUID** from the **Sets** dropdown list. Check the **Specified direction (h k l)** checkbox and set the direction to **0 0 1**. Click the **Analyze** button.

This contains a plot of the concentration profile of the fluid in the x, y, and z directions. The z-direction plot shows that the confined fluid has a higher density close to the wall surfaces indicating that the wax is sticking to the Fe surface under shear.

You can also average the concentration profile over a number of frames. This enables you to look for time dependency of the profile.


Check **Frames to average** and set the value to **6**. Click the **Analyze** button and close the dialog.


A chart is generated with multiple lines where each line shows the averaged concentration profile. In this very short example, the concentration profile does not have time to vary dramatically.

A visual inspection of the trajectory also supports the view that the tridecane sticks to the walls.

Make the output **Layer.xtd** the active document and open the **Display Style** dialog. On the **Lattice** tab change the **Style** setting to **In-Cell** and close the dialog.

This changes the display so that all the atoms are translated into the cell.

Press the **UP** arrow key twice to realign the view. Click the **Animation Mode** arrow  on the **Animation** toolbar and select **Options** to open the Animation Options dialog. Check the **Recalculate atom visibility every frame** checkbox and close the dialog.

Click the **Play** button .

As the animation progresses, you should see the wax moving toward the metal walls.

Select **File | Save Project** from the menu bar.

This is the end of the tutorial.

Calculating the solvation free energy of propionic acid in *n*-octanol

Purpose: Introduces the use of Forcite to calculate the free energy of solvation.

Modules: Forcite Plus, COMPASS, Amorphous Cell

Time: 🕒🕒🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

The free energy to transfer a solute from its vapor phase to a solvent, or solvation free energy, is important for understanding a wide range of chemical and physical processes. For example, it determines the solubility, the amount that will solvate in the solvent when it is in contact with the solute vapor. Knowledge of the relative solubilities of a compound in two or more solvents is key to the design of a solvent extraction process, a major separation technology. The most widely used parameter for relative solubility is $\log P$, which quantifies the partitioning in water and *n*-octanol. A positive value of $\log P$ indicates that the solute preferentially solvates in *n*-octanol, typical for apolar compounds. $\log P$ is used extensively as a predictor of the degree of adsorption of drugs and the activity of agrochemicals and environmental toxins in the body.

The solvation free energy can be obtained directly from a simulation, using the thermodynamic integration method. In this method the interaction of the solute with the solvent is gradually increased from zero to full interaction (or vice versa), in a number of steps. For each coupling strength a simulation is performed and the derivative of the solvation free energy is calculated. Once all derivatives have been calculated, the free energy is obtained as the integral. Since each step requires a long simulation run (typically a few 100 ps), free energy calculations are computationally expensive.

In practice a solvation free energy calculation is carried out over three runs: starting from a solute molecule in vacuum, the charges are gradually reduced to zero, whilst keeping all other interactions the same. The free energy change in this process is called the ideal contribution. Then the chargeless molecule is coupled to the solvent by switching on the van der Waals interaction in a number of steps. The free energy change in this process is called the van der Waals contribution. Finally the charges are re-introduced on the solute molecule, which is now submerged in the solvent. The free energy of this step is the electrostatic contribution. The total solvation free energy then follows as the sum of ideal, van der Waals, and electrostatic contributions.

Introduction

This tutorial shows you how to perform a solvation free energy calculation. You will calculate the solvation free energy of propionic acid (also known as propanoic acid) in *n*-octanol. Propionic acid is a liquid fatty acid found naturally in sweat, in milk products, and as a product of bacterial fermentation. In the form of its propionates it is used as a mold inhibitor in bread and as an ingredient in perfume. You will calculate the solvation free energy in octanol. Combined with the experimental solvation free energy in water of -6.36 kcal/mol ([Wolfenden, 1981](#)), you will determine the $\log P$ value of propionic acid.

Note: Since the calculations in this tutorial require very long simulation runs, the output of a long production run is provided for comparison. The example project *SolvationFreeEnergy.stp* is located in the share\Examples\Projects\Forcite directory, from the top level of your Materials Studio installation.

For Windows users who are not administrators, you should copy the *SolvationFreeEnergy.stp* project and associated *SolvationFreeEnergy_Files* folder to a location where you have write permissions. Then open the new copy of the *SolvationFreeEnergy.stp* project.

This tutorial covers:

- [Getting started](#)
- [Sketching a molecule of propionic acid and n-octanol](#)
- [Constructing an amorphous cell of propionic acid in n-octanol](#)
- [Equilibrating the structure](#)
- [Running the solvation free energy calculation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

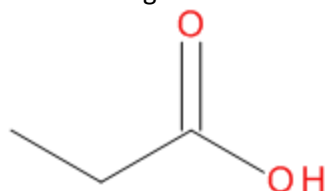
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **SolvationFreeEnergy** as the project name, click the **OK** button.

The new project is created with *SolvationFreeEnergy* listed in the Project Explorer.

2. Sketching a molecule of propionic acid and n-octanol

The first stage is to create a structure for propionic acid:



Select **File | New...** from the menu bar to open the New Document dialog. Select **3D Atomistic** and click the **OK** button.

Rename the new document **Propionic acid**.

Using the tools on the Sketch toolbar, draw a propionic acid molecule, ensuring that you adjust the hydrogens and clean the structure. Right-click in the document and select **Display Style** to open the Display Style dialog. On the **Atom** tab set the **Display style** to **CPK** and close the dialog.

To prepare the molecule for subsequent calculations you will optimize the geometry using charge groups. Once the charge groups are defined they will be available in subsequent calculations without the need to recalculate them.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog. Change the **Task** to **Geometry Optimization**.

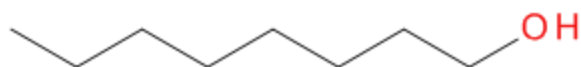
On the **Energy** tab select **COMPASS** from the **Forcefield** dropdown list. Ensure that **Charges** is set to **Forcefield assigned**. Set both the **Electrostatic** and **van der Waals** summation methods to **Group based**.

Click the **More...** button for **Forcefield** to open the Forcite Preparation Options dialog. Click the **More...** button for **Charge groups** to open the Forcite Charge Groups dialog. Set the **Method** to **Divide-and-conquer**. Close both dialogs.

Click the **Run** button to start the calculation.

A new folder, Propionic acid Forcite GeomOpt, is created in the Project Explorer. When the calculation is complete, the minimized structure is stored in the new folder. The output structure has COMPASS charges assigned and is divided into neutral charge groups. You can verify this by coloring the molecule by Charge Group, and labelling the atoms by Charge.

Use the same procedure for n-octanol:



Select the project root and create a new **3D Atomistic Document**, rename it **n-Octanol**.

Sketch an octanol molecule, leaving display style at default settings.

As before, perform a geometry optimization using charge groups. Since you use the same settings as above you can just press Run.

Ensure that **n-Octanol.xsd** is the active document, click the **Run** button on the Forcite Calculation dialog to start the calculation. Close the dialog.

A new folder, n-Octanol Forcite GeomOpt, is created in the Project Explorer, which will contain the optimized structure on completion, with charge groups assigned.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

3. Constructing an amorphous cell of propionic acid in n-octanol

Next you will create an input structure for the Solvation Free Energy calculation using the Amorphous Cell module. The structure will contain one molecule of propionic acid and several solvent molecules.

Select **Modules | Amorphous Cell | Calculation** from the menu bar to open the Amorphous Cell Calculation dialog.

In the **Composition** table, click in the **Molecule** column and select the optimized structure **Propionic acid.xsd** in the Propionic acid Forcite GeomOpt folder from the dropdown list. Ensure that the **Loading** is set to **1**.

Click on the next row and select the optimized structure **n-Octanol.xsd**. Set the **Loading** of n-Octanol to **100**.

The experimental density of octanol is 0.824 g/cm^3 . Construct the system at this density. The box length will be about 3 nm. Use the same energy settings in the Amorphous Cell calculation as you used in Forcite.

On the **Setup** tab, set the **Density** to **0.824**. Click the **Options...** button to open the Amorphous Cell Options dialog. Check the **Include non backbone torsions** checkbox and close the dialog.

On the **Energy** tab, select **COMPASS** from the **Forcefield** dropdown list. Set the **Electrostatic** summation method to **Group based**.

In the Project Explorer click on the tree root, then click the **Run** button to start the calculation. Close the dialog.

Note: Since valid charge groups are present on the input structures, Amorphous Cell will not recalculate them; it is not necessary to undo the automatic charge group calculation. Group based summation for van der Waals interaction is not available in Amorphous Cell and can be replaced by Atom based summation.

A new folder, Propionic acid AC Construct, is created in the Project Explorer, which will contain the solvated molecule structure in a trajectory document on completion. Amorphous Cell will always output a trajectory document, in case multiple frames are requested. In the following, however, it is more convenient to proceed with a structure document, so you will copy the structure over first.

Select the project root and create a new **3D Atomistic Document**, rename it **PA_nOct**.

Right-click in the Amorphous Cell structure **Propionic acid.xtd** and select **Copy**. Right-click in the new document **PA_nOct.xsd** and select **Paste**.

Before continuing, save and close all the open documents.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

4. Equilibrating the structure

Before you start the Solvation Free Energy calculation you should equilibrate the initial structure. The Amorphous Cell calculation will have performed a geometry optimization, but the structure may still contain stress points and density inhomogeneities that will need to be relaxed dynamically. Running dynamics with a thermostat is a way to remove the excess heat from the system. The NHL thermostat is a good thermostat for both equilibration and production runs.

Make sure **PA_nOct.xsd** is the active document. Open the **Forcite Calculation** dialog and set the **Task** to **Dynamics**, click the **More...** button to open the Forcite Dynamics dialog.

Set **Ensemble** to **NVT**. Set **Total simulation time** to **10** ps. On the **Thermostat** tab, select **NHL** for **Thermostat** and set **Q ratio** to **1.0**. Close the dialog.

Note: The default *Q ratio* of 0.01 is chosen such that the temperature oscillations that can occur with the Nosé thermostat are damped, allowing faster equilibration. The NHL thermostat is an extension of the Nosé thermostat, with its own damping mechanism. This means you can use a higher *Q ratio* with NHL. For a *Q ratio* of 1 the impact of the thermostat is sufficiently weak that you can use the same value in both equilibration and production runs.

On the **Energy** tab, set both the **Electrostatic** and **van der Waals** summation methods to **Group based**.

Click the **Run** button to start the calculation and close the dialog.

A new folder **PA_nOct Forcite Dynamics** is created in the Project Explorer. Chart and status text documents will appear shortly, recording the progress of the calculation. The equilibration may take a few minutes to complete, depending on the speed of your computer.

Tip: You can speed up the calculation by running the dynamics calculation in parallel, where multiple cores and licenses are available.

In a real calculation you would equilibrate for much longer, say 100 ps, followed by an equilibration with a barostat of about the same time to adjust the cell dimensions.

Note: If you want to continue with the next step without waiting for the equilibration run to complete, you can import a prepared structure from the Examples folder, found in the project **Examples\Projects\Forcite\SolvationFreeEnergy.stp**. This structure was equilibrated with 100 ps NVT dynamics, followed by 100 ps NPT dynamics. Results may differ depending on which structure you continue from.

Before continuing, save all open documents and clear the work space.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

5. Running the solvation free energy calculation

Continue the calculation with the final structure of the equilibration run, as found in the **PA_nOct Forcite Dynamics** folder (or the equivalent structure from the Examples folder).

Open the *3D Atomistic* document (not the trajectory) in the Forcite dynamics folder, **PA_nOct.xsd**.

This 3D Atomistic document contains the final structure from the dynamics calculation.

Select **Modules | Forcite | Calculation** to open the Forcite Calculation dialog. Set the **Task** to **Solvation Free Energy** and click the **More...** button to open the Forcite Solvation Free Energy dialog.

As mentioned in the introduction, the total solvation free energy is calculated as the sum of three contributions: *Ideal*, *van der Waals*, and *Electrostatic*. Each contribution requires a separate Solvation Free Energy calculation. You can use the same input structure for all contributions, and run the

calculations in any order. It is also possible to run all three contributions in a single calculation, which performs a sequence using the same settings in all runs.

In this tutorial you will run through the individual contributions one-by-one, starting with the Ideal contribution. You will use the default Thermodynamic integration algorithm throughout. To speed up the calculations in the tutorial you will reduce the number of time steps to 1000 for equilibration, and 5000 for production. In a real simulation you would run much longer. The simulation in the Examples folder was run with 50000 steps equilibration and 100000 steps production. You will run the coupling parameter from 0 to 1, which means that the charges will be decreased from full COMPASS charges to zero. You can also run the coupling parameter in the reverse direction, and the result should be the same, on average. For the Ideal contribution you may decrease the number of coupling parameter steps.

Set the **Contribution** to **Ideal**. Set the **Equilibration steps** to **1000** and the **Production steps** to **5000**. Set the Coupling parameter **Steps** to **5**.

The Dynamics and Geometry Optimization settings, as well as the Energy tab settings, may be left at their current values, that is those used in the previous steps in this tutorial. Before running the calculation you should specify which molecule in the structure is the solute molecule, by creating a set.

In the structure double-click on any atom in the solute molecule to select the molecule. Click the **Add** button to create a set called *SoluteAtoms*.

Click the **Run** button to start the calculation.

A new folder `PA_nOct Forcite FreeEnergy` is created inside the Dynamics folder. After a short while a status text document will appear, recording the progress of the calculation. The calculation of the Ideal contribution only takes a few minutes to complete, since it involves just a single molecule in an empty box. On completion a report document, a chart document, and a study table document are returned.

Open the report document `PA_nOct.txt` and scroll down to the section containing the solvation free energy results.

The Ideal contribution of the Solvation free energy of propionic acid should be about 25.5 kcal/mol. Since this is the free energy cost of removing charges on the molecule, it will be close to minus the electrostatic energy of the optimized structure, as calculated above. You can verify this by looking up the electrostatic energy in the report document of the geometry optimization run of propionic acid (around -26.2 kcal/mol).

Note: The free energy values quoted in this tutorial are taken from a much longer run, available in the Examples folder. As the simulations in this tutorial are much shorter, your results may be different.

The solvation free energy is determined by integrating the free energy derivatives as calculated in the simulation. The integral as a function of the coupling parameter is shown in the chart.

Open the chart document `PA_nOct FreeEnergy.xcd`. Confirm that the value at coupling parameter 1 matches the reported solvation free energy.

The data in the chart is also contained in the study table document, in the column $A(\lambda)$. The actual free energy derivate values are contained in the column labelled $\langle d E/d \lambda \rangle$.

Open the study table document **PA_nOct.std**. Select the first column by clicking on the header **A**. Hold down the **CTRL** key and click header **D** to select the fourth column. Click the **Quick Plot** button



You should see a straight line from a value of about 50 kcal/mol to 0 at coupling parameter 1. The free energy corresponds to the area under the line, which in this case is simply half the initial value.

Before proceeding with the other contributions, save all open documents and clear the work space.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

Continue with the Electrostatic contribution to the Solvation free energy. As the free energy derivative for electrostatics will be approximately linear, you can use the same number of coupling parameter steps as for the Ideal contribution.

Open the same input structure document as used in the previous step, **PA_nOct.xsd**.

On the Forcite Solvation Free Energy dialog, set **Contribution** to **Electrostatic**.

Click the **Run** button to start the calculation.

A new folder **PA_nOct Forcite FreeEnergy (2)** is created in the Dynamics folder. After a short while a status text document will appear recording the progress of the calculation. The calculation of the Electrostatic contribution takes much longer, since it involves all molecules in the system.

Note: The Progress as reported in the Job Explorer is that of individual dynamics runs, rather than the complete Solvation Free Energy run. After each equilibration or production run, this progress is reset to 0.

Tip: Each contribution in the free energy of solvation calculation is independent. Providing that you have the appropriate licenses and CPUs available these can be run simultaneously.

As before, on completion report, chart and study table documents are returned. The Electrostatic contribution can be found in the report document.

Open the report document **PA_nOct.txt** and scroll down to the section containing the solvation free energy data.

The Electrostatic contribution for propionic acid in octanol will be about -29.4 kcal/mol, close to the Ideal contribution, and close to the electrostatic energy of an optimized molecule. The sum of the Ideal and the Electrostatic contribution is about -3.9 kcal/mol, indicating that about 3.9 kcal/mol is stored in the electrostatic interaction between propionic acid and n-octanol.

Note: The free energy values quoted in this tutorial are taken from a much longer run, available in the Examples folder. As the simulations in this tutorial are much shorter, your results may be different.

Before proceeding with the final contribution, save all open documents and clear the work space.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

The van der Waals contribution is the most difficult to determine since the free energy derivative is non-linear. This means you need to have sufficient number of coupling parameter steps to capture the

curvature. You can use the same number of equilibration and production steps as for the Electrostatic contribution, but increase number of coupling parameter steps.

Open the same input structure document as used in the previous step, **PA_nOct.xsd**.

On the Forcite Solvation Free Energy dialog, set **Contribution** to **van der Waals**. Set the number of Coupling parameter **Steps** to **10** and close the dialog.

Click the **Run** button to start the calculation and close the dialog.

A new folder PA_nOct Forcite FreeEnergy (3) is created in the Project Explorer. Since you have used twice as many steps as for the Electrostatic contribution, this run will take about twice as long.

On completion, open the resulting chart document.

Open the chart document **PA_nOct FreeEnergy.xcd**.

Note how the free energy as a function of the coupling parameter is non-monotonous. After an initial dip the free energy becomes positive, indicating the cost to create a cavity in the octanol solvent. Once a cavity is created, the attractive dispersion interaction with the solvent dominates, and the free energy turns negative. The final value should be negative, and about -2.8 kcal/mol.

Open the text document **PA_nOct.txt** and confirm that the van der Waals contribution to the solvation free energy is about -3 kcal/mol.

You should now have obtained all contributions to the solvation free energy.

The total sum is:

$$25.5 - 29.4 - 2.8 = -6.7 \text{ kcal/mol}$$

Tip: You can run all contributions in a single calculation by selecting **All** for Contribution. The calculation provided in the Examples folder was run this way. In such a calculation, all graphs are returned in a single chart document. A single study table is returned with separate data sheets for each contribution.

Finally, to calculate $\log P$ for propionic acid, you could repeat a calculation using water as solvent, instead of octanol. Here we shall use the experimental hydration free energy of propionic acid of -6.36 kcal/mol ([Wolfenden, 1981](#)). Since this value is slightly less negative than the calculated value for octanol, propionic acid is predicted to be more soluble in octanol, and $\log P$ is expected to be positive.

$\log P$ is obtained by the equation:

$$\log P = 0.434 (A[\text{water}] - A[\text{octanol}]) / RT$$

Where 0.434 corresponds to $^{10}\log e$, R is the gas constant ($1.987 \cdot 10^{-3}$ kcal/mol/K), T the temperature in the simulation (298 K), and $A[x]$ the solvation free energy in solvent x . Substituting the above data gives $\log P = 0.25$, in excellent agreement with the experimental value of 0.246 ([Vitas-M Lab](#)).

Select **File | Save Project** from the menu bar.

This is the end of the tutorial.

References

Wolfenden, R.; Andersson, L.; Cullis, P. M.; Southgate, C. C. B., "Affinities of amino acid side chains for solvent water", *Biochemistry*, **20**(4), 849–855 (1981).

Log *P* data obtained from Vitas-M Lab (ID: STL168039),
<http://www.vitasmlab.com/userfiles/sdf2/stl168039.sdf>.

GULP tutorials

The following tutorial illustrates how to utilize GULP's capabilities.

- [Calculating the properties of diamond](#)
- [Forcefield fitting with GULP: SnO₂ library derivation](#)

Calculating the properties of diamond

Purpose: Introduces the GULP module for calculating the properties of ionic materials and molecular solids.

Modules: Materials Visualizer, GULP

Time: 

Prerequisites: Sketching simple molecules, Docking molecules onto surfaces Visualizer Tutorial

Introduction

Typically, classical simulations techniques in Materials Studio have concentrated on simulating condensed phases of liquids or soft materials and molecular structures. GULP provides tools that allow the simulation of ionic materials and molecular solids, previously the domain of computationally expensive quantum mechanics calculations. GULP includes 2D surface and molecular calculations besides its traditional 3D crystal structures.

This tutorial will take you through a simple calculation of the mechanical properties of diamond using GULP. You will then create a surface of diamond and calculate the surface energy.

This tutorial covers:

- [Getting started](#)
- [To optimize and predict mechanical properties](#)
- [To calculate the surface energy of diamond](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **diamond** as the project name, click the **OK** button.

The new project is created with *diamond* listed in the Project Explorer. You will load the crystal structure of the system you will be studying. In this tutorial, you will be working with diamond.

Click the **Import** button  on the toolbar to open the Import Document dialog. Navigate to **Examples\Documents\3D Model** and double-click on **C.msi**.


You should change the symmetry of diamond to P1.

On the menu bar, select **Build | Symmetry | Make P1**.

For many simulations, it is necessary to convert a higher symmetry crystal structure to P1 symmetry. For example, during a molecular dynamics simulation when the atoms will move away from their equilibrium positions and the intermediate positions will not satisfy the symmetry constraints of the higher symmetry space group. The use of P1 symmetry in this tutorial allows to generate elastic constants for the same orientation as was used in the Brenner et al. (2002) paper.

2. To optimize and predict mechanical properties

Now you are ready to optimize the structure. This will be a very quick calculation as the structure you loaded has been previously optimized.

Click the **GULP** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the GULP Calculation dialog with several task options available. You will carry out a geometry optimization.

Change the **Task** to **Geometry Optimization**.

GULP has many different forcefield libraries which use a variety of techniques from two-body interactions to many-body interactions. As you are working with diamond, you will use the [Brenner](#) potential for the calculations. The Brenner potential is a bond order potential that can be applied to systems containing carbon, hydrogen and oxygen. It has seen much use in simulating structures such as diamond and carbon nanotubes.

Select **Brenner** from the **Forcefield** dropdown list and click the **View...** button.

The forcefield libraries are stored as text files and you can view them to see information such as references and charges.

Close the **GULP Forcefield Library: Brenner** view.

A variety of properties can be obtained from GULP energy calculations.

Select the **Properties** tab

You will see several properties available. These are all very quick to calculate on a small system like the diamond unit cell so you can leave these all checked on.

Click the **Run** button. Close the GULP Calculation dialog.

When the job has completed a new folder, called C GULP GeomOpt, contains the following files:

- C.xsd is the optimized structure. Because phonon properties are obtained during the frequency calculation this display includes the reciprocal lattice and Brillouin zone and path.
- C.xtd contains frames showing the structure after each optimization step.
- C.gin is a text document containing the GULP input file.
- C.gout is a text document containing the GULP output.

Open **C.gout**. Press the **CTRL + F** keys and find **Elastic Constant**.

Compare the C11, C12, and C44 values in GPa with those published by Brenner et al. (2002). To convert GPa to Mbar, simply divide the value in GPa by 100.

	Brenner (in Mbar)	GULP (in Mbar)
C11	10.7	10.74
C12	1.0	1.25
C44	6.8	7.21

3. To calculate the surface energy of diamond 111 surface

The surface energy can be calculated using the following equation:

$$\Delta U_{SE} = \frac{U_{surf} - U_{bulk}}{A}$$

where U_{surf} is the energy of the surface, U_{bulk} is the energy of the bulk system and A is the surface area. You already have the energy of bulk diamond from your previous calculation but this will have to be normalized by the number of atoms in the cell.

In **C.gout**, search for **Total Lattice Energy** and write down the value in eV.

This should be equal to -58.9507 eV. As you will have more atoms in the surface than the crystal, you will have to scale the bulk energy to match.

Change focus to the optimized **C.xsd**. In the **Properties Explorer**, change the **Filter** to **Symmetry System**. and note the **NumberOfAtoms**.


Now you can build the surface.

Select **Build | Surfaces | Cleave surface** from the menu bar to open the Cleave Surface dialog. Change the **Cleave plane** to **1 1 1** and the **Fractional Thickness** to **4.0**. Click the **Cleave** button and close the dialog.

A new structure, **C (1 1 1).xsd** is created. You should optimize this with the same settings as before.

Open the **GULP Calculation** dialog and click the **Run** button. Close the dialog.

As you are studying a larger system, the calculation will take longer than previously. When the calculation has finished, you can examine the output files.

Open **C (1 1 1).xtd** and click the **Play** button  on the **Animation** toolbar.

You will see that the atoms in the surface change their positions slightly.

In the **Properties Explorer**, change the **Filter** to **Lattice 2D**. Click the **Step Forward** button on the **Animation** toolbar to examine the individual frames.

You will see that the surface area changes slightly as well.

Note down the **CellArea** for the last frame of the trajectory. Change the **Filter** to **Symmetry System** and note down the **NumberOfAtoms**.

The surface area should be approximately 22.475 Å². The final piece of information you need is the energy of the surface structure.

Open **C (1 1 1).gout**. Search for **Total Lattice Energy**. Note down the value in eV for the optimized geometry.

The geometry optimized lattice energy for the surface is -221.201 eV. You can now calculate the surface energy. Remember to scale the bulk energy by the ratio of the number of atoms in the surface to the number of atoms in the bulk.

This is the end of the tutorial.

References

Donald W Brenner, Olga A Shenderova, Judith A Harrison, Steven J Stuart, Boris Ni and Susan B Sinnott, *J. Phys.: Condens. Matter* 2002, **14**, 783.

Forcefield fitting with GULP: SnO₂ library derivation

Purpose: Explains how to use the Forcefield fitting task in GULP to obtain new potential parameters or to refine the existing ones.

Modules: Materials Visualizer, GULP

Time: 🕒 🕒

Prerequisites: none

Introduction

The current libraries in GULP do not have parameters to describe the SnO₂ bulk structure. Therefore, to be able to model this material and to calculate its different properties with GULP, new forcefield parameters have to be derived. The Forcefield fitting task in GULP can be used to obtain those. The bulk modulus, some elastic constants and the experimental structure of SnO₂, have been used as observables in the forcefield fitting procedure.

This tutorial covers:

- [Getting started](#)
- [To define the forcefield types and functional forms](#)
- [To define the observables used in the fitting](#)
- [Fitting procedure](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.


Open the **New Project** dialog and enter **ff_library** as the project name, click the **OK** button.

The new project is created with *ff_library* listed in the Project Explorer. You will load the crystal structure of the system you will be studying later.

2. To define the forcefield types and functional forms


The first step when performing a forcefield fitting task is to define the forcefield types and functional forms that describe the different interactions in the system. For the case under consideration, you need to define Buckingham parameters for the O-O, Sn-O and Sn-Sn two body terms.

When creating a new library you can proceed in two different ways, you can create a new library file (.lib) from scratch or you can modify an existing one. In this tutorial you will create a new library from scratch for the SnO₂ case. A library is just a text document, so you must open a text document.

Click the **New** button  on the toolbar and select **Text Document** from the dropdown list. **Rename** the new text file to **SnO2.lib**.

You will be prompted that changing the extension may make the file unusable.

Click the **Yes** button to change the file extension.

Click the **GULP** button  on the **Modules** toolbar and choose **Calculation** from the dropdown list.

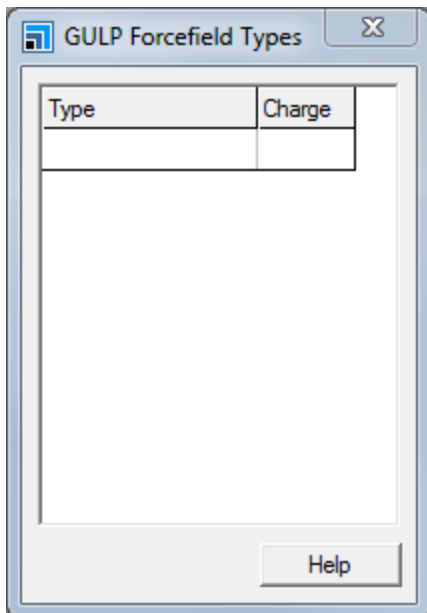
This opens the GULP Calculation dialog.

Change the **Task** to **Fit Forcefield**. Select **Browse...** from the **Forcefield** dropdown list to open the Choose GULP Forcefield dialog, then choose **SnO2.lib** from the dropdown list. Change the **Charges** to **Forcefield assigned** and click the **More...** button.

This opens the GULP Fit Forcefield dialog, before entering the potentials parameters, the atom types should be defined.

Click the **Types...** button.

This opens the GULP Forcefield Types dialog which lists atom types and charge definitions.

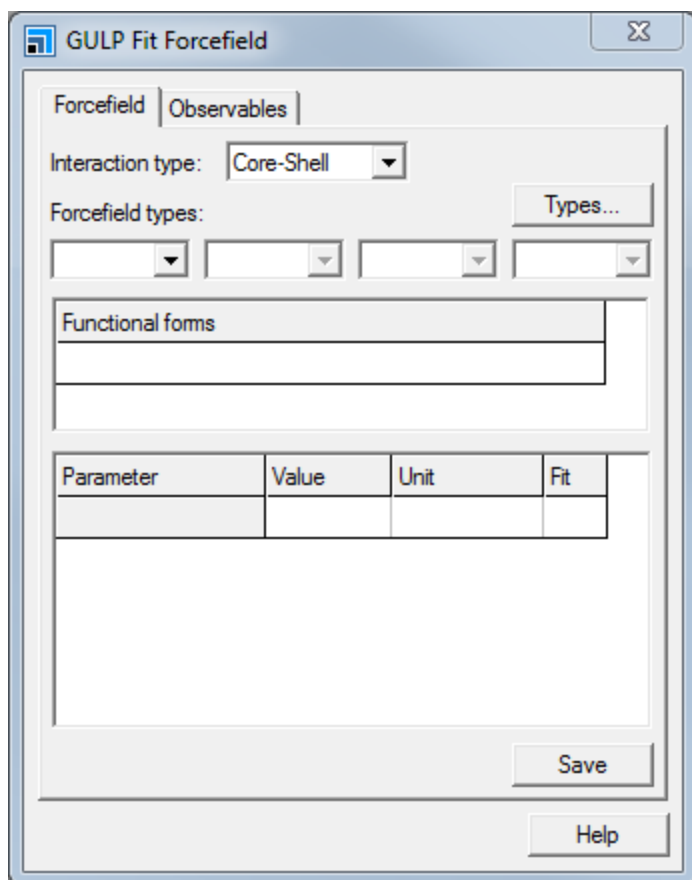


GULP Forcefield Types dialog

You are going to add two new atom types, Sn core and O core, with appropriate charges.

In the **Type** box enter **O core** and in the **Charge** box enter **-1.025**. On the next line, enter **Sn core** and **2.050**. Close the **GULP Forcefield Types** dialog.

You can now define the potential parameters on the GULP Fit Forcefield dialog.



GULP Fit Forcefield dialog, Forcefield tab

You need to define the functional form for each combination of potentials, O core - O core, Sn core - Sn core, and Sn core - O core.

Change the **Interaction type** to **Two-body**. In the **Forcefield types** section select **O core** as the first forcefield type and **O core** also for the second. In the **Functional forms** section, select **Buckingham (buck)** from the dropdown list.

Repeat this for the **O core - Sn core** and **Sn core - Sn core** combinations.

Next, you need to enter the following parameters for each case (these initial values are taken from *Bandura et al. J. Phys. Chem. B 2006, 110, 8386-8397*):

Potential Pair	A (eV)	rho (Å)	C (eV*Å ⁶)	rmax (Å)
O core - O core	5000	0.273	48.7	15.0
O core - Sn core	100000	0.169	16.0	15.0
Sn core - Sn core	1000000	0.205	6.3	15.0

Change the **Forcefield types** back to **O core** and **O core**. Choose the **Buckingham(buck)** functional form. Scroll down the **Parameter** box and enter the values for the parameters as listed above. Repeat this for **O core - Sn core** and **Sn core - Sn core**.

Initially you will only fit the A parameters for the three two-body terms. You will then use the obtained A parameters to fit the rho parameters, and finally those to fit the C ones. You need to indicate that the A parameters are the ones you want to fit.

For each pair potential, in the **Fit** column check the corresponding box for the Buckingham **A parameter**.

Click the **Save** button.

A new `.lib` file (`SnO2_2.lib`) with all the defined atom types and parameters is created, containing:

```
species
Sn core 2.05
O core -1.025

buck 1
Sn core Sn core 1000000.0000000000 0.2050000000 6.3000000000 &
  0.0000000000 15.0000000000 1 0 0
Sn core O core 100000.0000000000 0.1690000000 16.0000000000 &
  0.0000000000 15.0000000000 1 0 0
O core O core 5000.0000000000 0.2730000000 48.7000000000 0.0000000000 &
  15.0000000000 1 0 0
```


Close the **GULP Fit Forcefield** dialog.

3. To define the observables used in the fitting

To obtain the Buckingham parameters for the SnO_2 library, the following observables have been used in the fitting:

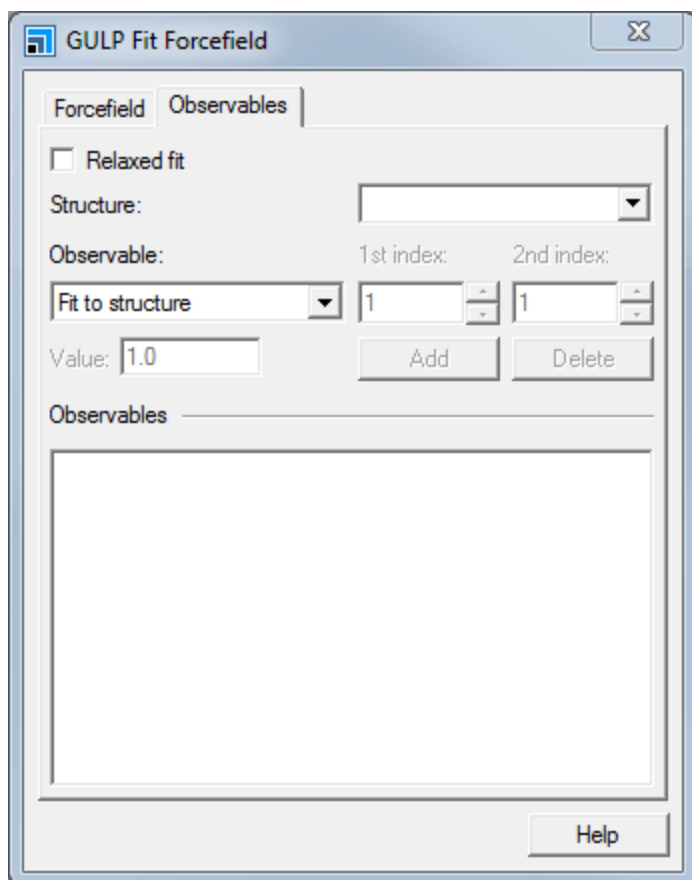
1. Experimental SnO_2 structure
2. Experimental bulk modulus: 212.3 GPa
3. Experimental elastic constants: $C_{11} = 261.7$, $C_{33} = 449.6$, $C_{44} = 103.1$, and $C_{66} = 207.4$ GPa.

Before defining all the above observables in the GULP Fit Forcefield dialog, you need to open the SnO_2 structure.

Click the **Import** button  on the toolbar to open the Import Document dialog. Navigate to the **Structures\metal-oxides** folder and double-click on **SnO2.msi**.

Once you have imported the structure, you can proceed to define all the observables in the dialog.

On the **GULP Calculation** dialog, check that the **Forcefield** is `\SnO2_2`. Open the **GULP Fit Forcefield** dialog and select the **Observables** tab.



GULP Fit Forcefield dialog, Observables tab

You will perform a relaxed fitting to obtain the SnO_2 library. The relaxed fit option fits to structural displacements on relaxation rather than to the derivatives. This also means any observables are fitted to the optimized rather than experimental structure.

Check the **Relaxed fit** checkbox. Select **SnO2.xsd** from the **Structure** dropdown list. To define the experimental structure as observable select **Fit to structure** from the **Observable** dropdown list.

As you want to fit to the structure, you need to add it to the observables.

Click the **Add** button.

The SnO_2 structure will appear in the Observables list on the GULP Fit Forcefield dialog. Now you will add the other observables that you want to fit to.

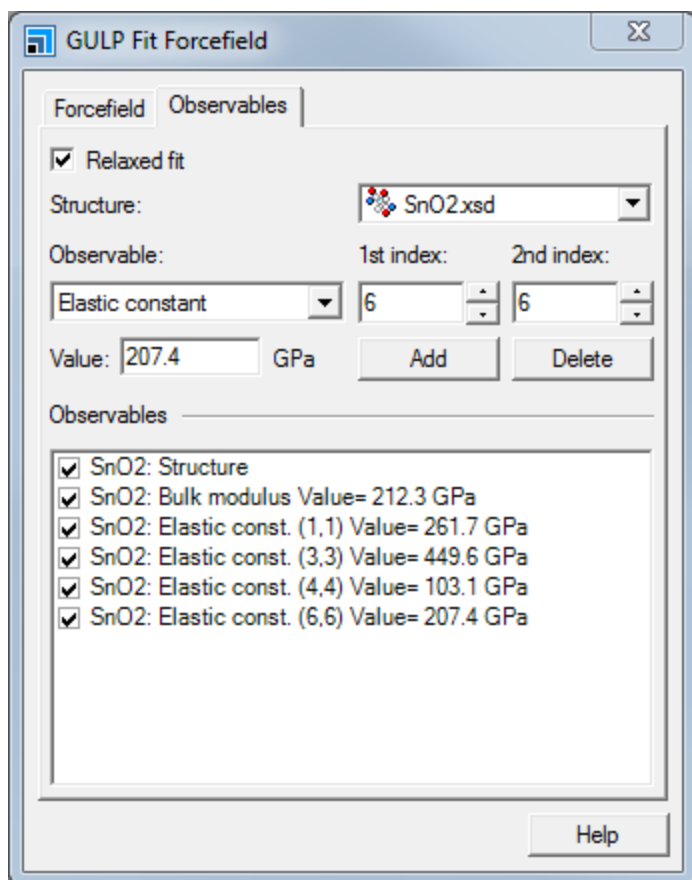
Change the **Observable** to **Bulk modulus**. Set the **Value** to **212.3** and click the **Add** button.

Change the **Observable** to **Elastic constant**. Ensure that the **1st Index** is set to **1** and the **2nd Index** is set to **1**. Set the **Value** to **261.7**. Click the **Add** button. Repeat this for:

1st Index = 3, 2nd Index = 3 and Value = 449.6

1st Index = 4, 2nd Index = 4 and Value = 103.1

1st Index = 6, 2nd Index = 6 and Value = 207.4.



GULP Fit Forcefield dialog Observables tab with values set as required

Close the **GULP Fit Forcefield** dialog and leave the GULP Calculation dialog open.

4. Fitting procedure

Now that the functional forms and observables have been defined, you can run the fitting calculation.

Click the **Run** button on the **GULP Calculation** dialog.

When the calculation is finished, the results of the fitting can be found in the `.gout` file. The new library is returned in the `.lib` file.

Open the GULP output file, **SnO2_2.gout**.

Tip: The contents of your output file may vary from this example.

In the `.gout` calculation you will find the new A parameters and also the value of the sum of squares, which gives an indication about the quality of the fitting, for example:

```
**** Fit completed successfully ****
```

```
Final sum of squares =      4.302300
```

```
Final gradient norm  =      0.000286
```

Final values of parameters :

Parameter No.	Parameter Original	Parameter Final	Parameter Type	Species
1	1000000.000000	404423.175101	Buckingham A	
2	100000.000000	88619.438577	Buckingham A	
3	5000.000000	4053.048025	Buckingham A	

Final values of numerical parameter gradients :

Parameter No.	Parameter Gradient	Parameter Type	Species
1	-0.000013	Buckingham A	
2	-0.000182	Buckingham A	
3	-0.000220	Buckingham A	

Final values of residuals :

Observable no.	Type	Observable	Calculated	Residual	Error(%)
1	Bulk modulus	212.30000	211.95855	0.11659	-
2	Elastic Const	261.70000	268.06136	0.40467	-
3	Elastic Const	449.60000	448.42642	0.01377	-
4	Elastic Const	103.10000	97.62695	0.29954	-
5	Elastic Const	207.40000	203.19004	0.17724	-
6	Structure	4.73727	4.68035	3.24018	-

1.202	7	Structure	3.18638	3.18995	0.01269	
0.112	8	Structure	0.30700	0.30506	0.03762	-
0.632						

 Comparison of initial and final observables :

Observable no.	Type	Observable	Initial	Final
1	Bulk modulus	212.30000	198.30781	211.95855
2	Elastic Const	261.70000	255.18258	268.06136
3	Elastic Const	449.60000	457.46019	448.42642
4	Elastic Const	103.10000	97.16571	97.62695
5	Elastic Const	207.40000	188.18899	203.19004
6	Structure	4.73727	4.76579	4.68035
7	Structure	3.18638	3.27295	3.18995
8	Structure	0.30700	0.30498	0.30506

The .lib document will also be updated with the optimized value of A.

Open **SnO2_2 GULP Fit\SnO2_2.lib**.

The value for A has changed from 5000 to 4053.048.

As stated above, you will use the results obtained here for the A parameters to fit the rho parameters, and then again to obtain the C parameters. To this end, you need to modify the .lib file used in the calculation, you should define the parameters obtained here as new values for the calculation and indicate which parameters you want to fit.

Open the **GULP Calculation** dialog. Select **Browse...** from the **Forcefield** dropdown list to open the **Choose GULP Forcefield** dialog. Select the **SnO2_2.lib** document in the **SnO2_2 GULP Fit** folder.

The new forcefield document is imported.

Open the **GULP Fit Forcefield** dialog and check that the **Forcefield types** are **O core** and **O core**. Scroll down to the fitted parameters.

The value for A has been updated to 4053.

Note: The value for your forcefield may not be exactly the same as this example due to minor differences in calculations, this is expected.

Check the **Fit** checkbox for the **rho** parameter. Repeat this for the **O core - Sn core** and **Sn core - Sn core** pair potentials. Click the **Save** button.

A new forcefield, SnO2_2 GULP Fit\SnO2.lib, is created.

On the **GULP Calculation** dialog, change the **Forcefield** to **SnO2_2 GULP Fit\SnO2.lib** and click the **Run** button.

Once the calculation is complete, you need to fit for C.

Repeat the last few steps, opening the newly optimized forcefield and fitting for C.

The final library obtained for SnO₂ after fitting A, rho and C, is:

species

O core -1.025

Sn core 2.05

keyword

buck 1

O core O core 4053.0480000000 0.2729750000 43.4236690000 0.0000000000 &
15.0000000000 0 0 0

O core Sn core 88619.4390000000 0.1689920000 16.2778010000 & 0.0000000000
15.0000000000 0 0 0

Sn core Sn core 404423.1800000000 0.2049250000 39.3054100000 & 0.0000000000
15.0000000000 0 0 0

This is the end of the tutorial.

Kinetix tutorials

The following tutorials illustrate how to utilize Kinetix's capabilities.

- [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#)
- [Multi-site modeling of CO oxidation on a Pt\(1 1 1\) surface](#)

Simple modeling of CO oxidation on a Pt(1 1 1) surface

Purpose: Introduces the Kinetix module for setting up a simple kinetic Monte Carlo simulation.

Modules: Materials Visualizer, Kinetix

Time: 🕒🕒🕒

Prerequisites: None

Background

Kinetic Monte Carlo (kMC) simulation, in the Kinetix module, is a method that studies the kinetics at a surface. It is characterized by atomic scale spatial resolution and time scale comparable to laboratory kinetic experiments. It can simulate systems over long times (about nine orders of magnitude longer than molecular dynamics) because it only simulates the reactions of the atoms and molecules in the system. Kinetix module uses the CARLOS program (<http://www.win.tue.nl/~johanl/projects/nCarlos>) developed at Eindhoven Technical University to carry out the simulation.

The precise positions of atoms and molecules and their velocities are not included in Kinetix simulations. The configuration of a system is assumed to be near a particular minimum of its potential energy surface. A consequence is that the exact time that reactions occur and which reactions occur is not determined. Instead probability distributions for these times and reactions are generated.

Introduction

A complete kMC simulation needs a complex specification, with many different reactions specified, each of which requiring detailed knowledge of reaction probabilities.

In this tutorial you will set up the processes involved in a simple oxidation/reduction (ORR or redox) reaction, specifically CO oxidation on a Pt(1 1 1) surface, using a simplified set of processes to model the reactions. This is similar to the model described by [Ziff et al., 1986](#) for the oxidation of CO on a Pt(100) lattice, referred to as the ZGB model.

The minimum set of processes consists of: CO adsorption, dissociative O₂ adsorption, CO₂ formation, and CO₂ desorption. The last two processes can be combined to give:

- CO(gas) → CO(ads)
- O₂(gas) → 2O(ads)
- CO(ads) + O(ads) → CO₂(gas)

Although more complete modeling of the reactions would involve other processes such as diffusion and O₂ desorption this tutorial will be restricted to just these three processes. Later in the tutorial further processes will be added to make the simulation more realistic.

Kinetix uses two document types specific to this type of simulation. A Processes document contains the specifications of the lattice and species involved in a simulation and the reactions and other processes

that can occur during a simulation. A Configuration document contains the description of the specific configuration(s) of species on the simulation grid. The simulation acts on the configuration document using the details in the processes document to determine how the configuration should evolve over time.

The following steps will be covered here:

- [Getting started](#)
- [Specifying the processes](#)
- [Creating an initial configuration](#)
- [Running a Kinetix simulation](#)
- [Analyzing the results of a Kinetix simulation](#)
- [Adding further processes](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ORR_simple** as the project name, click the **OK** button.

The new project is created with *ORR_simple* listed in the Project Explorer. You will create a basic processes document describing the simulation lattice and the species that will be involved in the simulation.

Click the **Kinetix** button  on the **Modules** toolbar and select **Process Builder** from the dropdown list to open the Kinetix Process Builder dialog.

This can be used to specify the geometry of the lattice on which the simulation will be performed. You will be working with a hexagonal lattice and because you will be using only one lattice site per cell, you should set the symmetry to the maximum possible. The lattice dimension corresponds to the distance between the metal atoms in a Pt crystal, or more specifically in the (1 1 1) surface cleaved from such a crystal.

Enter **Hexagonal ZGB model** in the **Description** text box. Set the **Type** for the lattice to **Hexagonal**, the **Symmetry** to **p 6 m m**, and the **Length** to **2.77 Å**. Click the **Create** button and close the dialog.

This will create a new Processes document which you will use to specify the species and the processes involved in the simulation.

In the **Project Explorer**, right-click on **KinetixProcesses.xkp** and select **Rename** from the shortcut menu. Change the name to **ZGBProcesses.xkp**.

You will now specify the species that will be used in the simulation. Note that there is always a definition corresponding to a vacancy (a lack of any species at a specific site). By default this has the symbol **V**.

Select the **Species** tab, enter **CO** in the first empty cell in the **Name** column and press the TAB key. Enter **O** in the next row and press the TAB key.

The default properties (radius, charge, and color) of the species will suffice for this tutorial, although they can be changed later if desired.

2. Specifying the processes

Kinetix does not take the gas phase into account so the exact processes [above](#) cannot be used. A Kinetix simulation models the changes at a particular site or sites in a configuration, accounting for the species populating the site(s) before and after the process. The absence of any species at a site is described as a vacancy, indicated by the symbol **V**. The ORR processes can be represented as:

- $V \rightarrow CO$
- $2V \rightarrow 2O$
- $CO + O \rightarrow 2V$

This description does not consider CO_2 as it is implicit in the last process. Because the model combines the CO_2 formation and its immediate desorption it is not explicit.

For each process you will define the reaction and sites involved, together with the details of the rates of the reactions. Reaction rates can be specified explicitly or using an Arrhenius expression. In this tutorial you will specify the reaction rates explicitly.

First specify the CO adsorption process.

Select the **Processes** tab of **ZGBProcesses**. Ensure that the **process of type** is set to **Adsorption** and click the **Add** button.

A new process, named *NewProcess* will be added to the list and the *Process Details* tab provides further options.

Enter **COAds** as the **Identifier** and **CO adsorption** as the **Description**.

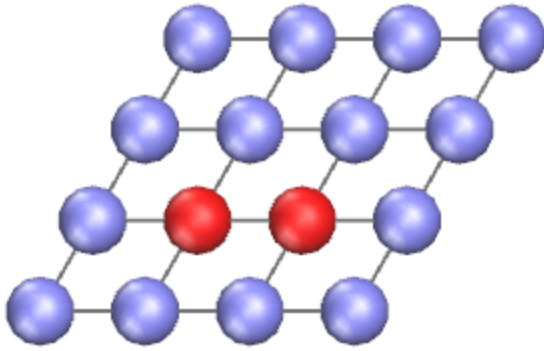
Change the **Specification type** to **Rates** and set the **Rate coefficient** to **0.55**. On the **Process Sites** tab select **CO** from the **Adsorbate(s)** dropdown list.

Next you will specify the O_2 adsorption process. This is different from the CO adsorption process, it is a dissociative process where the O_2 molecule creates two separate O species when it is adsorbed.

On the **Processes** tab click the **Add** button to create a new process.

On the **Process Details** tab enter **O2Ads** as the **Identifier** and **O2 adsorption** as the **Description**. Change the **Specification type** to **Rates** and set the **Rate coefficient** to **0.15**.

On the **Process Sites** tab check the **Dissociative adsorption** checkbox. Select the **Site View** tab to review the site set up:



Site view showing dissociative adsorption process

This is a view of the sites used in the specification of the current process, and the role that each site plays in the process. The red color indicates that the specification is incomplete or incorrect for that site. In the current situation this is because you have not yet specified the species involved in this adsorption process.

On the **Process Sites** tab select **O** from the **Adsorbate(s)** dropdown lists.

On the *Site View* tab the colors of the sites will change from red to white when the adsorbate is specified.

Right-click in the **Site View** and select **Site View Colors** from the shortcut menu to open the Kinetix Site View Colors dialog. Review the coloring of the sites and close the dialog.

Lastly you will specify the CO_2 formation process. This uses a different type of process and a different method of specifying the process rate to indicate that the formation and desorption should happen immediately when a given pattern occurs. An alternative way of considering this is as a process with an infinitely large rate coefficient.

On the **Processes** tab select **Desorption** as the **process of type** and click the **Add** button. On the **Process Details** tab enter **CO2Des** as the **Identifier** and **CO2 formation and desorption** as the **Description**. Change the **Specification type** to **Immediate**.

On the **Process Sites** tab check the **Associative desorption** checkbox and select **CO** and **O** from the **Species** dropdown lists.

You have now specified the processes to be used in the first simulation, you should check the processes are appropriate before proceeding.

On the **Site View** tab click the arrow buttons for the **Process number** to scroll through the processes defined.

Check that none of the processes are shown as invalid, indicated by red sites. Check that the **Multiplicity** reported is correct. This should be **1** for **COAds**, **3** for **O2Ads**, and **6** for **CO2Des**.

For each process review the **Process Details** and **Process Sites** tabs, checking the details for each process.


Before you continue, save the project.

Select **File | Save Project** from the menu bar.

3. Creating an initial configuration

In addition to these processes you also need an initial configuration for the simulation. A configuration is the way in which the adsorbates are distributed over the sites. The occupation of every site is necessary for a complete specification of a configuration.

You want to start with an empty surface where all sites are vacant. You can define such a configuration with the Configuration Builder.

Click the **Kinetix** button  on the **Modules** toolbar and select **Configuration Builder** from the dropdown list to open the Kinetix Configuration Builder dialog.

This allows you to specify the size of the simulation. A larger simulation will reduce the statistical noise in the results, at the expense of extra computation time. A large simulation is not easy to visualize (and will be slow), so it is desirable to specify a smaller range of the total simulation to display. The portion of the simulation displayed can be manipulated to review the results and check that they are representative of the whole simulation.


Change the **Configuration size** to **64 × 64**. and ensure that the **Type of configuration** is set to **Constant**. In the **Species to fill** section select **V** from the **Adsorption sites** dropdown list. Click the **Create** button and close the dialog.

A new document called `KinetixConfiguration.xkc` will be created.

Rename the newly created configuration document to **ZGB.xkc**. Select **File | Save Project** from the menu bar.

4. Running a Kinetix simulation

You are now ready to carry out a simulation.

Click the **Kinetix** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Kinetix | Calculation** from the menu bar.

This opens the Kinetix Calculation dialog where a number of different simulation tasks are available. These provide control over the length of the simulation and how parameters such as temperature, pressure, and potential vary with time. Simple *Rate coefficients* have been specified as the reaction rates for each of the processes rather than an *Arrhenius* expression, so there is no dependency on temperature, pressure, or potential. In this situation you should use the *Constant conditions* task.

Ensure that **ZGB.xkc** is the active document. On the Setup tab of the Kinetix Calculation dialog select **Constant conditions** from the **Task** dropdown list. Click the **More...** button to open the Kinetix Constant Conditions dialog.

For this simulation the only parameters on the *Kinetix Constant Conditions* dialog of interest are the *Simulation time* and *Sampling interval*. The rate coefficients specified mean that the default values for these parameters are satisfactory for the current simulation.

Close the **Kinetix Constant Conditions** dialog.

On the Setup tab choose **ZGBProcesses.xkp** from the **Processes** dropdown list.

Inspect the contents of the other tabs on the **Kinetix Calculation** dialog, all the default values for the settings are appropriate for a simple initial investigation.

The *Processes* tab lists the processes that are defined in the selected processes document, and allows you to decide which to use. It can be useful to repeat simulations using different processes, for example an initial simulation with adsorption, diffusion and desorption processes to generate a realistic starting configuration for a second simulation which might omit the adsorption processes to model temperature programmed desorption.

The *Job Control* tab controls details about where and how the job will be run. The *More...* button opens the Kinetix Job Control Options dialog which allows you to control features such as updates from the server while the calculation proceeds.

The frequency with which results are generated are controlled by the *Sampling interval* and *Configuration output every* options on the task details dialogs. Two types of raw results are created - one containing summaries of the concentrations, process rates and so on, and another which contains periodic snapshots of the actual configuration. The frequency of each is individually controlled. These outputs are used for analysis and the configurations can be displayed directly. They can also be used to *Restart* a simulation if, for example, you find that the initial simulation was not long enough.


Click the **Run** button and close the dialog.

A new folder, entitled ZGB Kinetix ConstCond, opens in the Project Explorer. The calculation should take less than a minute to complete. Six documents are generated in the new folder, as follows:

- ZGB - Calculation - the state file containing a copy of the current application state.
- ZGBProcesses.xkp - a copy of the original processes document.
- ZGB.kin - the input for the Carlos program.
- ZGB.kout - the main text output from the Carlos program, giving an overview of the input and the simulation performance. There are other output files containing more detailed results that are hidden within the Project Explorer which are accessed by the Analysis functionality.
- ZGB.xkc - the configuration at the end of the simulation.
- ZGBTraj.xkc - a multi-frame document containing snapshots of the configuration at points during the simulation, as requested by the parameters on the Output tab of the Kinetix Calculation dialog.

5. Analyzing the results of a Kinetix simulation

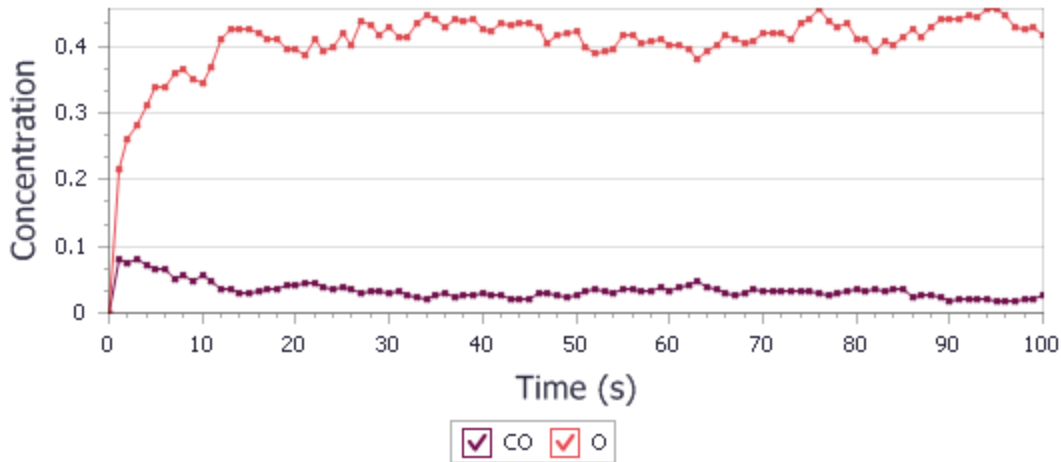
Next you will generate charts of how the average concentrations and reaction rates evolve with time.

In the Project Explorer, open **ZGB.kout** from the results folder. Click the **Kinetix** button  on the **Modules** toolbar and select **Analysis** to open the Kinetix Analysis dialog.

Select **Concentrations** and check the checkboxes for the **CO** and **O Species**. Click the **View** button.

A chart document is displayed showing the average concentration of each species as a function of simulation time. (The simulation is a Monte Carlo process involving random selections, so your results may not be identical to these.)

Kinetix Concentrations

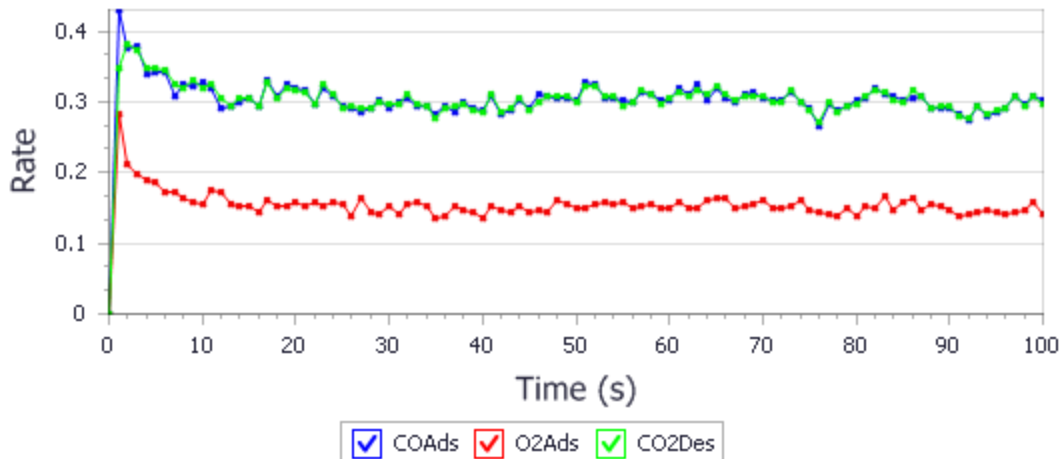


Average concentrations of species during the simulation

In the Kinetix Analysis dialog select **Rates** and check the checkboxes for the **COAds**, **O2Ads**, and **CO2Des** Reactions. Click the **View** button.

A chart document is displayed showing the average reaction rates in reactions per unit cell per second for each process as a function of simulation time.


Kinetix Reaction Rates



Average reaction rates of processes during the simulation

These charts show that the concentration of O quickly increases to about 0.4, and that of CO settles down to a low value, so that an approximate steady state is soon reached. These reaction rates for the COAds and CO2Des processes are approximately equal and that of the O2Ads is approximately half of the others, as would be expected to maintain the steady state.

It is now instructive to see how the configuration evolves with time.

In the Project Explorer, open **ZGBTraj.xkc** from the results folder. Click the **Play** button  on the Configuration Viewer to show an animation of the trajectory.

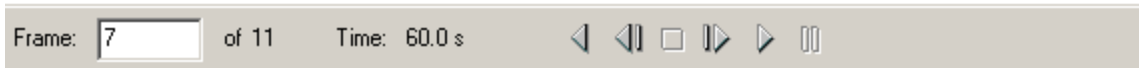
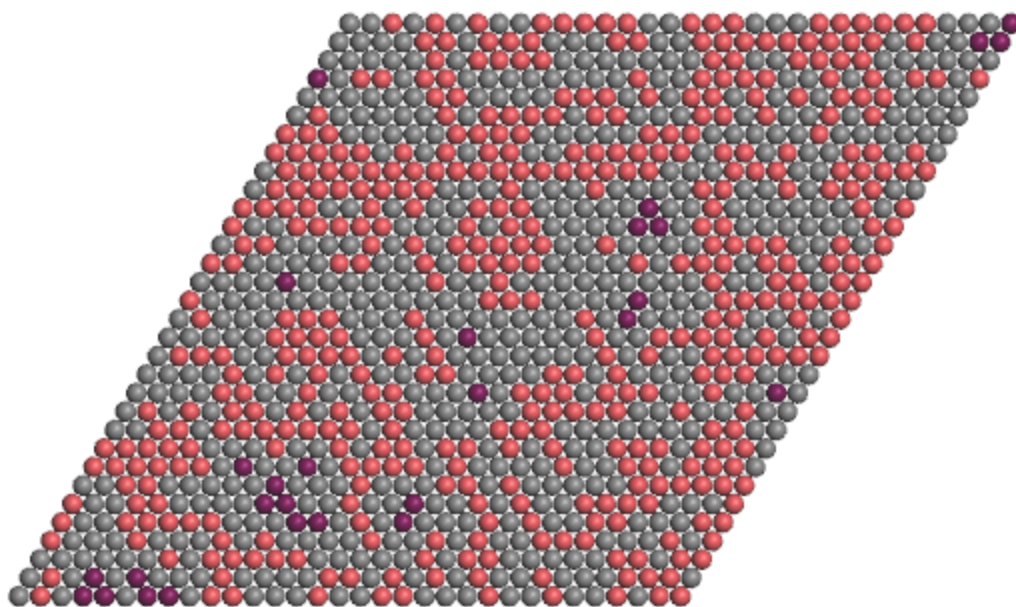
Click the **Stop** button .

Altering the display of the configuration document can be useful in the review and interpretation of results.

Right-click in **ZGBTraj.xkc** and select **Display Style** from the shortcut menu to open the Kinetix Configuration Display Style.

On the **Options** tab change the **Background color** to **white**. On the **Style** tab change both the **Radius scale** and the **Vacancy scale** values to **1.4** then close the dialog.

Your ZGBTraj .xkc view should look like this:



Configuration during the simulation

Inspection of the configuration shows that none of the CO species are adjacent to O species. This is as expected because the CO2Des process is specified to occur immediately that such a pair occurs.

The species in the configuration view are colored according to the colors originally defined in the ZGBProcesses .xkp document, but they can be altered if desired.

Right-click in **ZGBTraj.xkc** and select **Properties** from the shortcut menu to open the Kinetix Configuration Properties dialog showing the species used and their colors. Change the **Color** of one of the species and close the dialog.

Now save the project and close the open documents.

Select **File** | **Save Project** from the menu bar and then **Window** | **Close All**.

6. Adding further processes

Although the simulation so far has the necessary processes for adsorption of CO and O₂ and desorption of CO₂, it does not properly represent the full set of processes involved in the reactions. In particular those for diffusion of CO and O species. Diffusion is generally a much faster process than adsorption or desorption. Care must be taken in selecting the parameters to avoid spending too much of the calculation time on diffusion.

The desorption of CO or O₂, the converse of the adsorption processes, has also been omitted. Adsorption rate coefficients depend only weakly on temperature, but desorption rate coefficients have a strong dependence on temperature.

You will first add a process to describe diffusion of CO.

Open the original **ZGBProcesses.xkp** document and select the **Processes** tab. Choose **Diffusion** for the new process type and click the **Add** button.

On the **Process Details** tab enter **CODiff** as the **Identifier** and **CO diffusion** as the **Description**. Change the **Specification type** to **Rates** and the **Rate coefficient** to **25**.

On the **Process Sites** tab choose **CO** for the **Species**.

The diffusion process assumes that a species moves from one site to another that was previously vacant, leaving the original site vacant.

You will now add a similar process to describe diffusion of O.

On the **Processes** tab add another **Diffusion** process.

On the **Process Details** tab enter **ODiff** as the **Identifier** and **O diffusion** as the **Description**. Change the **Specification type** to **Rates** and the **Rate coefficient** to **15**.

On the **Process Sites** tab choose **O** for the **Species**.

By choosing rate coefficients of 25 and 15, these processes are much faster than the adsorption of CO and oxygen. However the CO₂ formation is currently described by an immediate process, so will occur whenever a CO species is at a site adjacent to one occupied by an O species. The CO₂ formation should occur with a rate coefficient intermediate between those of the adsorption processes and those of the diffusion processes.

On the **Processes** tab select the **CO2Des** process. On **Process Details** tab change the **Specification type** to **Rates** and enter a **Rate coefficient** of **5**.

You now need to add the processes for desorption of CO and O₂ as follows:

Process type	Identifier	Description	Specification type	Rate coefficient	Associative desorption	Species
Desorption	CODes	CO desorption	Rates	0.001	No	CO

Process type	Identifier	Description	Specification type	Rate coefficient	Associative desorption	Species
Desorption	O2Des	O2 desorption	Rates	0.001	Yes	O O

Add two new processes specified according to the table above.

This will be the final form of the processes document for this tutorial. Before continuing you should save the project.

Select **File | Save Project** from the menu bar.

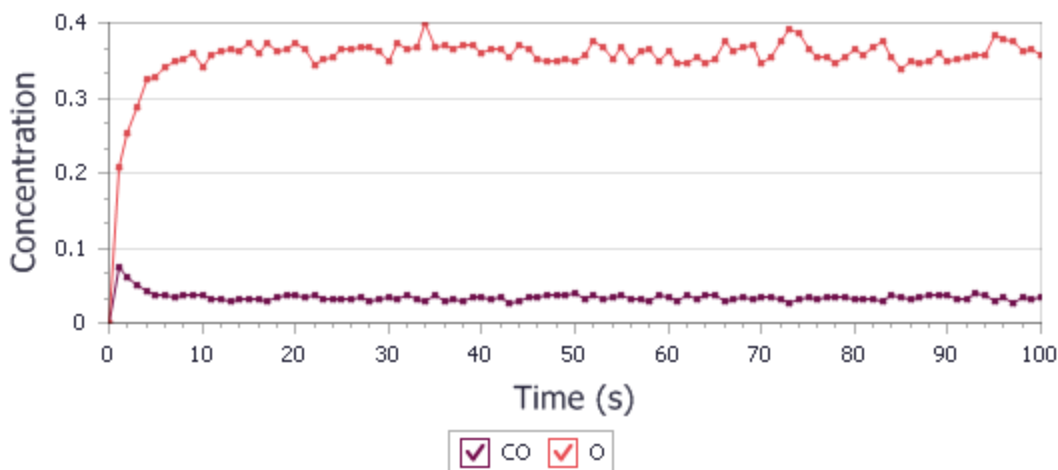
You will now rerun the simulation and compare some of the results with the previous run.

Make **ZGB.xkc** the active document. Open the **Kinetix Calculation** dialog and ensure that the **Constant conditions** task is selected. Click the **Run** button and close the dialog.

A new folder, named **ZGB Kinetix ConstCond (2)**, is added to the Project Explorer. When the job is complete the same set of documents will be created as for the previous run.

In the Project Explorer, open **ZGB.kout** from the new results folder. Open the **Kinetix Analysis** dialog and set up a **Concentrations** analysis of the **CO** and **O** species. Click the **View** button.

Kinetix Concentrations



Average concentrations of species during the simulation including diffusion

Comparison with the equivalent plot from the first run shows that the steady state concentration of O is lower than previously, and that the concentration of CO has increased.

Using the Kinetix Analysis dialog perform a **Rates** analysis for all of the **Reactions**. Click the **View** button.

The chart produced from this will immediately show that the simulation is dominated by the two diffusion processes. Although CO diffusion was specified with a higher rate coefficient than that for O diffusion, the O diffusion dominates the Rates chart because of the greater average concentration of O. You will now generate another Rates chart without the diffusion processes.

On the Kinetix Analysis dialog uncheck the **CODiff** and **ODiff** checkboxes. Click the **View** button and close the dialog.

Kinetix Reaction Rates



Average reaction rates of processes during the simulation including diffusion

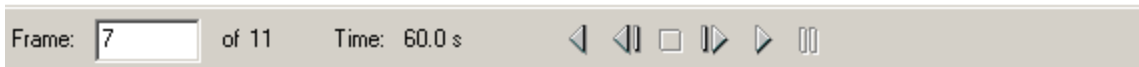
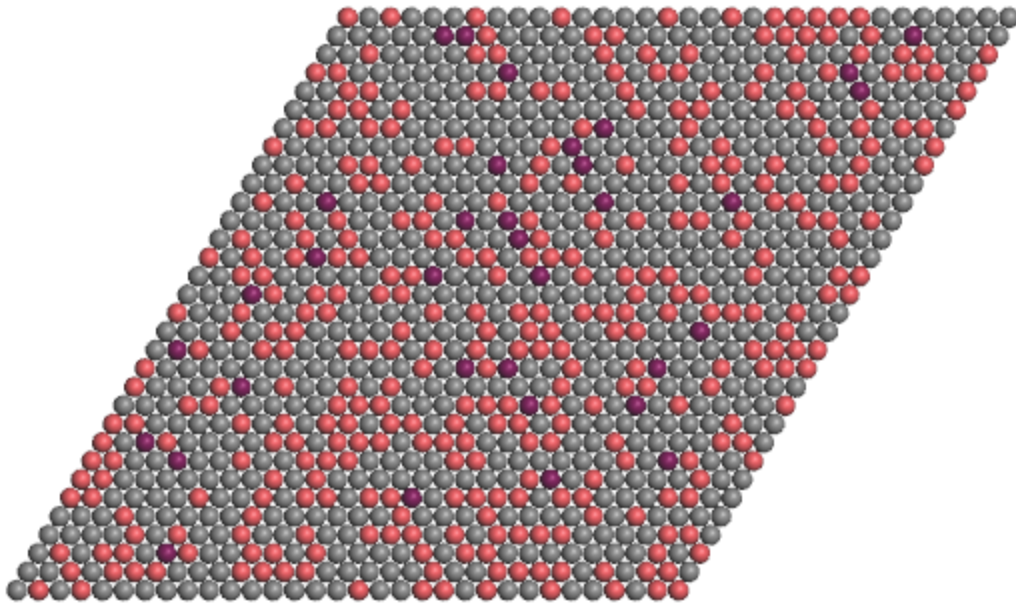
Comparison of this *Rates* chart with that from the first run shows that the rates of the three main processes of interest (COAds, O2Ads, and CO2Des) have all increased slightly, although they show the same relative values.

As expected, because of the very low rate coefficients specified for these processes, the CODes and O2Des processes have negligible contributions.

You should now inspect the new configuration evolution.

In the Project Explorer, open **ZGBTraj.xkc** from the new results folder. Modify the appearance in the same way that you did for the previous configuration document, and use the **animation controls** to step through the frames. **Stop** the animation.

Your new ZGBTraj.xkc view should look approximately like:



Configuration during the simulation including diffusion

The inclusion of the diffusion processes have allowed the CO and O species to move around the configuration, and the change of the CO2Des process to use a rate coefficient of 5 means that it is possible for CO species to exist in lattice sites adjacent to O species.

Although the second version of this simulation is more realistic than the initial simple run, due to the inclusion of the diffusion and desorption processes, there is still scope for improvements to the model. These improvements are discussed in the [Multi-site modeling of CO oxidation on a Pt\(1 1 1\) surface](#) tutorial.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

R.M. Ziff, E. Gulari, Y. Barshad, "Kinetic Phase Transitions in an Irreversible Surface-Reaction Model", *Phys.Rev.Lett.*, **56**, 2553-2556 (1986)

Multi-site modeling of CO oxidation on a Pt(1 1 1) surface

Purpose: Introduces Kinetix simulations on lattices with multiple sites.

Modules: Materials Visualizer, Kinetix

Time: 🕒🕒🕒

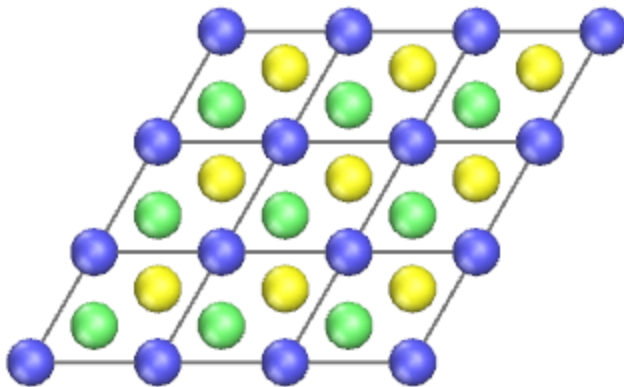
Prerequisites: [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#)

Background

The systems modeled by kinetic Monte Carlo (kMC) simulations, using the Kinetix module, can be described with varying degrees of sophistication.

The [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#) tutorial created a model similar to the that described by [Ziff et al., 1986](#) but adapted for the Pt(1 1 1) surface. This uses a single site per lattice cell with all the adsorbates on the same lattice site. The first simulation incorporated processes just for the adsorption of CO and O₂ and desorption of CO₂. Subsequently further processes were added to simulate diffusion and desorption of CO and O₂. The addition of these latter processes changed the dynamics of the system, resulting in different concentrations in the final coverage.

However even the modified simulation in that tutorial is an over-simplification of the system. In most reaction systems the adsorbates do not all sit at the same type of site. In the system being modeled CO prefers to adsorb onto top sites but the oxygen atoms are found at the hollow sites. In a hexagonal lattice such as this, there are two hollow sites, the fcc site at position (1/3, 1/3) and the hcp site at position (2/3, 2/3). These two hollow sites are not equivalent. The oxygen atoms prefer the fcc sites, but at high coverages they can also be found at the hcp sites.



Lattice showing top sites (blue) and hollow sites (fcc green, hcp yellow)

The difference between the hollow sites is modeled by specifying different processes acting at each of the types of site, each with different reaction rates for otherwise similar processes.

In the previous tutorial the rate coefficients were arbitrary to illustrate the types of processes that might be involved in a simple model, and how they can interact. To run a realistic simulation it is necessary to use realistic rate coefficients. Determining these is often the most difficult part of setting up a realistic kinetic Monte Carlo simulation. In practice you can obtain the rate coefficients from either calculated or

experimental data or, in some cases, they can be estimated from similar systems for which data is available.

Introduction

Because you will be using a more complex lattice than in the earlier tutorial it is necessary to define more processes to model all the possible reactions. In addition the specification of the individual processes will be more complex.

For example, the distance between adjacent sites in the new lattice will be only 1.6 Å. This is too small for adjacent sites to both be occupied so you will need to add specifications to ensure that this cannot happen.

The rate of a particular process can be dependent on the species occupying neighboring sites. This can be modeled in the form of lateral interactions which will be introduced here.

The following steps will be covered here:

- [Getting started](#)
- [Creating the processes document](#)
- [Adding the adsorption processes](#)
- [Adding the desorption processes](#)
- [Adding the diffusion processes](#)
- [Reviewing the processes document](#)
- [Running the simulation](#)
- [Analyzing the results](#)
- [Adding lateral interactions](#)
- [Using lateral interactions and running the simulation](#)
- [Analyzing the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ORR_MultiSite** as the project name, click the **OK** button.

The new project is created with *ORR_MultiSite* listed in the Project Explorer.

2. Creating the processes document

You will create a basic processes document describing the simulation lattice and the species that will be involved in the simulation.

Click the **Kinetix** button  on the **Modules** toolbar and select **Process Builder** from the dropdown list.

As in the previous tutorial, you will be working with a hexagonal lattice. However because you will be using more than one lattice site per cell you will need to think carefully about the symmetry. Inspection of the lattice diagram above, and in particular the different nature of the fcc and the hcp hollow sites, shows that the desired symmetry specification is $p\ 3$.

Enter **Hexagonal ZGB model** as the **Description**. Select **Hexagonal** from the **Type** dropdown list and **p3** from the **Symmetry** dropdown list. Set the **Length** to **2.77 Å**. Click the **Create** button and close the dialog.

This will create a new processes document called `KinetixProcesses.xkp`.

Rename the new document **ZGBMultiSite.xkp**.

The Processes document was created with a single lattice site, the top site at position (0,0) in the cell. You should now add the specification of the hollow sites.

On the **General** tab click the **Add Site...** button to open the Kinetix Add Sites dialog. Change the **Site type** to **Hollow**. Click the **Add** button and close the dialog.

In the processes document, two new sites are added to the *Sites* table on the *General* tab at (0.333, 0.333) and (0.667, 0.667).

You will now specify the species that will be used in the simulation, and specify radii for them. These radii will be used in the generation of minimum cutoff distances when creating interactions, and are also used in the display of simulations resulting from this document.

On the **Species** tab enter **CO** as the **Name** in the first empty row. Change the **Radius** to 1.3.

Add a second species, named **O** with a **Radius** of 1.3.

The other default properties (charge and color) of the species will suffice for this tutorial, although they can be changed later if desired.

3. Adding the adsorption processes

The adsorption processes used here will be superficially similar to those in the previous tutorial. However hollow sites will make the specification more complicated. In addition you must ensure that adsorption does not occur adjacent to occupied sites.

The rate coefficient for adsorption of CO can be calculated from ([Jansen, 2003](#)):

$$k_{\text{ads}}^{(\text{CO})} = \frac{P_{\text{CO}} A_{\text{site}} \sigma}{\sqrt{2\pi m_{\text{CO}} k_B T}}$$

Here P_{CO} is the pressure of CO, A_{site} is the area of a single site, σ is the sticking coefficient, m_{CO} is the mass of CO, k_B is the Boltzmann constant, and T is the temperature.

For a temperature of 1200 K, a CO pressure of 1 atm, and a sticking coefficient of 1.0 the rate coefficient for the CO adsorption is $9.68 \times 10^7 \text{ s}^{-1}$.

For oxygen adsorption a similar expression is used with a pressure of 0.5 atm. An additional factor of 3 is used in the denominator to account for the number of different possible orientations of the O_2 molecule. Thus a rate coefficient of $1.49 \times 10^7 \text{ s}^{-1}$ for the oxygen adsorption is obtained.

First specify the CO adsorption process.

Select the **Processes** tab of the processes document. Ensure that **process of type** is set to **Adsorption** and click the **Add** button.

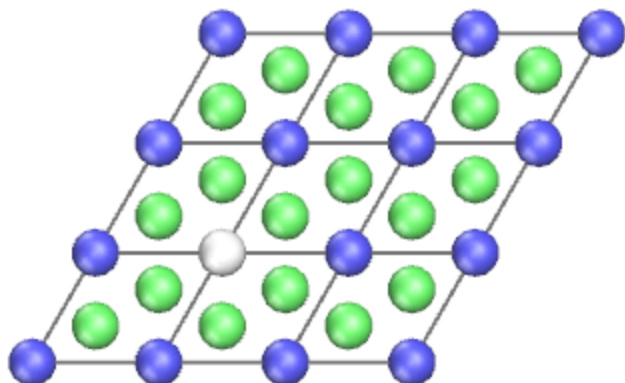
A new process, named *NewProcess* is added to the list on the *Processes* and the *Process Details* tab provides further options.

On the **Process Details** tab enter **COAds** as the **Identifier** and **CO adsorption** as the **Description**. Change the **Specification type** to **Rates** and set the **Rate coefficient** to **9.68e7 s⁻¹**.

On the **Process Sites** tab select **CO** from the **Adsorbate(s)** dropdown list.

You now need to specify the blocking sites, that is those sites at which the presence of a species will prevent the adsorption from occurring.

Select the **Site View** tab:



Site view showing adsorption process before blocking sites added

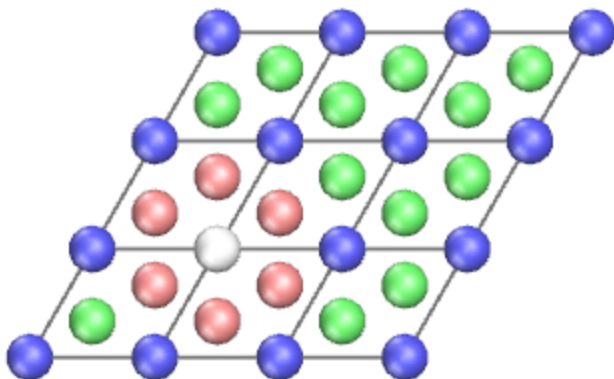
The white site represents the site where the adsorption will occur. The 6 neighboring sites should be defined as "blocking". This is achieved by specifying that the process is enabled only if these sites are vacant.

On the **Process Sites** tab select **V** from the **with enabling species** dropdown list in the **Site environment** section.

In the **Site View**, hold down the **CTRL** key and select each of the 6 sites surrounding the one colored white.

On the **Process Sites** tab click the **Add selected sites** button.

Six sites will be added to the list in the *Site environment* section, with a *Nearest distance* of 1.599 Å. This is the distance to the nearest active site in the current process. In the *Site View* these sites are now colored pink, to indicate their new role as contributing to the site environment requirements for the process. The *Site View* now looks like this:

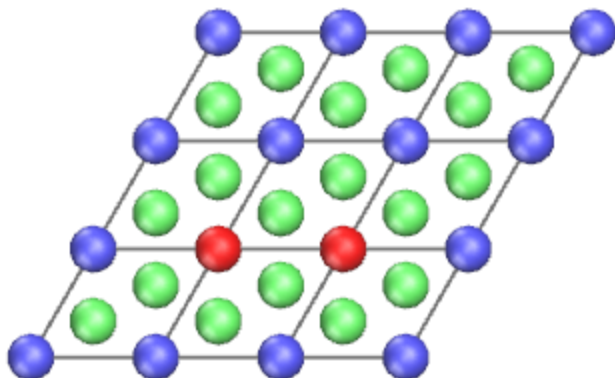


Site view showing adsorption process after blocking sites added.

Next you will specify the O_2 adsorption process. There are two possible sites for the adsorption so you will need to specify a separate process for each site.

On the **Processes** tab click the **Add** button. On the **Process Details** tab enter **O2Adsf** as the **Identifier** and **O2 adsorption onto fcc site** as the **Description**. Change the **Specification type** to **Rates** and set the **Rate coefficient** to $1.49e7 s^{-1}$.

On the **Process Sites** tab check the **Dissociative adsorption** checkbox and select the **Site View** tab:



Site view showing dissociative adsorption process before any corrections

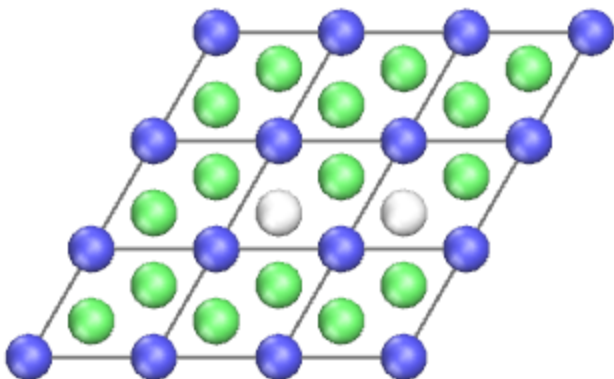
The active sites, shown in red, are not in the fcc hollow sites. The red color indicates that the species for these sites have not been set.

On the **Site View** tab select one of the fcc hollow sites.

On the **Process Sites** tab click the **+** button for one of the **Adsorption site(s)**. Select **O** from the corresponding **Adsorbate(s)** dropdown list.

Repeat this procedure for the other fcc site and the second **Adsorption site**, also populating it with **O**.

The *Site View* should now look like this:



Site view showing dissociative adsorption process on fcc sites

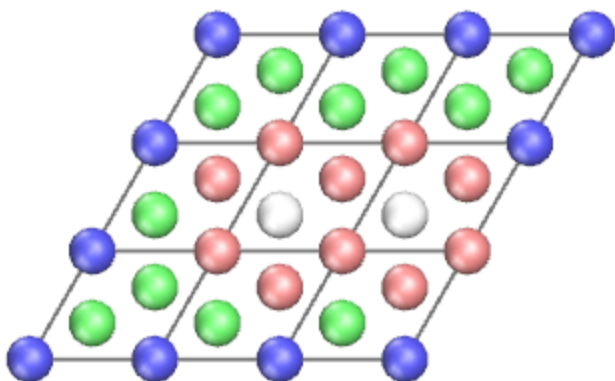
This process has a *Multiplicity* of 3 as there are three different orientations determined from the symmetry defined for the lattice. This is the reason for the extra factor of 3 in the calculation of the rate coefficient for the oxygen adsorption processes.

To complete the specification of this process, you need to add the blocking sites. There will be 10 surrounding two adsorption sites.

On the **Site View** select the 10 sites surrounding the two white sites occupied by O species.

On the **Process Sites** tab click the **Add selected sites** button to populate these sites with vacancies.

Ten sites will be added to the *Site environment* list, each with a *Nearest distance* of 1.599 Å. The *Site View* should now look like this:



Site view showing dissociative adsorption process on fcc sites after blocking sites added

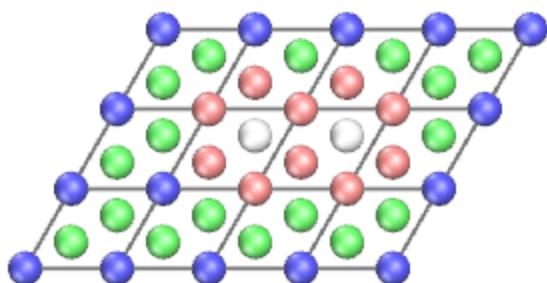
Tip: If you make any mistakes during the specification of processes, you can either *Undo* the last change(s) to the document, or you can *Delete* the process concerned and enter a new one.

The third adsorption process that you will need to add is that for O₂ onto the hcp sites. There will be one extra step here because one of the necessary blocking sites is not currently shown in the *Site View*.

Right-click in the **Site View** and select **Display Style** from the shortcut menu to open the Kinetix Site View Display dialog. Change the **U Max** value to **2**.

Repeat the procedures used for the **O2Adsf** process to create a similar process **O2Adsh** using the hcp hollow sites. Use the same value ($1.49e7 \text{ s}^{-1}$) for the **Rate coefficient**.

The *Site View* should now look like this:



Site view showing dissociative adsorption process on hcp sites after blocking sites added

On the **Kinetix Site View Display** change the **U Max** back to 1 and close the dialog.

Notice that although one of the blocking sites lies outside the display range specified for the *Site View* it is still shown. This is so that you always see the important sites relating to the current process regardless of the display parameters.

Before continuing you should save the project.

Select **File | Save Project** from the menu bar.

If you wish, you can compare your document at this stage with a version (ZGBMultiSite Stage 1.xkp) provided in the Examples library.

Select **File | Import...** from the menu bar to open the Import File dialog. Choose **Kinetix Files** from the file types dropdown list for the **File name**. Navigate to **Examples/Kinetix/Processes** and select **ZGBMultiSite Stage1.xkp**. Click the **Open** button.

4. Adding the desorption processes

As with the adsorption processes, there will be more desorption processes than in the previous tutorial. There will need to be two versions of the CO_2 formation desorption process, one using oxygen from the fcc hollow site and the other using oxygen from the hcp hollow site. Similarly there will be two processes for desorption of oxygen.

Desorption processes are simpler to specify than the equivalent adsorption processes, because there is no need to specify any blocking sites.

For these desorption processes you will give the rate coefficients by specifying the *Prefactor* and *Activation energy* for an *Arrhenius expression*.

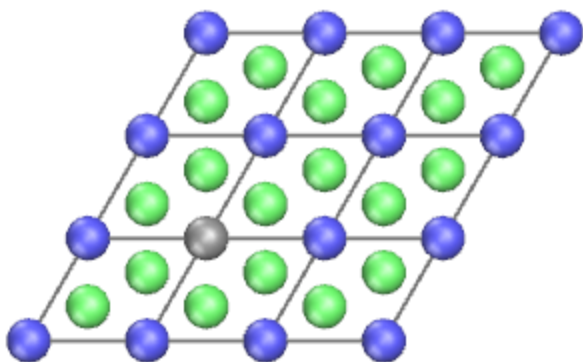
The rate coefficient for CO desorption has been obtained from temperature-programmed desorption spectra ([van Bavel et al., 2003](#)). Experimental measurements indicate that the prefactor used for the CO desorption on Pt(111) should be $1.0 \times 10^{13} \text{ s}^{-1}$, for many processes the observed value is close to this.

For oxygen desorption the results from kMC simulations correlate with experimental temperature-programmed desorption spectra ([Jansen et al., 2005](#)). However, this only provides parameters for desorption from the fcc sites - due to the experimental conditions all the oxygen atoms were located at fcc sites. To get usable parameters for oxygen desorption from hcp sites the activation energy is modified by the difference in adsorption energy of atomic oxygen between fcc and hcp sites, as calculated by [Offermans et al.](#).

The activation energies for the CO₂ formation have been calculated by [Yakovkin and Petrova](#). First you will specify the CO desorption process, the reverse of the CO adsorption process.

Add a new **Desorption** process with **CODes** as the **Identifier** and **CO desorption** as the **Description**. Change the **Prefactor** to **1.0e13 s⁻¹** and the **Activation energy** to **33.2 kcal/mol**.

Set up the process sites and species so that the Site View is displayed as below, ensuring that the top site has been selected in the Site View and that **CO** has been chosen as the **Species** on the Process Sites tab.

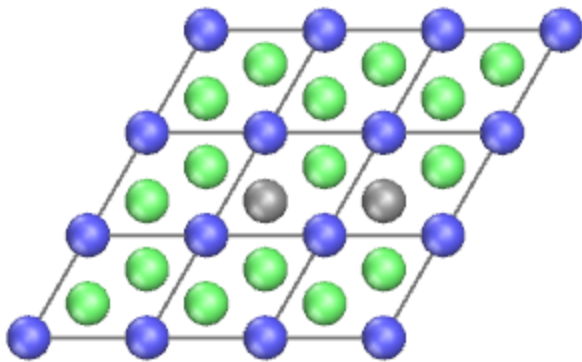


Site view showing CO desorption process from a top site

Next you will specify the process for O₂ desorption from fcc sites, the reverse of the O₂ adsorption onto fcc sites.

Add a new **Desorption** process with **O2Desf** as the **Identifier** and **O₂ desorption with fcc site oxygen** as the **Description**. Change the **Prefactor** to **7.2e18 s⁻¹** and the **Activation energy** to **61.8 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that the fcc sites are chosen and that **O** is chosen as the species for these sites.

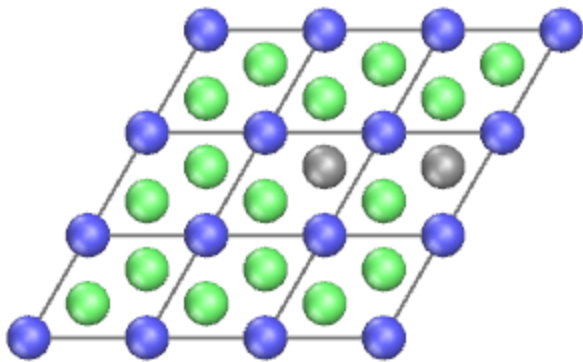


Site view showing associative desorption process from fcc sites

Next you will specify the process for O₂ desorption from hcp sites, the reverse of the O₂ adsorption onto hcp sites.

Add a new **Desorption** process and enter **O2Desh** as the **Identifier** and **O2 desorption with hcp site oxygen** as the **Description**. Change the **Prefactor** to **7.2e18 s⁻¹** and the **Activation energy** to **45.1 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that the hcp sites are chosen and that **O** is chosen as the species for these sites.

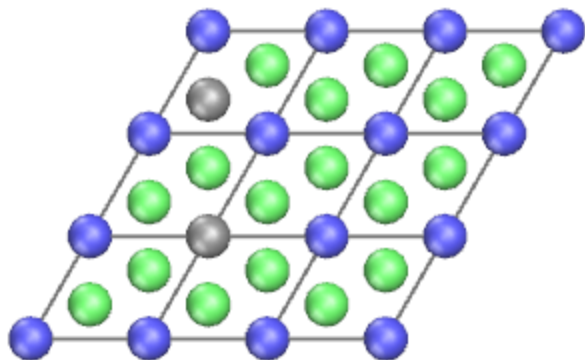


Site view showing associative desorption process from hcp sites

Now you will specify two versions of a process for CO₂ formation and desorption. First you will use oxygen from an fcc site. Note that the site used for the O is not the fcc site adjacent to the top site used for the CO. This is because of the distances concerned, and the decision that species cannot be present on adjacent sites (by use of the blocking sites in the adsorption processes, and later on in the diffusion processes).

Add a new **Desorption** process and enter **CO2Desf** as the **Identifier** and **CO2 desorption with fcc site oxygen** as the **Description**. Change the **Prefactor** to $1.0e13 \text{ s}^{-1}$ and the **Activation energy** to **51.9 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that **CO** is specified for the top site and **O** for the fcc site.

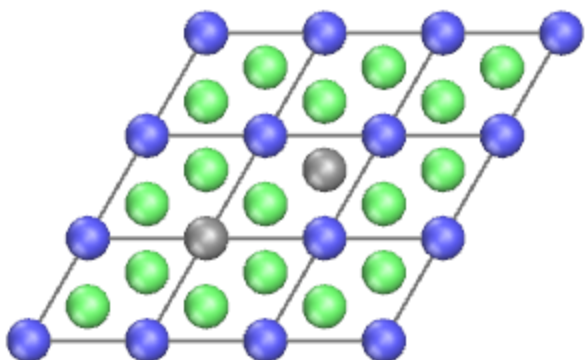


Site view showing associative desorption process from top and fcc sites

Finally, for the desorption processes, you will add a process for CO_2 formation and desorption using oxygen from an hcp site.

Add a new **Desorption** process and enter **CO2Desh** as the **Identifier** and **CO2 desorption with hcp site oxygen** as the **Description**. Change the **Prefactor** to $1.0e13 \text{ s}^{-1}$ and the **Activation energy** to **26.5 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that **CO** is specified for the top site and **O** for the hcp site.



Site view showing associative desorption process from top and hcp sites

You have now added all the desorption processes. Before continuing you should save the project.

Select **File** | **Save Project** from the menu bar.

If you wish, you can compare your document at this stage with a version (ZGBMultiSite Stage 2.xkp) provided in the Examples library.

5. Adding the diffusion processes

There are more diffusion processes than in the previous tutorial. CO can diffuse from a top site to an adjacent top site, as before. But this system has three-fold symmetry (rather than six-fold) to allow for the different treatment of the fcc and hcp sites. So you must specify two versions of the CO diffusion process so that it has the correct multiplicity.

Because, following diffusion, a previously vacant site becomes occupied, blocking sites around the destination should be added. However, to simplify the calculation you can take advantage of the vacancies in all sites adjacent to the source.

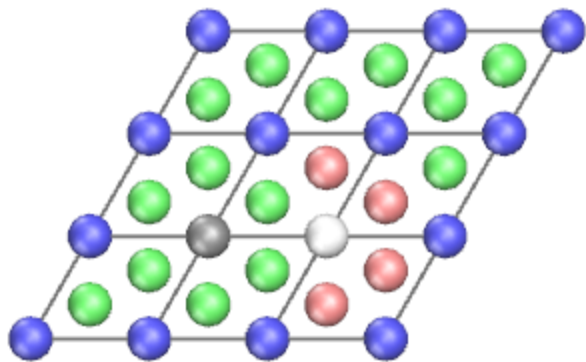
Diffusion is generally much faster than adsorption or desorption. This can mean that using realistic rate coefficients for diffusion would lead to almost all the simulation time being spent on diffusion which is inefficient and unnecessary. The role of diffusion in almost all reaction systems is to equilibrate the adlayer, this can also be accomplished using smaller rate coefficients than those observed by experiment. A pragmatic approach is to start with small rate coefficients for diffusion and increase them over a number of short simulations. The results will change as long as diffusion is not fast enough to equilibrate the adlayer. When the results become constant it is no longer necessary to increase the diffusion rate coefficient as this indicates that the adlayer is at equilibrium.

For CO diffusion the rate coefficient can be small; the same order of magnitude as for the desorption process. In this case it is desirable to use the same activation energy for the diffusion process as the equivalent desorption process. Thus the two rate coefficients will have the same ratio irrespective of simulation temperature.

For oxygen diffusion the process is much faster than the equivalent desorption. This is modeled as a process without a transition state, so for diffusion from fcc to hcp sites there is a significant activation energy while for the inverse diffusion from hcp to fcc sites the activation energy is effectively zero.

Add a new process of type **Diffusion**. Specify **CODiff** for the **Identifier** and **CO diffusion** for the **Description**. Change the **Prefactor** to **2.0e13 s⁻¹**, and the **Activation energy** to **33.2 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that the species for the source site is **CO**.

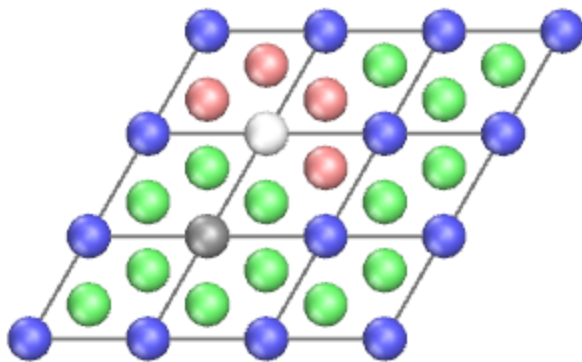


Site view showing the first CO diffusion process between top sites

The *Multiplicity* of the diffusion process you have just added is 3, this confirms that you will need a second version of it as there are six possible equivalent CO diffusion processes. You will now add the second version of the CO diffusion process using the same specification parameters for different sites. The identifier can be the same as the previous one, so that the statistics for the two processes will be merged in the simulation results.

Add a new process of type **Diffusion**. Specify **CODiff** for the **Identifier** and **CO diffusion** for the **Description**. Change the **Prefactor** to $2.0e13 \text{ s}^{-1}$, and the **Activation energy** to **33.2 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that **CO** is chosen for the species, and that the pair of sites used is 60 or 180 degrees different from the pair used in the previous process.

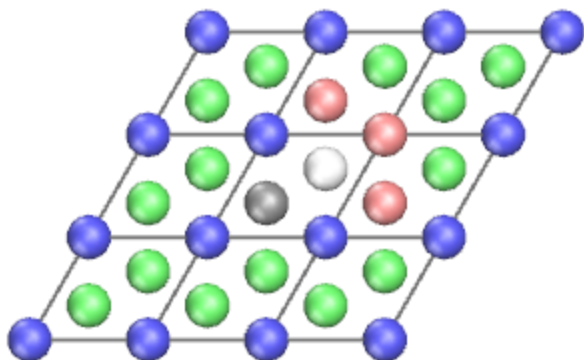


Site view showing the second CO diffusion process between top sites

You will now add processes for the diffusion of oxygen in both directions between the fcc and hcp sites. These processes, with their symmetry equivalents, allow diffusion of oxygen throughout the lattice. First specify the diffusion from the fcc site to the hcp site.

Add a new process of type **Diffusion**. Specify **ODiff_fh** for the **Identifier** and **Oxygen diffusion from fcc to hcp sites** for the **Description**. Change the **Prefactor** to $1.0e11 \text{ s}^{-1}$ and the **Activation energy** to **8.37 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that **O** is chosen for the species, and that you have the source and destination sites the correct way round, as indicated on the site view.



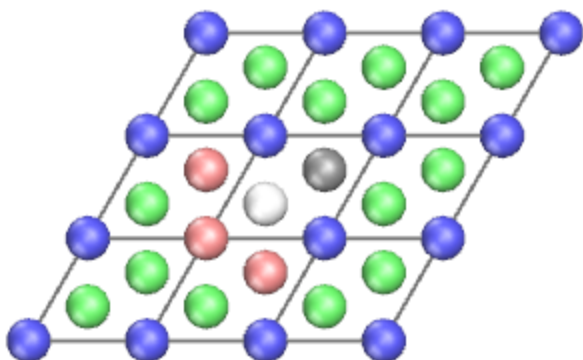
Site view showing O diffusion from fcc to hcp sites

You will now add the reverse process. You will use a different identifier and different process rates from the previous one.

Add a new process of type **Diffusion**. Specify **ODiff_hf** for the **Identifier** and **Oxygen diffusion from hcp to fcc sites** for the **Description**. Change the **Prefactor** to **1.0e11 s⁻¹**, and the **Activation energy** to **0.001 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that **O** is chosen for the species, and that you have the source and destination sites the correct way round, as indicated on the site view.

The activation energy for this process should be zero to reflect the lack of transition state, but the underlying server calculation requires that the value should be positive, so an arbitrarily low value of 0.001 is used.



Site view showing O diffusion from hcp to fcc sites

You have now added all the necessary diffusion processes. Before continuing you should save the project.

Click the **Save Project** button .

If you wish, you can compare your document at this stage with a pre-saved version of it in the file *ZGBMultiSite Stage 3.xkp* in the Examples library provided with Materials Studio.

6. Reviewing the processes document

At this point it is worth checking the processes you have entered.

Select the **Processes** tab, twelve processes should be listed:

Use	Index	Identifier	Type	Spec
<input checked="" type="checkbox"/>	1	COAdsf	Adsorption	Rates
<input checked="" type="checkbox"/>	2	O2Adsf	Adsorption	Rates
<input checked="" type="checkbox"/>	3	O2Adsh	Adsorption	Rates
<input checked="" type="checkbox"/>	4	CODes	Desorption	Arhenius
<input checked="" type="checkbox"/>	5	O2Desf	Desorption	Arhenius
<input checked="" type="checkbox"/>	6	O2Desh	Desorption	Arhenius
<input checked="" type="checkbox"/>	7	CO2Desf	Desorption	Arhenius
<input checked="" type="checkbox"/>	8	CO2Desh	Desorption	Arhenius
<input checked="" type="checkbox"/>	9	CODiff	Desorption	Arhenius
<input checked="" type="checkbox"/>	10	CODiff	Diffusion	Arhenius
<input checked="" type="checkbox"/>	11	ODiff_fh	Diffusion	Arhenius
<input checked="" type="checkbox"/>	12	ODiff_hf	Diffusion	Arhenius

Processes for the ZGB multi-site simulation


On the **Site View** tab click the arrow buttons for the **Process index** to scroll through the processes defined.

Check that none of the processes are shown as invalid, as would be shown by sites colored red in the **Site View**. Check that the **Multiplicity** seems as expected for each process. Errors in the multiplicity can occur either because the wrong sites have been specified, or the wrong species combination for an associative or dissociative process.

Scroll through the processes with both the **Process Details** and the **Process Sites** tabs showing, checking the details for each process.

7. Running the simulation


Before running the simulation, you will need a new configuration document. The one that you generated in the previous tutorial will not suffice because there are now three sites per lattice cell compared to a single one before.

Click the **Kinetix** button  on the **Modules** toolbar and select **Configuration Builder** from the dropdown list.

Change the **Configuration size** to **64 × 64**. Ensure that the **Type of configuration** is set to **Constant** and select **V** from the **Adsorption sites** dropdown list. Click the **Create** button and close the dialog.

A new document, `KinetixConfiguration.xkc` will be created. Note that this has a different appearance from that in the previous tutorial due to the multiplicity of sites per lattice cell.

Rename the newly created configuration document to **ZGBMultiSite.xkc** and **save** the project.

Click the **Kinetix** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Kinetix | Calculation** from the menu bar.

In this tutorial, you have not specified explicit rate coefficients (except for the adsorption processes). Using the Arrhenius expression the rate coefficients are highly dependent on the temperature. Hence you need to specify the desired temperature for the simulation. A variable temperature can be specified using the *Temperature programmed* task, but for this tutorial you will use a constant temperature.

Compared with the previous tutorial, the rate coefficients are extremely high. This means that the default values for the *Simulation time* and *Sampling interval* are no longer appropriate. Instead the simulation will happen very much faster than this, at a nanosecond time-scale. You can find this experimentally by running simulations with even shorter simulation times and sampling intervals, gradually increasing the sampling interval until a statistically meaningful number of reactions occur in each sampling interval.

Ensure that **ZGBMultiSite.xkc** is the active document, and that the **Constant conditions** task is chosen. Click the **More...** button to open the Kinetix Constant Conditions dialog.

Set the **Temperature** to **1200 K**. Set the **Simulation time** to **1.0e-7 s** and the **Sampling interval** to **1.0e-9 s** and close dialog.


On the **Setup** tab select **ZGBMultiSite.xkp** from the **Processes** dropdown list.

Click the **Run** button and close the dialog.

A new folder, entitled `ZGBMultiSite Kinetix ConstCond` opens in the Project Explorer. When the job is complete the same set of documents should be created as seen in the previous tutorial.

8. Analyzing the results

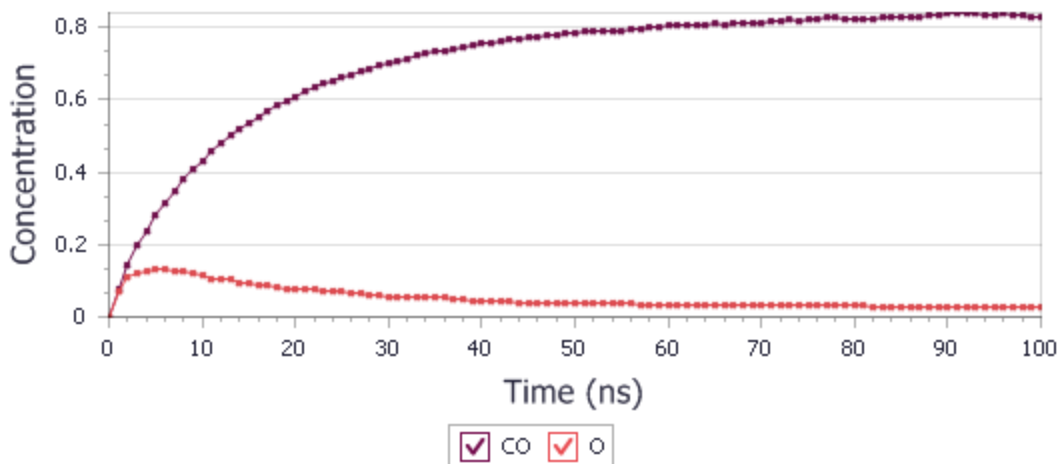
In the Project Explorer, open **MultiSiteZGB.kout** from the new results folder.

Click the **Kinetix** button  on the **Modules** toolbar and select **Analysis** from the dropdown list to open the Kinetix Analysis dialog.

Select **Concentrations** and check the **CO** and **O Species** checkboxes. Click the **View** button.

This will generate a chart similar to this:

Kinetix Concentrations



Average concentrations of species during the simulation

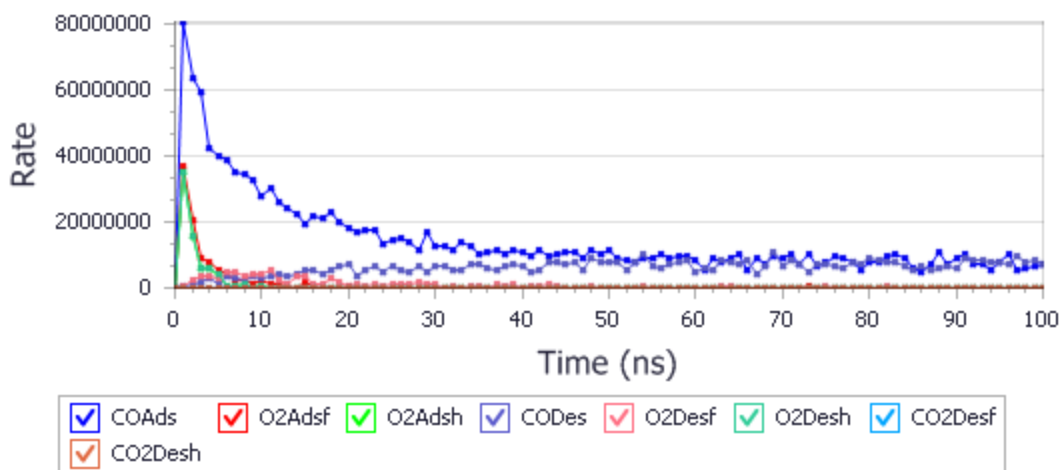
On the Kinetix Analysis dialog select **Rates** and check all the **Reactions** checkboxes. Click the **View** button.

The chart produced from this will immediately show that the simulation is dominated by the two diffusion processes. You will now generate another Rates chart without the diffusion processes.

On the Kinetix Analysis dialog uncheck the **CODiff**, **ODiff_fh**, and **ODiff_hf** checkboxes. Click the **View** button. and close the dialog

This will generate a chart similar to this:

Kinetix Reaction Rates



Average reaction rates of processes during the simulation

You should now inspect the new configuration evolution.

In the Project Explorer, open **ZGBMultiSiteTraj.xkc** from the new results folder. Use the **animation controls** to step through the frames. **Stop** the animation.

The chart documents and the configuration trajectory document are linked by point selection in the chart. As you step through the frames in the configuration trajectory the equivalent time point will be selected on one of the graphs in the each of the open charts. Conversely if a point is selected in one of the charts the configuration trajectory will change to show the frame nearest to the time of the chosen point.

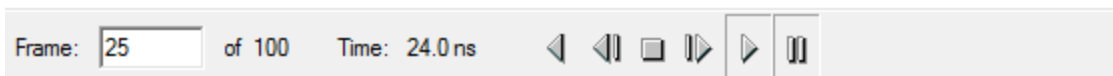
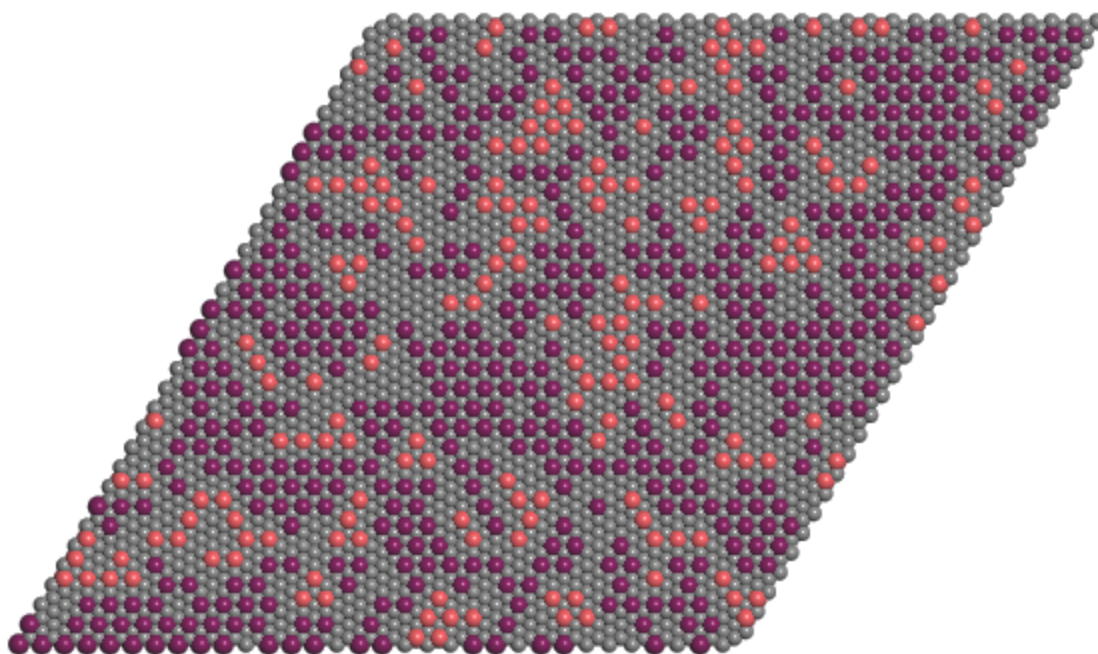
You should be able to confirm the correct use of the blocking sites. Each of the CO or O species should be completely surrounded by vacancies. You can now alter the display to give more emphasis to these species.

Right-click in **ZGBMultiSiteTraj.xkc** and select **Display Style** from the shortcut menu to open the Kinetix Configuration Display Style dialog.

On the **Options** tab change the **Background color** to **white**. On the **Style** tab change the **Radius scale** to **1.3**.

Close the dialog.

Your new ZGBMultiSiteTraj .xkc view should look approximately like:



Configuration during the simulation

The model used for the simulation in this tutorial is more sophisticated than that used in the [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#) tutorial. Consideration is given to multiple sites and their

different roles in the reactions. The reaction rates are specified using an Arrhenius expression, providing temperature dependence. However, another level of sophistication can be added to help make the model more realistic - lateral interactions.

9. Adding lateral interactions

Lateral interactions model the effect on a process (in modifying the activation energy) of species on nearby sites.

In Kinetix lateral interactions are described by specifying the change in the activation energy of a process for a combination of involved species and their neighbors. These are incorporated into the final descriptions of the processes when the input file is created for the server calculation.

Interactions are symmetric with respect to the species concerned. So the change in activation energy of a process involving species A when B is adjacent is the same for a similar process involving species B when A is adjacent.

Values for the lateral interactions between the oxygen atoms on fcc sites have been obtained from density-functional theory calculations ([Jansen et al., 2005](#)). It is assumed that the interactions for hcp sites have the same values. Values for the interactions between CO molecules have been taken from fits of kMC simulations to temperature-programmed desorption experiments of CO/Rh(100) ([Jansen, 2004](#)). Values for interactions between CO and oxygen and between oxygen atoms at different hollow sites have all been estimated, based on the distance between the sites and values of lateral interactions for other systems at similar distances.

You will need to add three sets of lateral interactions, for different combinations of the two species involved in an interaction. First you will add the interactions for the CO-CO combination.

On the **Interactions** tab of the original **ZGBMultiSite.xkp** select **CO** from each of the **Interactions** dropdown lists and specify a **cutoff** of **3.5 Å**. Click the **Add** button.

A new interaction will be added to the list in this tab, with the details listed on the *Interaction Details* tab. All possible combinations of sites between the minimum and maximum cutoff distances are listed. Some of these are irrelevant because, for example, CO can exist only on the top sites (with site index 1).

Many of the interaction details listed are related to each other by the symmetry defined for the lattice. Although these relationships are not shown in the list, they are honored when the lists are modified, such as by deletion of a detail item or modification of the interaction value.

You should remove the irrelevant interaction details from the list for this process, and specify the desired interaction value for the remaining details.

On the **Interaction Details** tab, select any row with **2** or **3** as the site index (the third component of the site description) for either **Site for CO** column. Press the **DELETE** key.

Repeat this to remove all interactions apart from those between top sites, so all remaining interactions should have site index 1 for both sites.

There should be six items remaining in the *Interaction Details* list.

Click in one of the **Interaction** cells and change the value to **6.69**. The two symmetry-related interaction rows will be updated automatically.

Repeat this procedure until all **Interaction** values are **6.69**.

Next you will add lateral interactions between *CO* and *O*. For this one you will make use of the fact that *CO* can exist only on the top site, and that *O* can exist only on a hollow site.

On the **Interactions** tab select **O** for the second interacting species and click the **Add** button.

On the **Interaction Details** tab select any row with site index **1** for the **Site for O** column and press the **DELETE** key.

Repeat this until all remaining **Site for O** have an index of 2 or 3.

Delete all the interactions where the **Site for CO** has an index of 2 or 3.

Change all the **Interaction** values to **2.39**.

There should also be six items remaining in the *Interaction Details* list for this interaction.

Next you will add lateral interactions between *O* and *O*. This is more complicated in that there will be two sets of interactions at different distances, hence with different interaction values.

On the **Interactions** tab select **O** for both the species and click the **Add** button.

On the **Interaction Details** tab delete all rows with a **Site for O** index of **1**.

There will be six interaction items between fcc sites (with a site index of 2), and six interaction items between hcp sites (with a site index of 3). These will all show a distance of 2.77 Å. Similarly there will be six interaction items between an fcc site and an hcp site, showing a distance of 3.199 Å.

Change the **Interaction** value to **6.21** for all those interaction items showing a distance of 2.77 Å.

Change the **Interaction** value to **2.39** for all those interaction items showing a distance of 3.199 Å.

The Interaction Details tab should look like:

Interaction index: 3

Interactions between: 0 and 0

Cutoff distance (Å) - min: 2.6 max: 3.5

	Site for O	Site for O	Distance	Interaction
	(0, 0/2)	(-1, -1/3)	3.199	2.39
	(0, 0/2)	(-1, 1/3)	3.199	2.39
	(0, 0/2)	(1, -1/3)	3.199	2.39
	(0, 0/3)	(-1, 1/2)	3.199	2.39
	(0, 0/3)	(1, -1/2)	3.199	2.39
	(0, 0/3)	(1, 1/2)	3.199	2.39
	(0, 0/3)	(-1, 0/3)	2.770	6.21
	(0, 0/3)	(-1, 1/3)	2.770	6.21
	(0, 0/3)	(0, -1/3)	2.770	6.21
	(0, 0/3)	(0, 1/3)	2.770	6.21
	(0, 0/3)	(1, -1/3)	2.770	6.21
	(0, 0/3)	(1, 0/3)	2.770	6.21

Process Details | Process Sites | Interaction Details

Interaction details tab

Before continuing you should save the project.

Select **File | Save Project** from the menu bar.

If you wish, you can compare your document at this stage with a pre-saved version of it in the file *ZGBMultiSite Stage 4.xkp* in the Examples library provided with Materials Studio.

10. Using lateral interactions and running the simulation

By default, any interactions that have been defined will be used to conditionally modify the activation energy for any process that uses an Arrhenius expression for the rate specification. In the simulation run earlier in this tutorial there were no interactions defined, so there were no such modifications.

For each such process, the extent to which the lateral interactions modify the activation energy is governed by the *Bronsted-Polanyi factor*, denoted by α . When the process is first created α is set to a value dependent on the type of the process. These default values are correct for your purposes, but you should check that they have not been accidentally altered.

On the **Process Details** tab check the details for each of the processes. For each **Desorption** process the **Use interactions** checkbox should be **checked** and the **Bronsted-Polanyi factor** should be **1.0**.

For each **Diffusion** process the **Use interactions** checkbox should be **checked** and the **Bronsted-Polanyi factor** should be **0.5**.

You can now run another simulation, and compare the results with the previous one which did not use lateral interactions.

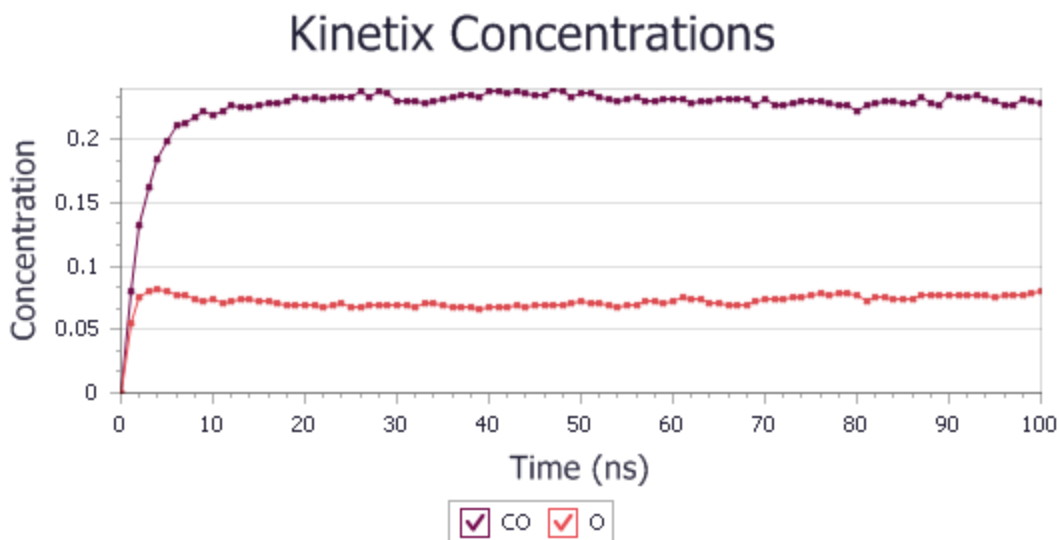
Open the **Kinetix Calculation** dialog. Ensure that the original **ZGBMultiSite.xkc** is the active document, and that the **Constant conditions** task is selected. On the **Job Control** tab uncheck the **Automatic** checkbox and set the **Job description** to **ZGB MultiSite With Interactions**.

Click the **Run** button and close the dialog.

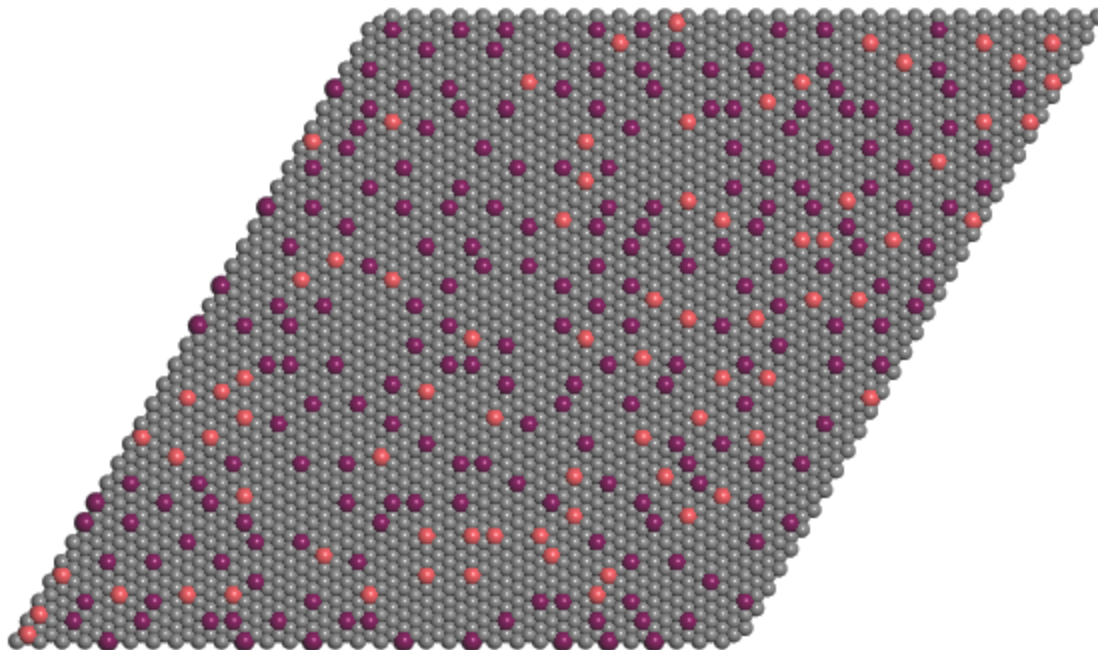
11. Analyzing the results

You should generate a chart of **Concentrations**, and also make the same changes to the display style of **ZGBMultiSite With InteractionsTraj.xkc** that you made for the earlier simulation.

These should look similar to the following:



Average concentrations during simulation with interactions



Configuration during simulation with interactions

You can now compare these results with those generated before you added the lateral interactions. You should be able to see immediately that the concentration of CO stabilizes at a value of about 0.23, much lower than previously, and that the oxygen concentration also stabilizes to about 0.06 whereas in the earlier simulation it dropped to about 0.03.

At this point you might like to export the trajectory in the form of an `.avi` files to play in a presentation. This is the end of the tutorial.

References

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- W.K. Offermans, A.P.J. Jansen, and R.A. van Santen, "Ammonia activation on platinum{111}; A density-functional theory study", *Surf. Sci.*, **600**, 1714-1734 (2006).
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- I.N. Yakovkin and N.V. Petrova, "Microscopic model of CO oxidation on Pt(111)", *Surf. Sci.*, **600**, 2600-2607 (2006).

R.M. Ziff, E. Gulari, Y. Barshad, "Kinetic Phase Transitions in an Irreversible Surface-Reaction Model", *Phys.Rev.Lett.*, **56**, 2553-2556 (1986)

Mesocite tutorials

The following tutorials illustrate how to utilize Mesocite's capabilities.

- [Coarse-grained molecular dynamics of a lipid bilayer](#)
- [Effects of surfactant on a lipid bilayer using DPD](#)
- [Effect of shearing on an oil droplet](#)
- [Calculating input parameters for a DPD simulation](#)

Coarse-grained molecular dynamics of a lipid bilayer

Purpose: Demonstrates how to set up and simulate a lipid bilayer using the mesoscale modeling tools

Modules: Materials Visualizer, Mesocite

Time: 🕒🕒🕒

Prerequisites: Building mesoscale molecules Visualizer Tutorial

Background

Coarse-grained molecular dynamics enables the simulation of longer time and larger length scales than is available to atomistic molecular dynamics. This is achieved by representing groups of several atoms as a single unit or bead. A forcefield is parameterized for the interaction between each type of bead in the system. In general, coarse-grained forcefields have to be parameterized for each system to be studied. However, [Marrink et al.](#) have generated a coarse-grained forcefield, MARTINI, which is parameterized for a wide range of organic moieties, focusing on simulations of biomolecular materials such as lipids.

Dipalmitoylphosphatidylcholine (DPPC) is a phospholipid and the major constituent of pulmonary surfactant. It is also used for research purposes in the study of liposomes, lipid bilayers, and models of biological membranes.

Materials Studio includes a slightly modified version of the MARTINI forcefield, MS Martini, which can be used to run coarse-grained molecular dynamics simulations of bead structures.

Introduction

In this tutorial, you will use Mesocite to run a coarse-grained molecular dynamics simulation of a lipid bilayer using the MS Martini forcefield. You will use the mesostructure building tools to build an initial starting structure and perform some equilibration of the bilayer.

This tutorial covers:

- [Getting started](#)
- [To create lipid and solvent molecules](#)
- [To apply the forcefield types and modify the forcefield](#)
- [To build the bilayer](#)
- [To optimize and equilibrate the structure](#)
- [To simulate the bilayer and analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CG_bilayer** as the project name, click the **OK** button.


The new project is created with *CG_bilayer* listed in the Project Explorer.

You can access the mesostructure building tools through the Build menu or using the Mesostructure toolbar. To use the toolbar make sure it is visible.

Select **View | Toolbars** from the menu bar and ensure the **Mesostructure** toolbar is enabled.

2. To create the lipid and solvent molecules


The first step is to define the bead types to be used in building molecules for lipid and solvent. You will use the same representation as used by Marrink et al. where 1 bead represents approximately four heavy atoms with an average mass of 72 g/mol and an effective radius of 2.35 Å.

Click the **Bead Types** button  on the Mesostructure toolbar to open the Bead Types dialog. Click the **Properties...** button to open the Bead Type Properties dialog. Click the **Defaults...** button to open the Bead Type Defaults dialog.

Set the **Mass** to **72** and the **Radius** to **2.35** and close the Bead Type Defaults and Bead Type Properties dialogs.

On the **Bead Types** dialog, define the following new bead types: **C**, **GL**, **NC**, **PO**, and **W**. Close the dialog.

With the defined bead types you can build the initial bead representations of the lipid and solvent.

Click the **Mesomolecule** button  on the Mesostructure toolbar to open the Build Mesomolecule dialog.

To build the lipid molecule in its characteristic conformation it is convenient to build the molecule in three steps. Start with the phosphate and choline head groups.

Define a repeat unit of **1** unit of **PO** and **1** unit of **NC**. Click the **Build** button.

Next add two glycerol beads to the phosphate group.

Delete the existing repeat unit definition and define a new repeat unit of **1** unit of **GL**. Select the **PO** bead in the structure and check the **Add to branch points** checkbox. Click the **More...** button to open the *Mesomolecule Branches* dialog and verify that **Branch from selected beads** is checked and the **Number of branches to attach** is set to **2**.

Close the dialog and click the **Build** button.

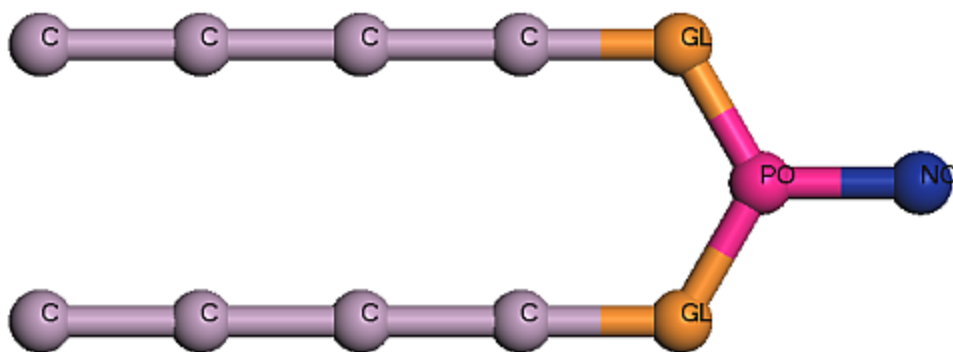
Tip: Use the *Label* dialog to apply *BeadTypeName* labels to your document.

Finally add the carbon tails to both glycerol beads. You will add four tails and delete the two that are not needed in order to generate a suitable starting geometry for the structure.

Delete the existing repeat unit definition and define a new repeat unit of **4** units of **C**. Select the two **GL** beads in the structure and click the **Build** button.

In the resulting structure delete the two branches that point out in the direction of the head group.

You should have a mesomolecule that looks the same as the image below.



Initial bead structure of the lipid in ball and stick display style, with the beads labeled by their *BeadTypeName*

Save the document and **close** the view. In the Project Explorer, **rename** the document to **DPPC.xsd**.

Finally build a solvent molecule. This will be a single bead of type **W**, representing four water molecules.

Delete the existing repeat unit definition and define a new repeat unit of **1** unit of **W**. Click the **Build** button and close the dialog.

Save and close the new document, then **rename** it to **solvent.xsd**.

3. To apply the forcefield types and modify the forcefield

You will use the MS Martini forcefield to perform all of the calculations in this tutorial. MS Martini is based on the MARTINI forcefield developed by Marrink et al. and has been parameterized to study lipid bilayers and other organic moieties. The basic forcefield uses an equilibrium bond distance of 4.7 Å and an equilibrium angle of 180° for all the forcefield types. For bonds that are non-linear (for example cis-unsaturated bonds) Marrink et al. have used a modified angle of 120° and they use this non-linear cis bond angle to represent the GL-PO-GL bond angle. This non-linear cis bond angle is not included in MS Martini by default and you will need to make a small modification to the provided forcefield to allow for its use.

As you are going to modify the existing MS Martini, you need to import it into the project.

Select **Modules | Mesocite | Forcefield Manager** from the menu bar to open the Mesocite Forcefield Manager. Select **MS Martini** and click the >> button to open the forcefield. Close the dialog.

Save and close the document, **rename** it to **MS Martini CIS.off**.

First you will define the forcefield types on the beads. These are the types listed in the MARTINI paper parameterizing the DPPC lipid.

BeadTypeName	MS Martini Forcefield Type	Charge
C	C1	0
GL	Na	0
PO	Qa	-1.0
NC	Q0	1.0
W	P4	0

As there are no bead typing rules in Mesocite, you need to manually assign forcefield types to the beads. You can do this using the Properties Explorer, or using the Mesocite dialog. In the following you will use the Mesocite dialog.

Select **Modules | Mesocite | Calculation** from the menu bar.

This opens the *Mesocite Calculation* dialog. The Setup tab is used to define the task, the Energy tab defines the forcefield and non-bond terms, and the Job Control tab is used to specify the calculation settings. As you will customize the forcefield, you should select the imported version of Martini rather than the standard version.

Select the **Energy** tab and select **Browse...** from the **Forcefield** dropdown list. On the Choose Forcefield dialog select **MS Martini CIS.off**.

Click the **More...** button for the **Forcefield** to open the Mesocite Preparation Options dialog.

The Mesocite Preparation Options dialog displays a list of all the forcefield types in the current forcefield. You can now assign selected types to selected beads in the lipid and solvent structures.

Open the **DPPC.xsd** document. In the 3D Viewer hold down the **ALT** key and **double-click** on any **C** bead.

All the beads of BeadTypeName C are selected.

Select **C1** in the list of forcefield types and click the **Assign** button. Repeat this for the **GL**, **PO**, and **NC** bead types, assigning the forcefield types in the table [above](#).

Two bead types, NC and PO, also have charges assigned. You need to assign the charges using the Properties Explorer or the Charges dialog.

Select the **PO** bead and, in the **Properties Explorer**, set the **Charge** to **-1**. Repeat this for the **NC** bead setting the **Charge** to **1**. Save and close the document.

Finally you need to specify the forcefield type of the solvent bead to be high polarity (P4).

Open the **solvent.xsd** document. Select **P4** on the Mesocite Preparation Options dialog, click the **Assign** button and close the dialog. Save and close the document.

Now you will modify the forcefield by adding an explicit bond angle term for the GL-PO-GL bond angle, which corresponds to the angle between forcefield types Na-Qa-Na.

Open the forcefield document **MS Martini CIS.off** and select the **Interactions** tab. Choose **Angle Bend** from the **Show interaction** dropdown list. In the empty row, set both **Fi** and **Fk** to **Na**, and set **Fj** to **Qa**. Change the **Functional Form** to **Cosine Harmonic**.

For the GL-PO-GL bond angle, Marrink et al. used an equilibrium bond angle, or T0, of 120° and a force constant of 10.8 kcal/mol (45 kJ/mol).

Set **T0** to **120** and **K0** to **10.8**. Save and close the forcefield document.

You are now ready to use the Mesostructure Template builder to build the mesomolecules into a bulk structure.

4. To build the bilayer

In this part of the tutorial, you will build the bulk structure containing the bilayer and the water using the Mesostructure builder. You will build a box which is $64 \times 64 \times 100 \text{ \AA}$. Into this box, you will add a slab former to pack with the DPPC lipid.

To calculate the depth of the slab you will use the experimental area per lipid, which is about 65 \AA^2 , and the fact that in Martini 1 solvent bead represents four water molecules ([Marrink et al.](#)). First determine the volume of a bead, using the density and molar weight of water.

Water has a density of 1 g/cm^3 and molar weight of 18 g/mol . Hence the volume of 1 water molecule is $18/N_{\text{av}} \text{ cm}^3$, or $18/N_{\text{av}} 10^{24} \text{ \AA}^3 = 29.9 \text{ \AA}^3$, where $N_{\text{av}} = 6.02 \times 10^{23}$ is Avogadro's number. As there are four water molecules per bead, the volume of a bead is $4 \times 29.9 = 119.6 \text{ \AA}^3$.

Now determine the number of lipid beads using the experimental area per lipid.

The total area of the slab is $64 \times 64 = 4096 \text{ \AA}^2$. As the area per lipid is 65 \AA^2 there are $4096/65 = 63$ lipids on either side of the bilayer, or $2 \times 63 = 126$ in total. Each lipid contains 12 beads, therefore the slab contains $126 \times 12 = 1512$ lipid beads.

Using the number of beads and their volume, you can calculate the depth of the slab.

There are 1512 lipid beads with a volume of 119.6 \AA^3 per bead, so the total volume is $1512 \times 119.6 = 180835 \text{ \AA}^3$. Since the area is 4096 \AA^2 , the depth must be $180835/4096 = 44 \text{ \AA}$.

Now you can build the template, starting with a system former.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. Change both the **X** and **Y Extents** to **64** and the **Z Extent** to **100**. In the **Filler** text box, enter **solvent**. Click the **Build** button.

A new template document is created containing a single blue system former. Add a slab of depth 44 \AA to the template.

Change the **Former type** to **Slab**. Change the **Depth** to **44** and the **Orientation** to **Along Z**.

You will need to use the surface packing to pack the lipid heads onto both surfaces.

Check the **Enable surface packing** checkbox and enter **lipid** in the **Filler** text box. Click the **Add** button and close the dialog. **Save** the document.

Now that you have built the template, you need to fill it with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog.

You need to specify the components that you want to associate with the fillers.

Click in the **Mesoscale Molecule** column for the **solvent** filler and select **solvent.xsd**. For the **lipid** filler select the **DPPC** structure.

Confirm that the target **Density** is set to **1 g/cm³**.

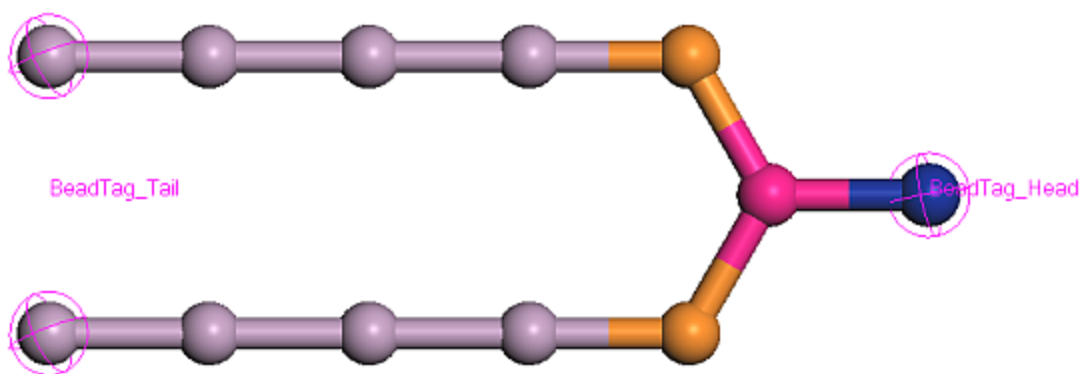
On the **Options** tab, **uncheck** the **Randomize conformations** checkbox.

Before building the mesostructure, you need to define the head and tail beads on the lipids so that the lipid heads stick to the surface of the slab former.

Click the **More...** button to open the Bead Packing Options dialog. Change focus to the lipid structure in **DPPC.xsd**.

Select the **NC** head bead and click the **Create bead Head set from selection** button. Select both terminating tail beads, change the **Bead tag** to **Tail** and click the **Create bead Tail set from selection** button. Close the dialog.

The labeled DPPC bead structure is shown below.



Prepared DPPC lipid structure

You can now build the mesostructure.

Make the template the active document. On the **Build Mesostructure** dialog, click the **Build** button and close the dialog.

A 3D Atomistic Structure document is returned containing the solvent and lipid molecules packed in different former areas of the template.

In the Project Explorer, **rename** the document to **bilayer.xsd**.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

You have now prepared the initial structure. The next stage is to equilibrate the structure and perform a production run.

5. To optimize and equilibrate the structure

The structures generated by the Mesostructure Builder are very rough and will have overlapping beads. Therefore, before trying to run some dynamics on this structure, you should optimize the geometry first to remove close contacts and any initial stresses in the system.

The optimization is best carried out in two steps, by first optimizing the intermolecular interactions, keeping the internal conformation rigid, followed by an optimization of all degrees of freedom. This reduces the chance that bead overlap is resolved by introducing unrealistic bond lengths or angles.

Open the **Mesocite Calculation** dialog, on the **Setup** tab change the **Task** to **Geometry Optimization** and click the **More...** button to open the Mesocite Geometry Optimization dialog. Check the **Keep motion groups rigid** checkbox.

By keeping motion groups rigid, the distance between all atoms in a motion group is fixed during the optimization. To keep all molecules rigid, define motion groups for each molecule.

Open **bilayer.xsd**, click the **More...** to open the Motion Groups dialog. Click the **Assign automatically** button and close the dialog. Close the **Mesocite Geometry Optimization** dialog.

Now you can perform an initial geometry optimization.

On the **Mesocite Calculation** dialog, click the **Run** button.

The optimization may take a few minutes to complete. You can look at the live update charts to see the energy profile.

Open **bilayer Energies.xcd**.

You should see a very high initial energy which drops rapidly. This is due to the overlaps from the initial model build process, which are gradually removed by the optimizer.

Once you have completed this initial optimization, the next stage is to run another minimization, this time without constraining the motion groups and allowing the cell parameters to be optimized.

Open **bilayer Mesocite GeomOpt\bilayer.xsd**.

Open the **Mesocite Geometry Optimization** dialog and **uncheck** the **Keep motion groups rigid** checkbox. **Check** the **Optimize cell** checkbox and close the dialog.

Click the **Run** button.

Now that you have removed the major overlap using optimization, you can use dynamics at a fixed temperature and pressure to equilibrate further.

Make sure that **bilayer Mesocite GeomOpt\bilayer Mesocite GeomOpt\bilayer.xsd** is the active document. On the **Setup** tab change the **Task** to **Dynamics** and click the **More...** button to open the Mesocite Dynamics dialog. Set the **Time step** to **40 fs** and change the **Ensemble** to **NPT**.

The time step of 40 fs is the time step used by Marrink et al. in their parameterization of the MARTINI forcefield. The NPT ensemble is used to equilibrate the pressure and temperature in the system. You will initially use the Velocity scaling thermostat to equilibrate the temperature in the system and the Andersen barostat to relax the residual stress. Velocity scaling is a very approximate thermostat and is only useful for quickly bringing the system closer to equilibrium.

Select the **Thermostat** tab and set the **Thermostat** to **Velocity Scale**. On the **Barostat** tab set the **Barostat** to **Andersen** and close the dialog.

Click the **Run** button on the Mesocite Calculation dialog.

The structure should now be suitable to carry out a production run and analyze the results.

6. To simulate the bilayer and analyze the results

The final production run will be a long NPT dynamics with the Nose thermostat and Andersen barostat.

Make **bilayer.xtd** in the **bilayer Mesocite Dynamics** folder the active document.

Open the Mesocite Dynamics dialog and select the **Thermostat** tab, set the **Thermostat** to **Nose**. On the **Dynamics** tab set the **Frame output every** to **250** steps and close the dialog.

Tip: In a real calculation you would run a much longer production run, monitoring the density plot to assess when it is converged.

You can restart the calculation so that the velocities on the atoms from the previous simulation are used as starting velocities for this simulation. As you have already performed some equilibration of the velocities, restarting enables you to re-use those velocities.

On the **Mesocite Calculation** dialog, check the **Restart** checkbox and click the **Run** button. On the warning dialog click the **Yes** button. Close the **Mesocite Calculation** dialog.

This calculation will take several minutes to complete. When the calculation completes, you can change focus to the trajectory and perform some analysis.

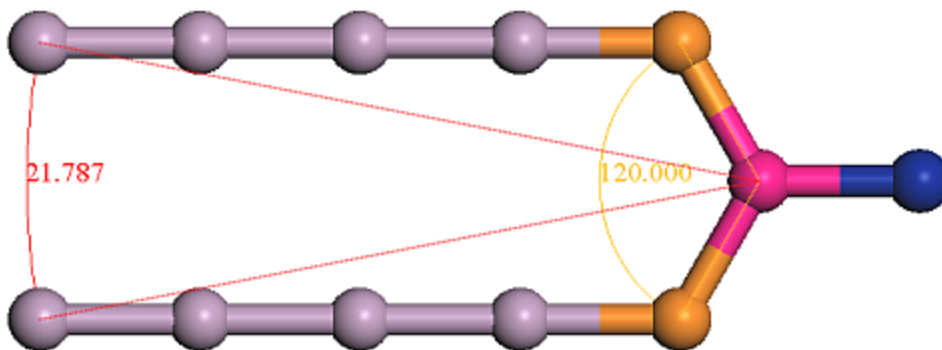
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

You are now ready to perform some analysis on the structure.

For this analysis, you will look at the difference in the angle distribution between the GL-PO-GL bond angle and the C-PO-C angle. Initially, you will edit the DPPC molecule and add GL-PO-GL and C-PO-C angle monitors. You will perform a pattern match against the trajectory to find all the GL-PO-GL and C-PO-C angles and then analyze the angle distributions.

Open the trajectory document in the **bilayer Mesocite Restart** folder and the initial DPPC structure.

Make **DPPC.xsd** the active document. Define two bond angles as illustrated below. Select the **GL-PO-GL** bond angle.



The two bond angles that can be used in the analysis

Now you can use the pattern matching tools to create two sets of these bond angles on the trajectory.

Select **Edit | Find Patterns** from the menu bar to open the Find Patterns dialog. Select **DPPC.xsd** as the **Pattern document** ensuring that the GL-PO-GL angle is still selected. Change the **Match property** to **BeadTypeName**. Make **bilayer.xtd** the active document and click the **Find** button.

Angle monitors are created on all the GL-PO-GL bond angles in the system and they are all selected. You can create a set of these so that you can select them later and use the set in the analysis.

Click the **New Sets...** button to open the Define New Set dialog. Enter the name **GLPOGLAngles** and click the **OK** button. In **bilayer.xtd**, deselect the angles.

You can now use the Find Patterns tool to find the C-PO-C angle that you defined and create a set for those angles.

Change back to **DPPC.xsd** and select the **C-PO-C** angle. Make **bilayer.xtd** the active document and, on the **Find Patterns** dialog, click the **Find** button.

Click the **New Sets...** button to open the Define New Set dialog and enter the name **CPOCAngles**. Click the **OK** button and close the **Find Patterns** dialog. Click anywhere in **bilayer.xtd** to deselect the angles.

You have created two sets containing the two different angles. Now you can analyze their distribution.

Select **Modules | Mesocite | Analysis** from the menu bar to open the Mesocite Analysis dialog.

There are many different types of analysis that you can perform on a trajectory. For this example, you will perform an Angle distribution analysis.

In the **Analysis** section, select **Angle distribution**. Select **GLPOGLAngles** from the **Sets** dropdown list and click the **Analyze** button.

Select **CPOCAngles** from the **Sets** dropdown list and click the **Analyze** button.

You should see two different charts. The restricted GL-PO-GL angle has a peak centered around 100° and for the C-PO-C angles there is a broader peak spread between 10° and 80°. This shows the flexibility of the tails in comparison to the constrained head angle.

This is the end of the tutorial.

References

S.J. Marrink, H.J. Risselada, S. Yefimov, D.P. Tieleman, A.H. de Vries., "The MARTINI forcefield: coarse grained model for biomolecular simulations.", *J. Phys. Chem. B*, 111:7812-7824, 2007.

Effects of surfactant on a lipid bilayer using DPD

Purpose: Demonstrates how to set up and simulate a lipid bilayer using the mesoscale modeling tools

Modules: Materials Visualizer, Mesocite

Time: 🕒🕒🕒

Prerequisites: Building bulk mesostructures Visualizer Tutorial

Background

The DPD method is designed to allow hydrodynamic behavior in fluids to be captured. In addition, the use of a soft potential allows much larger time steps than are traditionally available in either classical atomistic calculations or coarse-grained molecular dynamics.

The ability to study long time scales and to include hydrodynamic behavior makes DPD the perfect tool for studying lipid and surfactant systems. In this tutorial, based on a paper by [Groot and Rabone](#), you will simulate the effect of adding surfactant to a lipid membrane.

Introduction

In this tutorial, you will use Mesocite to run several mesoscale dynamics simulation of different lipid bilayers using the DPD method. You will use the mesostructure building tools to build an initial starting structure and perform some equilibration of the bilayers. You will then perform a production run and use the analysis tools to examine the structure of the bilayer.

This tutorial covers:

- [Getting started](#)
- [To create the input structure](#)
- [To equilibrate the structures](#)
- [To perform a production run](#)
- [To analyze the results](#)

Note: Completion of this tutorial entails running a DPD calculation. Depending on the configuration of your computer server, this calculation could take a considerable amount of time.

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DPD_lipid** as the project name, click the **OK** button.

The new project is created with *DPD_lipid* listed in the Project Explorer.

2. To create the input structures

The first step is to build mesomolecule models of water, lipid, and surfactant molecules. Groot and Rabone used a coarse graining approach where one bead represents three molecules of water (W). As

the volume of a water molecule at room temperature is about 30 \AA^3 , they defined the volume of a bead to be $(3 \times 30) = 90 \text{ \AA}^3$. At the standard density of 3 beads per unit volume, this translates to a fundamental length unit of $(3 \times 90)^{1/3} = 6.46 \text{ \AA}$. Likewise, given that the mass of a water molecule is 18 amu, the mass of a bead is $(3 \times 18) = 54 \text{ amu}$. You will use these mass and length units based on water in this tutorial. The length unit will also serve as the diameter of a bead, corresponding to a radius of $6.46/2 = 3.23 \text{ \AA}$.

In the coarse graining approach of Groot and Rabone, one bead also maps on three carbon atoms (C), or 1.5 ethylene oxide groups (E). These have slightly different densities and molecular weights. Whilst you could have beads with different masses in the DPD calculation, there has been little validation on the effect of this. Therefore, you will use same mass for all beads in this tutorial. As the C and E beads are used in both the lipid and surfactant molecules, you will differentiate between them using CL and EL for the lipids, and CS and ES for the surfactants. This is not essential for the calculation but does add clarity to the visualization of the bilayer.

Select **Build | Build Mesostructure | Bead Types** from the menu bar to open the Bead Types dialog. Click the **Properties...** button to open the Bead Type Properties dialog and click the **Defaults...** button to open the Bead Type Defaults dialog. Set the **Mass** to **54** and the **Radius** to **3.23**. Close the Bead Type Defaults and Bead Type Properties dialogs.

Define the following new bead types: **CL**, **CS**, **EL**, **ES**, **H**, and **W** and close the Bead Types dialog.

Note: The bead radius is used in the mesomolecule builder to determine the bond length. Otherwise it is used only for visualization and has no effect on the calculation. The bead mass, on the other hand, is used in the DPD simulation.

Now you have defined the bead types, you can create the structures.

Select **Build | Build Mesostructure | Mesomolecule** from the menu bar to open the Build Mesomolecule dialog. Build a mesomolecule of **1** unit of **W** and rename the new document to **water.xsd**.

Build a mesomolecule of **4** units of **ES** and **4** units of **CS**. Rename the document **surfactant.xsd**.

Build a mesomolecule of **2** units of **H** and **1** unit of **EL**.

In the resulting structure, select the **EL** bead. Define a sequence of **5** units of **CL**. Check the **Add to branch points** checkbox and click the **Build** button. Rename the document **lipid.xsd**. Close the dialog and click anywhere in the 3D Viewer to deselect any items.

It is convenient at this point to define forcefield types on the three molecules. This avoids having to type individually all the bulk structures that you are going to build later. You can assign forcefield types using the Properties Explorer or the Type facility of the Create DPD Forcefield dialog. In this tutorial you will use the Type functionality.

Select **Mesocite | Forcefield Manager** from the menu bar to open the Mesocite Forcefield Manager dialog. Click the **DPD...** button to open the Create DPD Forcefield dialog. Ensure that **lipid.xsd** is the active document and click the **Type** button. Repeat this for the documents **surfactant.xsd** and **water.xsd**. Close the Mesocite Forcefield Manager dialog.

Later in this tutorial you will use the other controls on the Mesocite Forcefield Manager dialog, you can ignore these for now.

Tip: You can use the Label dialog to verify the forcefield types, by applying a label for the ForcefieldType property of a bead.

Now you have built the components, you need to construct the cell containing these mesomolecules. You will build several cells containing varying concentrations of lipid and surfactant but keeping a fixed volume of water. You can use the Mesostructure template tools to pack the membrane molecules into a slab which will then force the bilayer to form. In this tutorial you will build a slab of 30 Å in a box of 90 × 90 × 90 Å, such that the solvent occupies 70% of the volume, and the membrane 30%.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. Change all the **Extent (X Y Z)** values to **90**. In the **Filler** text box, enter **solvent** and click the **Build** button.

To build the slab for the membrane you will add a slab former to the template, positioned in the middle of the box with a normal along the x direction.

On the **Build Mesostructure Template** dialog, change the **Former type** to **Slab**. Set the **Depth** to **30.0** and enter **membrane** in the **Filler** text box. Click the **Add** button and close the dialog.

Now that you have built the template, you need to fill it with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog. Make sure that the template is in focus.

You need to specify the components that you want to use as the fillers - you will fill the 'solvent' with water and 'membrane' with lipid and surfactant.

Click in the **Mesoscale Molecule** column for the **solvent** filler and select **water.xsd**. Repeat this for the **membrane** filler, selecting **lipid.xsd** and **surfactant.xsd**.

For the **membrane** filler, set the **Relative Amount** of **lipid** to **50** and **surfactant** to **50**.

This will build a box with 70% volume fraction of water beads and 30% volume fraction of 50/50 mixture of lipid and surfactant. Due to the differing number of beads in the lipid and surfactant molecules, this will not give you a molar ratio of 50:50.

Before building the box, you need to specify the target density. By setting the density to that of water (1 g/cm³) the resulting structure has a reduced density of 3 beads per cubic length scale. This follows from the mass scale of 53 amu and the length scale of 6.46 Å. A reduced density of 3 is the value most commonly used in DPD, and was also used in the study by Groot and Rabone.

On the Components tab, make sure the **Density** is set to **1 g/cm³**. Click the **Build** button. Rename the document **W70_L50_S50.xsd**.

As you will be repeating this for several runs, you should build several cells at concentrations ranging from 100% lipid to 100% surfactant.

Ensure that the template is the active document. Modify the **Relative Amount** to **lipid 20** and **surfactant 80**. Click the **Build** button. Rename the document **W70_L20_S80**.

Make the template the active document and modify the **Relative Amount** to **lipid 0** and **surfactant 100**. Click the **Build** button. Rename the document **W70_S100**.

Make the template the active document and modify the **Relative Amount** to **lipid 100** and **surfactant 0**. Click the **Build** button. Rename the document **W70_L100**. Close the dialog.

You have now built the initial structures. The next stage is to equilibrate the structures.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To equilibrate the structures

In this section of the tutorial, you will begin to equilibrate the structures by performing geometry optimization. The first step is to set up the forcefield. Since you have assigned forcefield types on the molecules, these should already be set on the structures built from them.

Open **W70_L50_S50.xsd**. Select **Modules | Mesocite | Forcefield Manager** from the menu bar and click the **DPD...** button to open the Create DPD Forcefield dialog.

You should see a matrix of forcefield types corresponding to those in the document. The values are currently displayed in physical units (based on kcal/mol and Å) whereas DPD work, including that of Groot and Rabone, has usually been carried out using reduced units. Mesocite DPD allows you to set up the calculation using either physical or reduced units (in which case the conversion to physical units will be performed automatically). You will use reduced units here.

Change the **Units** to **Reduced** and click the **More...** button to open the Mesocite DPD Units dialog.

You need to enter the Length and the Mass scales to be used for the unit conversion. As discussed earlier in the coarse graining method of Groot and Rabone, one length unit corresponds to 6.46 Å and one mass unit to the mass of a bead, 54 amu.

Change the **Length scale** to **6.46** and the **Mass scale** to **54**. Close the dialog.

It can be shown that the DPD repulsion parameters a_{ij} can be related to the Flory-Huggins Chi parameter χ as follows:

$$a_{AB}(\rho = 3) = 25 + 3.50\chi$$

where the a_{ij} are in reduced units.

Tip: There are various ways of estimating χ . You can derive it from Solubility Parameters, as calculated by Synthia or from Cohesive Energy Density calculations using Forcite Plus, COMPASS, and Amorphous Cell. There are various tables of χ values for polymers derived from experimental work. Alternatively, you can use the Blends module to get a first estimate of the value of χ . In many cases, you might use a mixture of these techniques based on what you have derived or have used in the past and fit them to reproduce a known mesoscale structure.

In this tutorial, you will use the "set1" values of a_{ij} as used by Groot.

	CL	CS	EL	ES	H	W
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CL	78					
CS	78	78				
EL	86.7	86.7	78			
ES	86.7	86.7	78	78		
H	104	104	79.3	79.3	78	
W	104	104	79.3	79.3	79.3	78

The diagonal elements used by Groot and Rabone are chosen such that a monomer bead fluid has the compressibility of water. This value scales with the number of water molecules represented by a bead (Groot and Rabone, 2001). The default value in Mesocite (25) is based on the case where a bead represents one water molecule (Groot and Warren, 1997). Since in the present case a bead represents 3 water molecules, the diagonal terms are about three times higher than the default.

On the **Create DPD Forcefield** dialog edit the matrix and set the **Repulsions** to the values shown in the table above. Click the **Create** button and close the dialog.

Tip: You can expand the dialog to see the whole matrix by dragging one of its corners.

When you click the Create button, a new Forcefield document is created and listed as `W70_L50_S50.off` in the project explorer. The values in the forcefield document are written in physical units and the forcefield is automatically set on the Energy tab of the Mesocite Calculation dialog.

Tip: As the interactions are stored in a forcefield document, you can add other interactions to the calculation such as bond angle terms to control rigidity of the bonds. You can also edit the Description of the forcefield to annotate it with references, updates, and so on.

You can change the name of the forcefield document so that it is not specific to a particular structure. As these are generated from set1 in the Groot and Rabone paper, you can indicate that in the name.

Rename the forcefield document **GrootRaboneSet1.off**.

When you change the name of the forcefield, this is updated on the Energy tab of the Mesocite Calculation dialog.

Select **Modules | Mesocite | Calculation** to open the Mesocite Calculation dialog and select the **Energy** tab.

You should see that the Forcefield is set to `\GrootRaboneSet1`. As DPD uses very short soft interactions, you can also decrease your calculation time by changing the van der Waals nonbond cutoff distance. Again, you should set this to the length scale that you used earlier. If you leave this at the default value, the calculation time will increase but without benefit.

Make **W70_L50_S50.xsd** the active document.

Click the **More...** button for the **Summation method** section to open the Mesocite Non-Bond Options dialog. Set the **Cutoff distance** to **6.46** and the **Spline width** to **0**. Close the dialog.

Note: It is important that you have the right 3D periodic structure in focus when you change the cutoff distance, since Mesocite has separate settings for periodic and nonperiodic structures.

Before starting the DPD calculation, you should optimize the structure.

Select the **Setup** tab on the **Mesocite Calculation** dialog and change the **Task** to **Geometry Optimization**. Click the **Run** button.

Note: You should always pre-optimize structures in this way. Although you may not obtain a perfectly optimized structure, the geometry optimization will remove discrepancies between the structure and the forcefield. In particular, the Mesostructure Builder has to estimate an initial connector length, and this may not be a good match for the spring parameters defined by the forcefield.

When the calculation is complete, you should see that the energy has dropped significantly indicating an improvement in the initial geometry.

Repeat the Geometry Optimization calculation on the other three structures.

When all the calculations are complete, tidy up the project.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To perform a production run

Now that you have performed some initial geometry optimization, you can run the DPD dynamics calculation and analyze the mean-squared displacement (MSD) of the water beads.

Ensure that the optimized **W70_L50_S50.xsd** is the active document.

On the **Mesocite Calculation** dialog, change the **Task** to **DPD** and click the **More...** button.

You will run 50,000 steps of DPD dynamics with a frame output every 2000 steps.

On the Mesocite DPD dialog change the **Number of steps** to **50000** and the **Frame output every** to **2000** steps. Close the dialog.

Note: Although you can change the temperature in Mesocite DPD, the repulsion matrix used by Groot and Rabone was parameterized for room temperature. In general, changing the temperature will in principle also require the repulsion matrix to be changed.

You are now ready to run the calculation.

With the optimized structure in focus click the **Run** button on the **Mesocite Calculation** dialog.

This calculation is quite long and will take some time to complete.

Repeat the DPD calculation on the other three optimized structures.

When all the calculations are complete, you can move onto the next step to perform the MSD analysis and compare the effect of adding surfactant to the lipid membrane on the diffusion of water.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

5. To analyze the results

The first part of the analysis is a visual inspection of the results. This will be easier if you change the visibility of the water beads. As you need them later in the analysis, you can create a set of the water

beads.

Change focus to one of the trajectories. Hold down the **ALT** key and double-click on one of the water beads. Select **Edit | Edit Sets** from the menu bar to open the Edit Sets dialog. Click the **New...** button to open the Define New Set dialog.

Enter the name **water** and uncheck the **Show set** checkbox. Click the **OK** button.

Repeat this for all the trajectories and close the dialog.

You can now access the set of water beads in the analysis without having them visible.

Right-click in the 3D atomistic document and select **Display Style** to open the Display Style dialog. On the **Bead** tab, change the **Display style** to **None**.

Repeat this for all the trajectories and close the dialog.

Apart from a visual inspection, you can also view the concentration profiles of the water molecules in the x-direction. You can use this to identify holes in the layer.

Select **Modules | Mesocite | Analysis** to open the Mesocite Analysis dialog. Select **Concentration profile**.

You can specify the frame range, specific beads, and the direction. If you don't choose a direction, you will automatically get the profiles in the X, Y and Z axis. You will examine the concentration profile in the x-direction for the water beads from frame 6 to the end of the trajectory.

Click the **Trajectory ...** button to open the **Trajectory Specification** dialog. Enter **6-END** and close the dialog. Select **water** from the **Sets** dropdown list and check the **Specified direction** checkbox. Click the **Analyze** button.

Repeat this for all trajectories, resetting the **Trajectory Specification** to **6-END** for each.

For each trajectory a study table and a chart is generated, containing the raw concentration data and a plot of concentration as a function of distance respectively.

You should see that as you increase the percentage of surfactant, the lipid bilayer becomes less stable. This results in the water beads moving through the bilayer. For the 100% lipid system, there are no holes in the bilayer and the water cannot penetrate from one side to the other. However, at 100% surfactant, the relative concentration of the water beads is high where the layer should be - indicating there are holes in the layer.

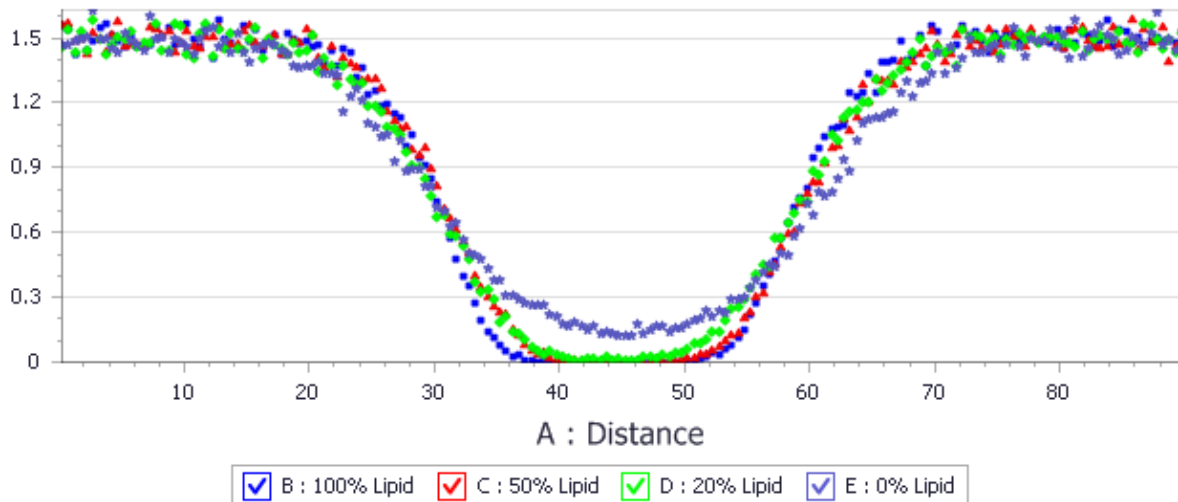


Chart containing the overlaid concentration profiles

Note: You can generate the above chart by copying and pasting data from the generated study tables into a new study table and using the Plot Graph functionality.



You can look at the mean-squared displacement of the water beads. You can calculate the overall mean square displacement and anisotropic components. You want to compare the MSD of the water beads in the XX direction.

Select **Modules | Mesocite | Analysis** and select **Mean square displacement**. Select **water** from the **Sets** dropdown list and check the **Include anisotropic components** checkbox. Click the **Analyze** button.

Repeat this for all trajectories.

The slope of the chart indicates the speed of the diffusion of the water beads with a steeper slope meaning fast diffusion. Examine the xx component of the diffusivity.

Right-click on the project root and select **New | Study Table Document** from the shortcut menu. Rename the new document **MSD_XX_comparison.std**.

In the **W70_L100 Mesocite MSD.std** study table select the **xx component** tab and select both columns. Click the **Copy** button . In **MSD_XX_comparison.std** select the first two columns and click the **Paste** button .

Right-click in the **MSD** column header and select **Properties** from the shortcut menu to open the Column Properties dialog. Amend the **Description** to **100% lipid**.

The xx components of the MSD for the other trajectories can be added to this.

For **W70_L50_S50 Mesocite MSD.std** choose the **xx component** tab and select and **Copy** only column **B**. Select column **C** in **MSD_XX_comparison.std** and **paste** the data, rename the column **50% lipid**.

Repeat this for **W70_L20_S80 Mesocite MSD.std** and **W70_S100 Mesocite MSD.std**, pasting into columns **D** and **E** of the new study table and amending the column names accordingly.

Now the columns in the comparison study table can be used to plot the XX MSD components for each combination of lipid, water, and surfactant.

Select all the columns in **MSD_XX_comparison.std** and click the **Quick Plot** button .

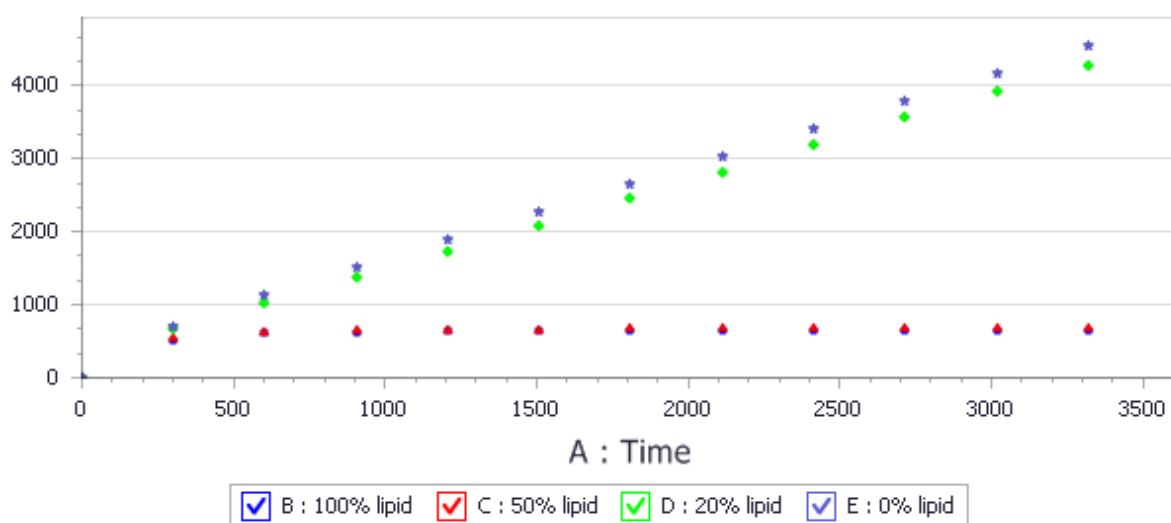


Chart containing the overlaid xx components of the diffusivity of the water beads

Again, as you increase the percentage of surfactant, the diffusivity increases. In the original paper, the membrane started to break down around 80% lipid content. If you run the calculation for longer, the diffusivity will tend to increase as the bilayer absorbs water.

This is the end of the tutorial.

References

R.D. Groot and K.L. Rabone, "Mesoscopic Simulation of Cell Membrane Damage, Morphology Change, and Rupture by Nonionic Surfactants", *Biophysical Journal*, 2001, **81**, 725-736.

R.D. Groot and P.B. Warren, "Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation", *J. Chem. Phys.*, 1997, **11**, 107.

Effect of shearing on an oil droplet

Purpose: Demonstrates the use of shearing in DPD and the effect on morphology of an oil droplet in water

Modules: Materials Visualizer, Mesocite

Time: 🕒 🕒

Prerequisites: Building bulk mesostructures Visualizer Tutorial

Background

Production of new materials often involves the use of processing conditions to affect the properties of the final product. A dispersion of oil in water forms a droplet with a distribution of sizes which can be controlled by shearing the system. DPD provides the capability to simulate shearing at a mesoscale level and visualize the effect of shear on a system.

This tutorial is inspired by some early work done on DPD, studying shearing effects on oil droplets, carried out by [Clark et al.](#) and [Jones et al.](#)

Introduction

In this tutorial, you will use Mesocite to run a DPD shearing calculation on an oil-water droplet. You will specify the initial conditions using the mesostructure builder, run an equilibration DPD calculation, and then perform a shear calculation and visualize the results.

This tutorial covers:

- [Getting started](#)
- [To create the input structure](#)
- [To equilibrate the structures](#)
- [To perform a shearing run](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DPD_shear** as the project name, click the **OK** button.

The new project is created with *DPD_shear* listed in the Project Explorer.

2. To create the input structures

The first step is to build mesomolecule models of water and oil. When working with DPD, you can either spend time accurately parameterizing the system by using molecular dynamics or other methods, use data from published simulations, or use your chemical intuition to derive the parameters and tune the parameters to a known system. As there have been several studies of oil/water systems, you will use parameters from a previous publication.

The inputs to the Mesocite DPD simulation require the parameterization of the contents of a bead. For this simulation, you will use the default parameters of bead mass of 100 amu. As a water molecule has a

mass of 18 amu, this means that one bead represents about 5 molecules of water. As the mass of a CH₂ oil group is 14 amu, each oil bead represents a chain of approximately 7 CH₂ groups.

Select **Build | Build Mesostructure | Bead Types** from the menu bar to open the Bead Types dialog.

Define the following new bead types: **Oil** and **Water**, close the Bead Types dialog.

Note: The bead radius is only used for visualization and has no effect on the calculation. However, the bead mass is used in the DPD simulation.

Note: Whilst you could have beads with different masses in the DPD calculation, there has been little validation on the effect of this. Therefore, you are advised to use the same mass for all beads.

Now you have defined the bead types, you can create the structures.

Select **Build | Build Mesostructure | Mesomolecule** from the menu bar to open the Build Mesomolecule dialog. Build a mesomolecule of **1** unit of **Water** and rename the new document to **water.xsd**.

Build a mesomolecule of **1** unit of **Oil** and rename the document **oil.xsd**. Close the **Build Mesomolecule** dialog.

Before continuing, you can set the forcefield type for the beads. The forcefield type is preserved when mesostructures are built, so defining this now will save time later. You can use the Properties Explorer to assign a forcefield type by selecting the bead and editing the ForcefieldType property. Alternatively, you can use the Type button which will set the forcefield type to the same value as the BeadTypeName. This is accessed from the Forcefield Manager for Mesocite.

Select **Modules | Mesocite | Forcefield Manager** from the menu bar to open the Mesocite Forcefield Manager. Click the **DPD...** button.

This opens the Create DPD Forcefield which enables you to create DPD specific forcefields by entering the repulsive interaction parameter in either physical or reduced units. It also enables you to assign forcefield types.

With **oil.xsd** in focus, click the **Type** button. Change focus to **water.xsd** and click the **Type** button.

Close the **Mesocite Forcefield Manager** dialog.

You can ignore the Repulsions that are displayed in the Create DPD Forcefield dialog at the moment. You will set these correctly in the next section.

Now you have built the components, you need to construct the cell containing these mesomolecules. You will build a mesostructure template which contains an oil droplet. In this example, you will use default values to build a box of 100 × 100 × 100 Å and place a droplet former of radius 20 Å.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. In the **Filler** text box, enter **water** and click the **Build** button.

This creates a new mesoscale document named **Mesostructure Template.msd**. You can either start this calculation from random starting conditions or you can define a droplet former. In this case, you will define a droplet former.

On the **Build Mesostructure Template** dialog, change the **Former type** to **Droplet**. Set the **Radius** to **20.0** and enter **oil** in the **Filler** text box. Click the **Add** button and close the dialog.

Now that you have built the template, you need to fill it with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog. Make sure that **Mesostructure Template.msdl** is in focus.

You need to specify the components that you want to use as the fillers - you will fill the 'water' filler with water and 'oil' filler with oil

Click in the **Mesoscale Molecule** column for the **water** filler and select **water.xsd**. Repeat this for the **oil** filler, selecting **oil.xsd**.

You can also control the density, the conformations of the mesoscale molecules, and the surface packing capabilities. In this example, you will leave these at their default values.

Click the **Build** button and close the dialog. Rename the new document **Water_Oil_20rad.xsd**.

You have now built the initial structure. The next stage is to equilibrate the structure.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To equilibrate the structures

The first step before equilibration is to create a DPD forcefield. You can choose whether to set up the DPD calculation in Physical or Reduced units. As most papers still refer to reduced units for the repulsive interactions, you will use reduced units.

Open the **Mesocite Forcefield Manager** dialog and click the **DPD...** button.

There are a variety of papers which quote interaction parameters ranging from 30 to 80 between the oil and water beads. As it is known that oil and water are very repulsive, you will use a value of 50.

Open **Water_Oil_20rad.xsd**. On the Create DPD Forcefield dialog, change the **Units** to **Reduced**. Set the value for the **Oil-Water** cell in the **Repulsions** grid to **50**.

Click the **Create** button and close the **Mesocite Forcefield Manager** dialog.

A forcefield document named **Water_Oil_20rad.off** is created. This will be used in the DPD calculation and is set as the current forcefield in the Mesocite Calculation dialog.

Note: If you are modifying the bead parameters such as the bead mass from their defaults, you should also set the Length and Mass scale before creating the forcefield. However, as you are using default parameters you do not need to change any of the settings.

Usually when dealing with output from the Mesostructure Builder, you are advised to perform a short geometry optimization before continuing with the DPD run. This is performed to equilibrate bond lengths in the system but, as you have no bonds between the particles, you can just run a DPD calculation.

Select **Modules | Mesocite | Calculation** from the menu bar. Select **DPD** from the **Task** dropdown list and click the **More...** button to open the Mesocite DPD dialog.

You should increase the number of steps so that you can see how stable the droplet is.

On the Mesocite DPD dialog change the **Number of steps** to **10000** and the **Frame output every** to **1000** steps. Close the **Mesocite DPD** dialog.

As the potential used in DPD is a soft harmonic potential which has finite range, you can also decrease your calculation time by changing the van der Waals non-bond cutoff distance. Again, you should set this to the value of the Length scale. If you leave this at the default value, the calculation time will increase but without benefit.

Make **Water_Oil_20rad.xsd** the active document.

Select the **Energy** tab and click the **More...** button for the **Summation method** section to open the Mesocite Non-Bond Options dialog.

Set the **Cutoff distance** to **8.0 Å** and the **Spline width** to **0 Å**. Close the dialog.

On the Energy tab, you should also see that the Forcefield is set to `\Water_Oil_20rad`.

You are now ready to perform a DPD equilibration run.

On the Mesocite Calculation dialog, click the **Run** button and close the dialog.

The calculation will take several minutes to complete. When the calculation is complete, you can animate the trajectory to see how the particles are moving in the box. You should set the Lattice Display Style to In-Cell to keep the beads in the cell.

Change focus to **Water_Oil_20rad.xtd**. Right-click and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Lattice** tab change the **Style** to **In-Cell**.

Hold down the **ALT** key and **double-click** on one of the **Water** beads. On the **Bead** tab of the Display Style dialog select **None**. Close the dialog.

You should also set the animation options for the trajectory so that the atom positions are updated and the animation stops at the last frame.

Click the **Animation Mode** button and select **Stop At End**. Click the **Animation Mode** button and select **Options** to open the Animation Options dialog.

Check the **Recalculate atom visibility every frame** checkbox and close the dialog. Click the **Play** button.

You should see the gray oil droplet beads move around in the solvent. You can also use an isosurface to visualize the bead positions.

Select **Modules | Mesocite | Analysis** from the menu bar to open the Mesocite Analysis dialog. Select the **Density field** option.

There are several options for creating density fields, including defining density fields for a set of beads, and the field resolution. However, you will use the default values.

Hold down the **ALT** key and **double-click** one of the **Oil** beads.

Click the **Analyze** button and close the dialog.

A new trajectory named `Water_Oil_20rad Mesocite Density Field.xtd` is created. This contains one density field and its respective isosurface. You can visualize the density field by animating the trajectory. Before animating, you should change the display options so that the isosurface is rendered.

Right-click in `Water_Oil_20rad Mesocite Density Field.xtd` and select **Display Options** from the shortcut menu. Uncheck the **Fast render on move** checkbox and close the dialog. On the Animation toolbar, click the **Play** button.

The animation should play and you should see the oil droplet moving around the box.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To perform a shearing run

The equilibration run demonstrated that the initial interaction parameters gave a reasonable interaction between the oil and solvent as the oil remained in a droplet through the simulation. Now you will use the shearing functionality to put a shear force on the structure. You will restart the calculation but not append the trajectory.

Ensure that the trajectory `Water_Oil_20rad.xtd` is the active document.
Open the **Mesocite Calculation** dialog and check the **Restart** checkbox on the **Setup** tab.

You will run another 10,000 steps but this time with shearing switched on.

Click the **More...** button to open the Mesocite DPD dialog. Check the **Enable shearing** checkbox and set the **Shear rate** to **0.1** reduced units. Close the dialog.

You have limited control over the direction of the shearing. For this calculation, it is not so important as you are just shearing a droplet so you can leave it at the default value.

You are now ready to run the calculation.

Click the **Run** button and click the **Yes** button on the warning dialog. Close the **Mesocite Calculation** dialog.

The calculation will take several minutes to complete. When completed, you can perform the same visual analysis as you did previously.

Hold down the **ALT** key and **double-click** on one of the **Oil** beads.

In the **Mesocite Analysis** dialog, check the **Exclude analyzed objects in output** checkbox and click the **Analyze** button. Close the dialog.

You should see that, under the initial shear, the oil droplet stretches but does not break. You could repeat the calculation with a higher shear rate, for example 0.30 using Reduced units, and you should see the oil droplet breaks.

Note: The shearing in DPD physically shears the cell by deforming and re-setting the cell parameters. If you choose to write out the frame more frequently, you will see the cell deforming. In this example, if you write out the frame every 250 steps, you will see a deformation.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Clark, A. T.; Lal, M.; Ruddock, J. N.; Warren, P. B.; "Mesoscopic Simulation of Drops in Gravitational and Shear Fields." *Langmuir*, **16**, 6342-6350, (2000)

Jones, J. L.; Lal, M.; Ruddock, J. N.; Spenley, N. A.; "Dynamics of a drop at a liquid/solid interface in simple shear fields : A mesoscopic simulation study.", *Faraday Discussions*, **112**, 129-142 (1999).

Calculating input parameters for a DPD simulation

Purpose: Illustrates how to obtain input parameters for a DPD simulation of a real system.

Modules: Materials Visualizer, Mesocite

Time: 🕒 🕒

Prerequisites: Building mesoscale molecules, Building bulk mesostructures Visualizer Tutorials

Background

One of the strengths of the DPD task in Mesocite is that hydrodynamic simulations can be performed on systems in which the chemical nature of the species is included. The chemistry of the system is imparted by the molecular architecture and the bead-bead repulsions. This tutorial explores the steps to calculate the bead-bead repulsions, and run a Mesocite DPD calculation in Materials Studio.

Note: This tutorial covers calculating DPD input parameters using solubility parameters. There are alternative methods available to obtain DPD input parameters which are not covered.

Introduction

The goal of this tutorial is to determine DPD input parameters for a system containing a mixture of SEBS and polypropylene (PP). SEBS is a triblock copolymer with polystyrene extremes and a copolymer of ethylene and butylene in the interior. The blocks are incompatible and phase separation is known to occur. The phase diagram of SEBS in polypropylene shows a variety of phases as a function of composition. You will consider the situation where the length of the individual blocks in SEBS is variable, and polypropylene has an average molecular weight of 20 000 amu.

This tutorial covers:

- [Getting started](#)
- [To determine the number of beads in each chain](#)
- [To calculate Flory-Huggins parameters for binary mixtures](#)
- [To convert Flory-Huggins parameters into DPD inputs](#)
- [Creating the input structure](#)
- [To simulate SEBS in PP matrix](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DPD_input** as the project name, click the **OK** button.

The new project is created with *DPD_input* listed in the Project Explorer.

2. To determine the number of beads in each chain

The number of beads in each chain depends on the model resolution. In principle the resolution can be chosen independent of the physical system being studied, and the polymer model be adjusted to match

the chosen resolution. Here you will choose the resolution such that the polymers are reasonably described by a simple bead-spring model.

The mean-square end-to-end distance (MSD) of a bead-spring model scales linearly with the number of beads. The MSD of a real bulk polymer also scales linearly with the number of monomers, but only after a certain number of monomers, due to correlation. This number is given by the characteristic ratio, C_∞ . The characteristic ratio is a measure of the stiffness of a chain and can be obtained experimentally.

Tip: The characteristic ratio (at 298 K) can be calculated for many polymers using the Synthia module in Materials Studio.

The characteristic ratio can be used to determine the number of beads in each chain: If one bead represents, on average, C_∞ monomers, the MSD scaling of the bead-spring model matches that of the real chain. With M_m the mass of the monomer and M_p the mass of the real chain, the number of beads in the polymer is thus given by

$$n_{DPD} = \frac{M_p}{M_m C_\infty}$$

The characteristic ratio of polypropylene is 6.7 ([Brandrup and Immergut, 1989](#)). The mass of a propylene monomer is 42 amu. Hence the mass of one propylene bead is $6.7 \cdot 42 = 281.4$ amu, and the polypropylene chain in this tutorial contains $20\,000/281.4 \approx 71$ beads.

Note: The characteristic ratio is the minimum number of monomers per bead to ensure that the MSD of the bead-spring model scales linearly. You could increase this further, for example to model very long chains. By increasing the bead mass, less beads are required to model a chain of a given length. Typically the bead mass is chosen such that the chain length in DPD does not exceed 100 beads.

You could derive bead masses from the characteristic ratios for the other species in the same way, but it is more common in DPD to fix the masses of all beads to be the same. In this tutorial you will fix the bead mass to be 281.4 amu, and consequently one bead represents 6.7 monomers of propylene, or $42/104 \cdot 6.7 = 2.7$ monomers of styrene.

Note: To accurately model the stiffness of polystyrene at this resolution would require angular interactions, which are ignored in this tutorial.

The choice of chain lengths in SEBS is quite arbitrary. In this tutorial you will use 10 beads in the styrene blocks and 20 in the central ethylene/butylene segment. Hence an SEBS chain has a molecular weight of $(10+20+10) \cdot 281.4 \approx 11\,000$ amu, about half that of PP.

3. To calculate Flory-Huggins parameters for binary mixtures

To parameterize a DPD bead-spring model you need to set up the interactions between all different species. You can identify three chemically distinct chemical units in this simulation: polystyrene (PS), polypropylene (PP), and the random copolymer of ethylene and butylene that makes up the central portion of the SEBS molecule (EB). Therefore you must obtain interaction parameters for each pair of these: PS-PP, PS-EB, and PP-EB.

The DPD interaction parameters are usually obtained in two steps: first the Flory-Huggins interaction parameters are determined, which are then converted to DPD parameters. There are various ways to obtain Flory-Huggins interaction parameters. Here you will calculate them from the solubility parameters δ_i ,

$$\chi_{ij} = \frac{v}{RT} (\delta_i - \delta_j)^2$$

where R is the gas constant, T the absolute temperature and v is the volume per mole beads.

The solubility parameter can be measured experimentally and are given in the table below:

Species	Solubility parameter (J/cm ³) ^{1/2}
PS	19.52
PP	16.06
EB	16.49

Tip: Solubility parameters can be calculated for many monomers using the Synthia module in Materials Studio.

The molar volume of polypropylene at 298 K is 49.0 cm³ per mole monomers. Since one bead represents 6.7 propylene monomers, the reference volume v is $6.7 \times 49.0 = 328.3$ cm³/mol.

Note: Since the reference volume scales with the number of monomers per bead, the product of chain length and interaction parameter, χN , is invariant under coarse-graining.

Using the solubility parameters given above, and $v/RT = 0.133$ cm³/J, the following Flory-Huggins parameters are obtained:

Species	PS	PP	EB
PS	0	1.59	1.22
PP	1.59	0	0.02
EB	1.22	0.02	0

4. To convert Flory-Huggins parameters into DPD inputs

Groot and Warren (1997) performed a series of DPD calculations on binary mixtures with a variety of repulsion parameters, a . They then computed Flory-Huggins parameters and found a linear relationship between χ and a . This relationship can be used to obtain input parameters for a pair of species with a known χ value.

The relationships that Groot and Warren obtained are for densities, in reduced units, of 3 and 5. As lower densities are more efficient you will use $\rho = 3$, for which the relationship is (in reduced units):

$$a_{ij}(\rho = 3) = 25 + 3.50\chi_{ij}$$

The first term is the self repulsion of beads. This value was chosen by Groot and Warren such that a pure DPD fluid has a compressibility similar to that of liquid water.

Using the above expression the following repulsion parameters are obtained for the DPD calculation:

Species	PS	PP	EB
PS	25.0	30.6	29.3
PP	30.6	25.0	25.1
EB	29.3	25.1	25.0

To ensure that the physical density corresponds to the reduced density of 3, for which the correlation was derived, the length scale must be set. As derived above, the bead volume is 328.3 cm³ per mole beads, or 545 Å³ for one bead. Hence 3 beads occupy a volume of $3 \times 545 = 1635$ Å³, corresponding to a cube with edge $1635^{1/3} = 11.8$ Å. This value must be chosen as length scale to match both the required

physical and reduced density. Half the length scale (5.9 Å) may be used as the bead radius for display purposes.

Note: Both physical and reduced units can be used as input to Mesocite. When using reduced units, Mesocite will automatically convert the values to physical units using the mass, length and energy scales specified.

5. To create the input structure

The first step is to define the bead types with which to build mesomolecule models of SEBS and polypropylene molecules.

Select **Build | Build Mesostructure | Bead Types** from the menu bar to open the Bead Types dialog. Click the **Properties...** button to open the Bead Type Properties dialog and click the **Defaults...** button to open the Bead Type Defaults dialog. Set the **Mass** to **281.4** and the **Radius** to **5.9**. Close the Bead Type Defaults and Bead Type Properties dialogs.

Define the following new bead types: **PP**, **PS** and **EB** and close the Bead Types dialog.

This defines three bead types, PP, PS, and EB, with the same mass and radius.

Note: The bead radius is used in the mesomolecule builder to determine the bond length. Otherwise it is used only for visualization and has no effect on the calculation. The bead mass, on the other hand, is used in the DPD simulation.

Now you have defined the bead types, you can create the mesomolecule structures.

Select **Build | Build Mesostructure | Mesomolecule** from the menu bar to open the Build Mesomolecule dialog. Build a mesomolecule of **71** units of **PP** and rename the new document to **PP.xsd**.

Build another mesomolecule containing **10** units of **PS**, **20** units of **EB**. and another **10** units of **PS**. Rename the document **SEBS.xsd**.

Close the dialog.

Tip: Mesostructure tools are also accessible from the Mesostructure toolbar.

Now you have built the components, you need to construct the cell containing these mesomolecules. The construction is a two-step process: first you create a template containing one or more formers; then you fill the formers with the molecules, or a mixture thereof. In this case you use a simple template containing just one system former of size $100 \times 100 \times 100$ Å.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. Ensure all the **Extent (X Y Z)** values are set to **100.0**. In the **Filler** text box, enter **SEBS_PP** and click the **Build** button. Close the template dialog.

A new template document is created `Mesostructure_Template.msd`, containing a system former displayed as a blue box. The next task is to fill the box with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog. Make sure that the template is in focus.

The dialog shows the **SEBS_PP** filler you defined earlier, and you can select the mesomolecules to be associated with this filler. In this case you will use a mixture of SEBS and polypropylene with the same mass of both components.

Click in the **Mesoscale Molecule** column for the **SEBS_PP** filler, selecting **PP.xsd** and **SEBS.xsd**.

Ensure that the **Relative Amount** is set to **1.0** for both components.

Note: The relative amount for a given type of molecule refers to the *mass* contained in molecules of this type, not to the *number* of those molecules in the system. Since in this case PP is about twice the mass of SEBS, there will be about half as many PP molecules than SEBS molecules in the structure.

Before building the mixture of polystyrene and SEBS, you need to specify the target density, either in reduced units (with the appropriate reduced unit scales set), or directly in physical units. Here you will set the density directly in g/cm^3 . The molecular weight of PP is 42 amu and molar volume is $49.0 \text{ cm}^3/\text{mol}$. Hence the density is $42/49 = 0.857 \text{ g/cm}^3$.

On the Components tab set the **Density** to **0.857 g/cm^3** . Click the **Build** button and close the dialog. Rename the document **SEBS_PP.xsd**.

Note: Alternatively you can set the density to 3 in reduced units, after specifying the Length scale (11.78 Å) and mass scale (281.4 amu) on the Reduced Units dialog.

You have now built the initial structure. The next stage is to simulate SEBS/PP matrix.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

6. To simulate SEBS in PP matrix

Now that you have determined all of the input parameters, you can perform a simulation.

Open **SEBS_PP.xsd**. Select **Modules | Mesocite | Forcefield Manager** from the menu bar and click the **DPD...** button to open the Create DPD Forcefield dialog.

As no force field types are assigned to the beads the Repulsions matrix is empty.

Press the **Type** button to assign force field types to beads in the active document.

You should see a matrix of forcefield types corresponding to those in the document. The values are currently displayed in physical units (based on kcal/mol and Å) whereas in DPD work, including that of Groot and Warren, has usually been carried out using reduced units. Mesocite DPD allows you to set up the calculation using either physical or reduced units (in which case the conversion to physical units will be performed automatically). You will use reduced units here.

Tip: When constructing multiple structures (for example, different concentrations of the polymers) you can avoid retyping the beads by assigning force field types directly on the input molecules before building the structures.

Change the **Units** to **Reduced** and click the **More...** button to open the Mesocite DPD Units dialog.

You need to enter the Length and Mass scales to be used for the unit conversion, as discussed earlier.

Change the **Length scale** to **11.8** and the **Mass scale** to **281.4**. Close the dialog.

You now need to enter the forcefield parameters for this simulation.


Species	EB	PP	PS
EB	25.0	25.1	29.3
PP	25.1	25.0	30.6
PS	29.3	30.6	25.0

On the **Create DPD Forcefield** dialog edit the matrix and set the **Repulsions** to the values shown in the table above. Click the **Create** button and close the dialogs.

When you click the Create button, a new Forcefield document is created and listed as SEBS_PP.off in the Project Explorer. The values in the forcefield document are written in physical units and the forcefield is automatically set on the Energy tab of the Mesocite Calculation dialog.

Tip: As the interactions are stored in a forcefield document, you can add other interactions to the calculation such as bond angle terms to control rigidity of the bonds. You can also edit the Description of the forcefield to annotate it with references, updates, and so on.

You can change the name of the forcefield document so that it is not specific to a particular structure. When you change the name of the forcefield, this is updated on the Energy tab of the Mesocite Calculation dialog.

Click the **Mesocite** button  on the **Modules** toolbar, then select **Calculation** from the dropdown list and select the **Energy** tab.

You should see the custom forcefield `\SEBS_PP` selected in the Forcefield chooser.

As DPD uses very short soft interactions, you can decrease your calculation time by changing the van der Waals nonbond cutoff distance. You should set this to the length scale that you used earlier. If you leave this at the default value, the calculation time will increase but without benefit since the interaction beyond the length scale is zero.

Make **SEBS_PP.xsd** the active document.

Click the **More...** button for the **Summation method** section to open the Mesocite Non-Bond Options dialog. Set the **Cutoff distance** to **11.8** and the **Spline width** to **0**. Close the dialog.

Note: It is important that you have the right 3D periodic structure in focus when you change the cutoff distance, since Mesocite has separate settings for periodic and nonperiodic structures.

Finally you can run the DPD simulation. You can leave all simulation parameters at their default value, but to save time you will reduce the length of the run.

Select the **Setup** tab and set the **Task** to **DPD**. Click the **More...** button next to the task to open the Mesocite DPD dialog. Set the **Number of Steps** to **1000** and change **Frame output every** to **100** steps. Close the Mesocite DPD dialog.

Click the **Run** button and close the Mesocite Calculation dialog.

Since this tutorial is concerned with the parameterization of the DPD simulation, it is not necessary to analyze the output of the job. If you do choose to analyze the results, you should begin to see the two polymers separating. However, a much longer calculation would be required to see the full effect. By changing the composition of the block copolymer different phases may be obtained.

Tip: You can restart calculations by checking the Restart checkbox on the **Setup** tab.

Select **File | Save Project** from the menu bar followed by **Window | Close All**.

This is the end of the tutorial.

References

Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd Edition, John Wiley & Sons Inc: New York (1989).

Groot R. D.; Warren, P. B. "Dissipative Particle Dynamics: Bridging the gap between atomistic and mesoscopic simulation", *J. Chem. Phys.*, **107**, 4423-4435 (1997).

MesoDyn tutorials

The following tutorials illustrate how to utilize MesoDyn's capabilities.

- [Running a simple MesoDyn simulation](#)
- [Obtaining input parameters for MesoDyn](#)
- [Using explicit charges and salt solutions](#)
- [Using pseudodynamics](#)

Running a simple MesoDyn simulation

Purpose: To introduce the MesoDyn calculation panel, launch a short simulation to the server and look at the results graphically. Also to look at restarting a simulation and shearing.

Modules: Materials Visualizer, MesoDyn

Time: 

Prerequisites:

Background

The large size and slow dynamics of mesoscale structures makes quantum mechanics or molecular modeling with atomistic detail prohibitively expensive. These structures are critical to the properties of materials and therefore methods have been developed to elucidate mesophase behavior. At such length scales, fast atomic degrees of freedom contribute only to effective potentials. MesoDyn uses such an approach. The Materials Studio implementation permits the user to perform simulations on Linux or Windows servers, while system setup and post simulation analysis can be done from the desktop PC.

Introduction

This tutorial uses most of the default values on the MesoDyn Calculation dialog to run a short simulation of phase separation of a symmetric diblock copolymer melt system. The default starting point is a homogeneous mixture. Repulsive interactions between the two blocks of the polymer will drive the system closer to its equilibrium state, which is a lamellar phase separated structure. The results are visualized using 2D and 3D graphics. Restarting a simulation and subjecting the system to a shearing force are also demonstrated.

This tutorial covers:

- [Getting started](#)
- [To set up a MesoDyn calculation](#)
- [To control the job settings and run the job](#)
- [To examine the results](#)
- [To restart the simulation with shear](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.

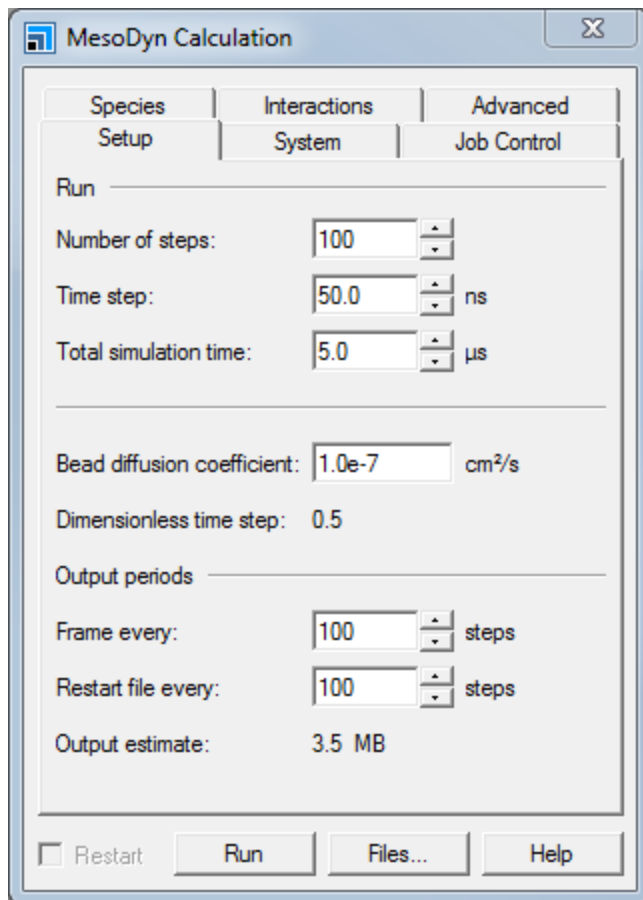
Open the **New Project** dialog and enter **MD_simple** as the project name, click the **OK** button.

The new project is created with *MD_simple* listed in the Project Explorer.

2. To set up a MesoDyn calculation

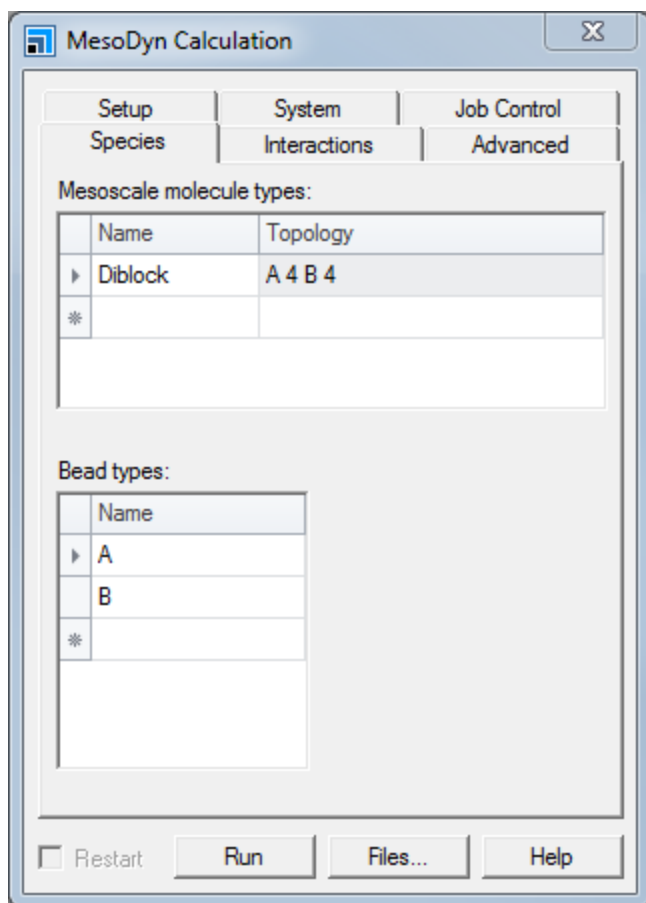
The first step is to open the MesoDyn Calculation dialog.

Click the MesoDyn button  on the **Modules** toolbar and select **Calculation** to open the MesoDyn Calculation dialog.



MesoDyn Calculation dialog, Setup tab

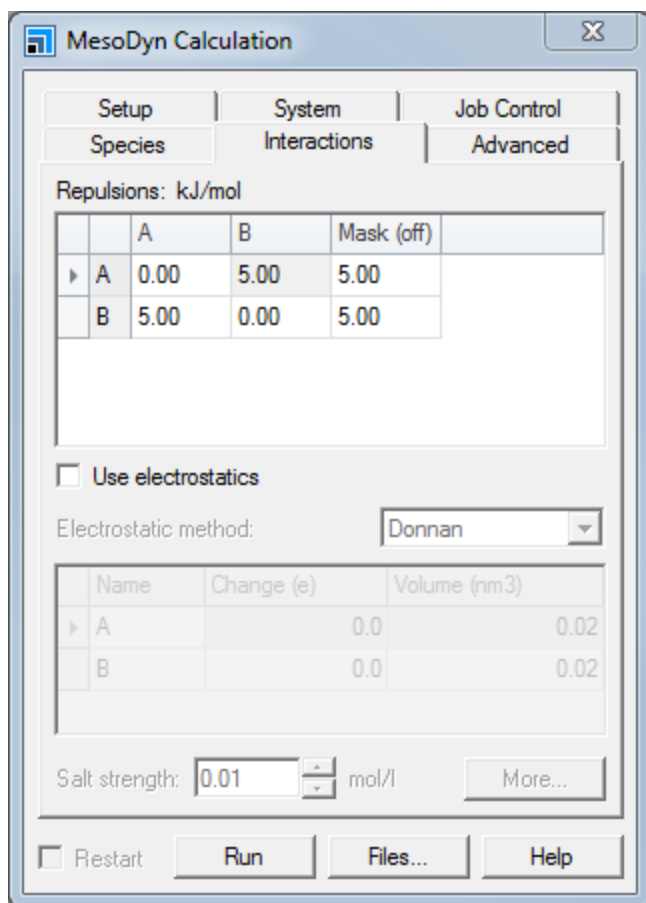
Select the **Species** tab and ensure that the default diblock copolymer consisting of bead types **A** and **B**, with topology **A 4 B 4** are defined in the Bead types and Mesoscale molecule types grids.



MesoDyn Calculation dialog, Species tab

The *Species* tab allows you to set the parameters that define bead types and molecular topology. Although the default diblock copolymer system used in this tutorial does not require modification of the default parameters on this tab, this is where you would define the *Mesoscale molecule types* and *Bead types* in other calculations.

Select the **Interactions** tab.



MesoDyn Calculation dialog, Interactions tab

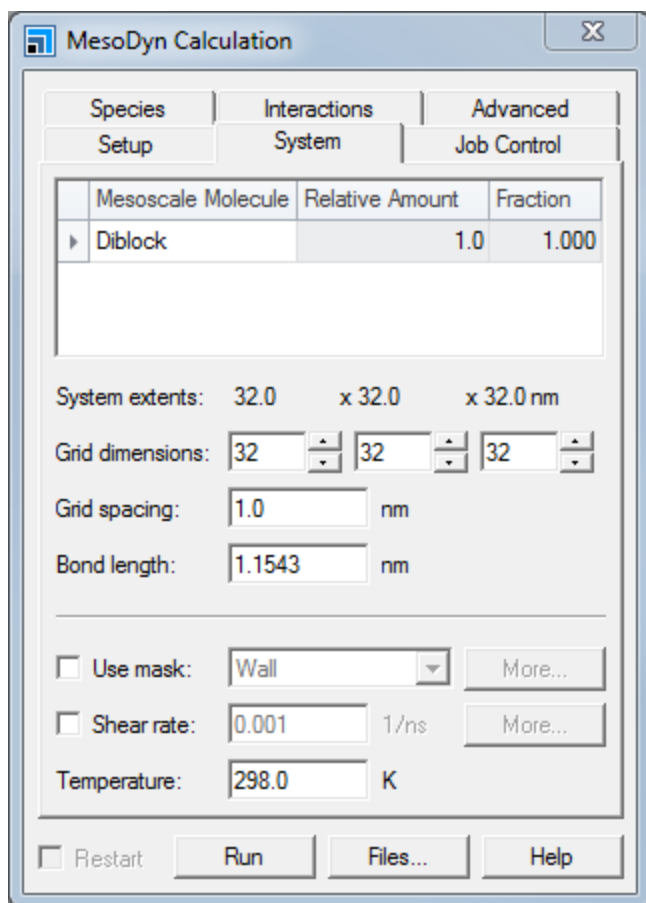
The repulsion of the beads is specified in the *Repulsions* panel. The values of the off-diagonal terms are greater than zero and this will tend to cause phase separation. The matrix of interactions is symmetric, so any changes made below the diagonal are reflected above the diagonal.

This tutorial does not involve the electrostatics functionality, so leave the option unchecked. Likewise, salt strength controls are not used.

Note: Values appear for bead-mask interactions even though the *Use Mask* control on the *System* tab is not checked. Mask status (*on* or *off*) is indicated in the *Mask* cell heading of the *Repulsions* panel.

For this tutorial, the default values are appropriate.

Select the **System** tab.



MesoDyn Calculation dialog, System tab

The *System* tab specifies the concentrations of individual molecules, cell size, and other external variables.

There is only one molecule in the system, so the composition cannot be changed. To shorten the length of the calculation, reduce the grid dimensions to 16×16×16.

Change the **Grid dimensions** value from 32 to **16** in all three dimensions.

Note: The bond length parameter, which defines the Gaussian chain, is fixed at 1.15 times the grid spacing. This ensures the isotropy of all grid restricted operators. The bond length is therefore approximately the same size as the lattice on which the density profiles will be reported.

Select the **Setup** tab.

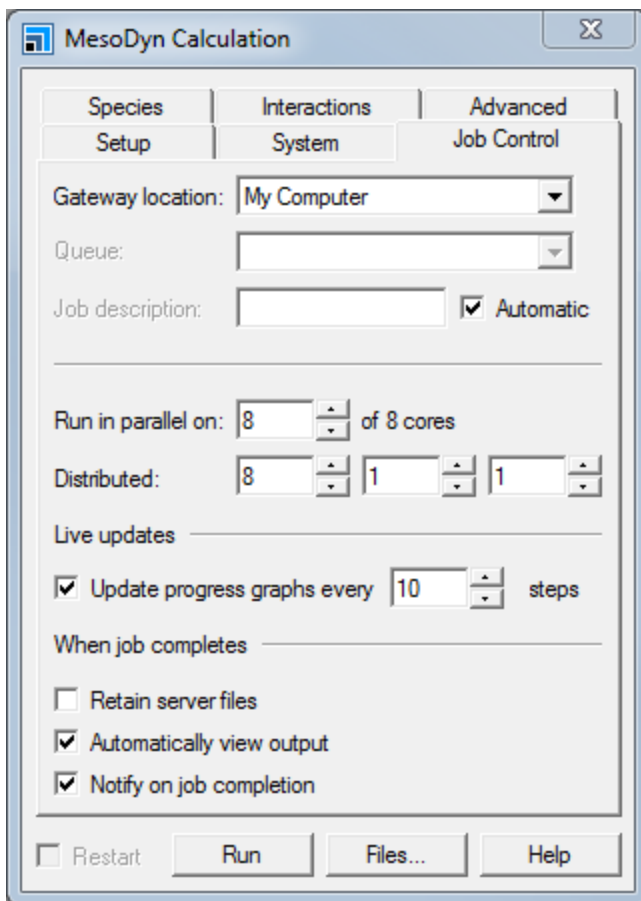
A lengthy simulation is not required for this tutorial, so the simulation will be configured to run for only 500 time steps of the default 50 ns each.

Change the **Number of steps** to **500**. Set the **Frame every** to **100** steps (five frames will be generated) and set the **Restart file every** to **500**.

Check the *Output estimate* and make sure the output files are not too large (compare with your available disk space).

3. To control the job settings and run the job

Select the **Job Control** tab.



MesoDyn Calculation dialog, Job Control tab

From this tab you can choose the gateway location where the calculation will run, which queue (if any) to submit the job to, and parallel simulation topology, as well as set various options such as the job description, live update settings, and what happens when the job completes. For now, simply change the update frequency and number of processors, if necessary.

Change the **Update progress graphs every** to **50** steps. Ensure that **Run in parallel on** is set to **1** processor.

Note: As you will later restart the run using shear, the processor topology must be supported by the shear protocol. Shear requires an N processor job to be distributed as $1 \times N \times 1$. If you want to use multiple processors in this tutorial you therefore have to ensure the topology is in this format. It is not possible to restart a run originally distributed as $N \times 1 \times 1$ by a run with shear, if $N > 1$.

Specify a name for the calculation.

Uncheck the **Automatic** checkbox and enter **MD_simpletut_run** as the **Job description**. Click the **Run** button.

The Job Explorer is displayed, indicating the status of the calculation. The run should take less than ten minutes on a standard PC.

Two chart viewers will open, displaying the files `FreeEnergy.xcd` and `OrderParameters.xcd`. These are the live documents that are updated regularly while the calculation is running. They display the free energy evolution and order parameters of the system, respectively. These can be useful visual aids to indicate the progress of your calculation, for example you can observe the free energy decreasing and the order parameters increasing during the run, indicating that phase separation is taking place.


4. To examine the results

A number of files have been saved under the `MD_simpltetut_run MesoDyn Dynamics` project. The `MD_simpltetut_run.mtd` file contains the density and potential fields - the concentration of that species throughout the box at the relevant instants of the simulation. Double-clicking this file in the Project Explorer displays the simulation cell with a colored-dot representation of the fields.

Make the `MD_simpltetut_run.mtd` file the active document.

By default only the density fields are displayed. The display shows each species (bead) in a single color, at all points in the cell where the concentration of that bead is greater than the field's mean value; so that if a species A ranges from 0 to 1 in its concentration, it will be displayed as a series of dots at each point in the cell where the concentration of A is greater than 0.5.

Select one of the beads for further examination.

Click the **Volumetric Selection** button  on the **Volume Visualization** toolbar to open the Volumetric Selection dialog. Uncheck the **B Density** checkbox and select the **A Density** field so that it is highlighted in blue.


The background of the icon and name turns dark blue and the frame of the cell turns yellow, indicating selection.

Right-click in `MD_simpltetut_run MesoDyn Dynamics\MD_simpltetut_run.mtd` and select **Display Style** from the shortcut menu to open the Display Style dialog.

Controls on the *Field* tab toggle the color of dots between a custom color and a range determined by the field value. The Color Maps tool on the Volume Visualization toolbar allows you to change the color spectrum used to indicate the field, select the range of field values that should be colored, specify any exclusions from the spectrum, and crop/clamp options for field points outside the indicated range.

On the **Field** tab click the **Color by field values** radio button.

The default display style is 32 colors in a blue to red spectrum (blue for low density, red for high). The range of densities is from 0 to 1. Points with densities below 0.5 are not displayed.

Click the **Color Maps** button  on the **Volume Visualization** toolbar to open the Color Maps dialog. Display the entire spectrum by clicking and dragging in the **Color range chooser**.

Hovering the cursor over the chooser indicates the density corresponding to each color and whether it is excluded. Excluded densities (that is, colors) are also indicated by horizontal gray lines through the corresponding colors. Clicking on any band toggles between excluded and included.

The default field display is low quality, dot size = 1. Increasing the quality increases the number of dots used to represent the field. Altering the dot size has a predictable effect on the image. You can display

the cell without the field visible by selecting the *Empty* radio button. The cell can be made invisible by unchecking the *Show box* checkbox. The entire field, including cell and dots, can be made invisible by unchecking the *Visible* checkbox.

The dot display of the field can be replaced by a 3D volume rendering of the fields by selecting the *Volume* radio button. This option is rather memory intensive and should be utilized with some caution.

Try some of these options for yourself.


The cell can be viewed with periodic replicas visible, using the *Display range* controls of the *Field* tab. The displayed range can be incremented in any of the three Cartesian directions (both positive and negative directions are permitted) and by non-integer amounts.

The other files created in the simulation are also of considerable interest.

- *FreeEnergy.xcd* shows the evolution of free energy during the simulation, which reaches equilibration asymptotically.
- *OrderParameters.xcd* shows the instantaneous value of the order parameter for each species (bead type) in the system.
- *MD_simpletut_run.MesoDyn_par* is a text version of the input parameters. This file may be edited and read back in to the *MesoDyn Calculation* dialog using the *Files* button.
- *MD_simpletut_run.MesoDyn_out* reports the completion status of the simulation and the numerics of the integration.

Slices and isosurfaces provide useful 2D and 3D representations of the phase morphology. These can be generated for any field in the system and color-coded in the same manner as fields themselves. Both options are available on the *Volume Visualization* toolbar.

First, create a 3D isosurface linking points with the same concentration of type A beads.

With no field selected, click the **Create Isosurface** button  on the *Volume Visualization* toolbar to open the *Choose Fields To Isosurface* dialog. Select the **A Density** field and click the **OK** button.

This creates a surface linking all the points in the cell that have the same density of type A beads. Use the *Display Style* dialog to control the coloring of this surface.

On the **Display Style** dialog select the **Isosurface** tab.


Custom coloring, using the Microsoft Custom Coloring Control, is the default. Coloring the surface by the potential energy experienced by the A beads along the surface is more useful here.

Select **A Potential** from the **Mapped field** dropdown list.

The coloring method automatically changes to *Color by mapped field*. Now the surface is color mapped by the potential energy of the A beads along this surface.

Select the surface and press the **DELETE** key to remove it.

It is also interesting to examine the system using 2D slices.

With no field selected, click the **Create Slices** arrow  on the **Volume Visualization** toolbar and select **Best Fit**.

This opens the *Choose Fields to Slice* dialog, select **A Density** and click the **OK** button.

The density of A beads in a slice through the system is displayed. You can use the Display Style dialog and *Color Maps* tools to manipulate the color mapping.

Select the **Slice** and press the **DELETE** key to remove it.

Choose one of the bead types on the **Volumetric Selection** dialog. Click the **Field Distribution** button



on the **Volume Visualization** toolbar.

A graph of the selected field's values is displayed.

Note: If the *Field Distribution* button is pressed while no field is selected in the Volumetric Selection dialog, a new dialog is displayed and you are prompted to select a field. You can select multiple fields, if desired.

Make the trajectory the active document and uncheck the checkboxes for all the density fields on the Volumetric Selection dialog. Check one of the potential fields.

A field is displayed which shows the potential felt by the selected species at each point in the box. You can use the *Field* tab in the Display Style dialog, and the Color Maps tool to control the appearance of the field.

Close any dialogs that remain open.

The MesoDyn Analysis dialog allows you to plot enthalpy, entropy, free energy, compressibility, order parameter and electrostatics as an evolution or an average. Parts of the run, for example equilibration stages, can be excluded from the graphing and averaging. The order parameter plot can be chosen for one or more of the species present. In this tutorial the two curves should be the same, since there are two components of equal density in the system.

Select **Modules | MesoDyn | Analysis** from the menu bar to open the MesoDyn Analysis dialog.

Select **Thermodynamics** and click the **View** button. Repeat this for each analysis type.

Select **Window | Close All** from the menu bar, followed by **File | Save Project**.

5. To restart the simulation with shear

In the Project Explorer, double-click on the **MD_simpletut_run MesoDyn Dynamics/MD_simpletut_run - Calculation** file.

This opens MesoDyn Calculation dialog. Note that the *Restart* checkbox is inactive. This function becomes active when an output file is the current document.

In the Project Explorer, double-click on **MD_simpletut_run.MesoDyn_out**.

Now the *Restart* checkbox is active.

Check the **Restart** checkbox on the MesoDyn Calculation dialog.

Several of the parameters on the MesoDyn Calculation dialog are now inactive. These are variables that cannot be altered in a restarted run.

Select the **Species** tab.

The bead definitions and molecular architecture of the system are fixed for the entire simulation, and the controls are grayed out, prohibiting modifications.

Select the **Interactions** tab.

Modifications to the repulsions are allowed, however leave all the settings on this tab as they are for this tutorial. Note that charges can be added to some of the beads at this stage, by checking *Use electrostatics* and selecting **Donnan** from the *Electrostatic method* dropdown list.

Select the **System** tab.

Most of the controls on this tab are inactive in *Restart* mode. A mask cannot be introduced in the middle of a run, however, if one had been defined at the start, it could be modified now. Temperature and shear options can be modified at this time.

Check the **Shear rate** checkbox, and input a rate of **0.001** 1/ns.

Select the **Setup** tab.

The value of *Number of steps* indicates how many steps (of length *Time step*) should be run beginning from the current configuration. Thus this number can be left unmodified or even decreased.

Leave the **Number of steps** set to **500**. Set **Frame every** to **100** steps. Set **Restart file every** to **500** steps.

Check that the estimated results folder is not too large (compare with your available disk space).

Click the **Restart** button. Wait for the restarted job to finish before continuing.

Output files are listed in the Project Explorer under the folder *MD_simpletut_run MesoDyn Dynamics/MD_simpletut_run MesoDyn Dynamics*. These files are much the same as those generated in the earlier run, however, the effect of the shear should be apparent. Note, for example, the initial decrease in order parameter as the shearing acts to mix the system.

The mesoscale trajectory document, *MD_simpletut_run.mtd*, contains structural information which, when compared with the results of the previous calculation, indicate the effect of the shear. Very clear lamellar order has developed under shear.

Complete the analysis by creating an isosurface of the A density field, to confirm the apparent lamellar structure.

Open the **Choose Fields To Isosurface** dialog, select **A Density**, and click the **OK** button.

This creates a surface linking the points where the A field falls to around half its maximum density. This is a reasonable approximation to the dividing surface in the system, and demonstrates clear lamellar order.

You can delete the files generated during this tutorial.

This is the end of the tutorial.

Obtaining input parameters for MesoDyn

Purpose: To demonstrate the necessary steps to obtain input parameters for a MesoDyn calculation of a real system.

Modules: Materials Visualizer, MesoDyn

Time: 🕒

Prerequisites: None

Background

The strength of MesoDyn is that full simulations are performed on systems in which the chemical nature of the species is included. The chemistry of the system is imparted through the molecular architecture and the bead-bead repulsions. This tutorial explores the steps required to perform these calculations in the Materials Studio environment. It should be noted that there are other ways to determine these parameters, some involving other simulation tools, others involving experimental data. Finally, it is recognized that alternative methods of parameterizing the simulation are not necessarily inferior in their predictive power.

Introduction

The goal of this tutorial is to determine MesoDyn input parameters for a system of a binary mixture of SEBS in polypropylene. SEBS is a triblock copolymer with polystyrene extremes and a copolymer of ethylene and butylene in the interior. The blocks are incompatible and phase separation is known to occur. The phase diagram of SEBS in polypropylene shows a variety of phases as a function of composition. The length of the individual blocks in SEBS varies from sample to sample, and you will assume block lengths at your convenience. The polypropylene in question has a molecular weight distribution centered around $M_p = 20000$, and this value will be taken as the polymer weight. Time will not permit simulation of all the input parameters, so some will be provided.

This tutorial covers:

- [Calculating Flory-Huggins parameters for binary mixtures](#)
- [Converting Flory-Huggins parameters into MesoDyn inputs](#)
- [To simulate SEBS in a polypropylene matrix](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Calculating Flory-Huggins parameters for binary mixtures

There are three chemically distinct chemical units in this simulation: polystyrene, polypropylene, and the random copolymer of ethylene and butylene that makes up the central portion of the SEBS molecule. The Flory-Huggins interaction parameters must be obtained for each pair of these, that is PS-PP, PS-EB, PP-EB (where PS is polystyrene, PP is polypropylene, and EB is a random copolymer of ethylene and butylene).

The solubility parameters can be obtained experimentally, by using quantitative structure property relationship (QSPR) methods (such as those available in the Synthia module), or from atomistic simulations.

Solubility parameters for the various components of the system, generated using QSPR methods with Synthia, are given in the table below:

Species	van Krevelen Solubility Parameter (J/cm ³) ^{1/2}
PS	19.52
PP	16.06
PE	16.80
PB	16.34
EB	16.49

The solubility parameters can be used to derive Flory-Huggins interaction values using:

$$\chi = \frac{V_{ref}(\delta_i - \delta_j)^2}{RT}$$

Where V_{ref} is a reference volume, taken to be the molar volume of one of the monomers (actually the mean volume of the two monomers).

The chain lengths are determined from the degrees of polymerization and the characteristic ratios of the polymers. According to the [Polymer Handbook](#), polypropylene has a characteristic ratio of 6.7. The following characteristic ratios are used in this tutorial:

Species	C_n
PS	9.9
PP	6.7
EB	7.32

The following molar volumes at 298 K, from Synthia, are used:

Species	Molar Volume (cm ³ /mol)
PS	96.98
PP	49.04
EB	48.89

These parameters are given for the homopolymers in [Bicerano's Prediction of Polymer Properties](#), and for the copolymer they are obtained using Quantitative Structure Property Relationships (QSPR), using the Synthia module.

Using the above data (and taking arithmetic means of the molar volumes as the input to the equation for the FH parameter) you can obtain a table of Flory-Huggins parameters for pairs of species in the system:

Species	PS	PP	EB
PS	0	0.35	0.270
PP	0.35	0	0.004
EB	0.270	0.004	0

Converting these parameters into MesoDyn input is covered in the [next section](#).

The expression for the MesoDyn chain length (N_{Meso}) is:

$$N_{Meso} = \frac{M_p}{M_m C_n}$$

where M_p is the polymer molecular weight, M_m is the monomer weight, and C_n is the characteristic ratio. Hence you should use a chain for PP of $20000/(42 \times 6.7) \sim 71$.

This is just about as long a chain as you should use routinely. However, if this calculation results in a chain of more than 100 MesoDyn beads, all is not lost. You can rescale the parameters, by increasing the interaction parameter by the same factor that you reduce the chain length (so that $\chi \times N$ remains constant).

The chain lengths in the SEBS are arbitrary. Choose 10 beads in the styrene blocks and 20 in the central ethylene/butylene segment. Again if the chain lengths are known experimentally, characteristic ratios (from experimental, QSPR, or RIS/RMMC calculations) should be used to determine N_{Meso} .

2. Converting Flory-Huggins parameters into MesoDyn inputs

The MesoDyn input parameter is related to the Flory-Huggins parameter through:

$$v^{-1} \varepsilon_{IJ} = \chi_{IJ} RT$$

where $v^{-1} \varepsilon_{IJ}$ is the input parameter.

Using the above expression to obtain the following table of MesoDyn input repulsions for pairs of species in the system:

Species	PS	PP	EB
PS	0.0	0.867	0.661
PP	0.867	0.0	0.0
EB	0.661	0	0.0

3. To simulate SEBS in a polypropylene matrix

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MD_input** as the project name, click the **OK** button.

The new project is created with *MD_input* listed in the Project Explorer.

Select **Modules | MesoDyn | Calculation** from the menu bar to open the MesoDyn Calculation dialog. Select the **Species** tab.

Each chemical species present and the connectivity of the molecules are specified on the *Species* tab.

In the **Bead types** text box enter: **PS** as A, **PP** as B, and **EB** as C. In the **Mesoscale molecules types** text box enter: **Polypropylene - PP 71** and **SEBS - PS 10 EB 20 PS 10**.

An interaction parameter must be input for each pair of species. This is accomplished on the *Interactions* tab.

On the **Interactions** tab enter the MesoDyn repulsions parameters as follows:

Species	PS (A)	PP (B)	EB (C)
PS (A)	0.0	0.867	0.661
PP (B)	0.867	0.0	0.0
EB (C)	0.661	0	0.0

Check the input parameters carefully before launching the simulation.

On the **System** tab ensure that the **Grid dimensions** are **16×16×16**. Ensure that the **Relative Amount** is set to **1** (the default) for both molecules. Set the **Temperature** to **298 K**.

On the **Setup** tab set the **Number of Steps** to **500**, save a **Frame every 50** steps, and set the **Restart file** to be created after **500** steps.

Note: These runs are much shorter than typical simulations. Run lengths in thousands of time steps are still considered quite short. It is prudent to check the hardware demands of the calculation before launching a full production run. The equilibration of the system can be inferred from the evolution of the free energy.

On the **Job Control** tab choose the server on which you will run the simulation. Uncheck the **Automatic** checkbox and enter **SEBS+PP** as the **Job description**. Set the live updates to **Update progress graphs every 50** steps.

Note: Generally you would turn off live updates for a full simulation, since there is a non-negligible overhead associated with this step.

Click the **Run** button.

When the run completes you may analyze the results using the usual tools. When you have finished, you can remove all the files created by this tutorial.

This is the end of the tutorial.

References

Bicerano, J. *Prediction of Polymer Properties*, 2nd Edition, Marcel Dekker: New York (1996).

Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd Edition, John Wiley & Sons Inc.: New York (1989).

Using explicit charges and salt solutions

Purpose: To introduce the MesoDyn electrostatics using the Donnan approximation.

Modules: Materials Visualizer, MesoDyn

Time: 

Prerequisites: [Running a simple MesoDyn simulation](#)

Background

MesoDyn in Materials Studio allows you the explicit use of charges with the Donnan approximation. This tutorial demonstrates how to input charges and run a simulation with electrostatics, and compare the results with a similar result using uncharged systems.

Introduction

The lack of direct inclusion of electrostatics in MesoDyn has often been considered a major limitation of the method. Full implementation of Poisson-Boltzmann charges requires some account of the long-ranged potentials, which would significantly reduce computational efficiency. As a first the ideas of Donnan are used, these ignore the long-ranged interaction by assuming perfect screening. With this approximation in place real charges can be assigned to the beads and the effect of charges on phase behavior can be simulated.

This tutorial covers:

- [Getting started](#)
- [To compare charged and non-charged systems](#)
- [To vary other parameters](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Charges can be used in MesoDyn by checking the checkbox on the *Interactions* tab, and assigning charges to each species. Under the limitations of the Donnan theory, the charged particles are assumed to reside in a salt solution. The strength of the salt solution can be specified on the *Interactions* tab.

It must also be determined whether the input interaction parameters should be changed so that they no longer include electrostatic interactions. In general if a bead has a net charge (even in a strongly polar system most beads will average to neutral) its interactions should include all contributions. However, if two species are to be treated as charged, then it is realistic to calculate χ in the absence of electrostatics.

1. Getting started


Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MD_salt** as the project name, click the **OK** button.

The new project is created with *MD_salt* listed in the Project Explorer.

2. To compare charged and non-charged systems

For this tutorial you will perform two calculations on the same system, one with and one without charges.

Click the MesoDyn button  on the **Modules** toolbar and select **Calculation** to open the MesoDyn Calculation dialog. Change the **Number of steps** to **400**.

Next, indicate that the terminal groups of the diblock are different species.

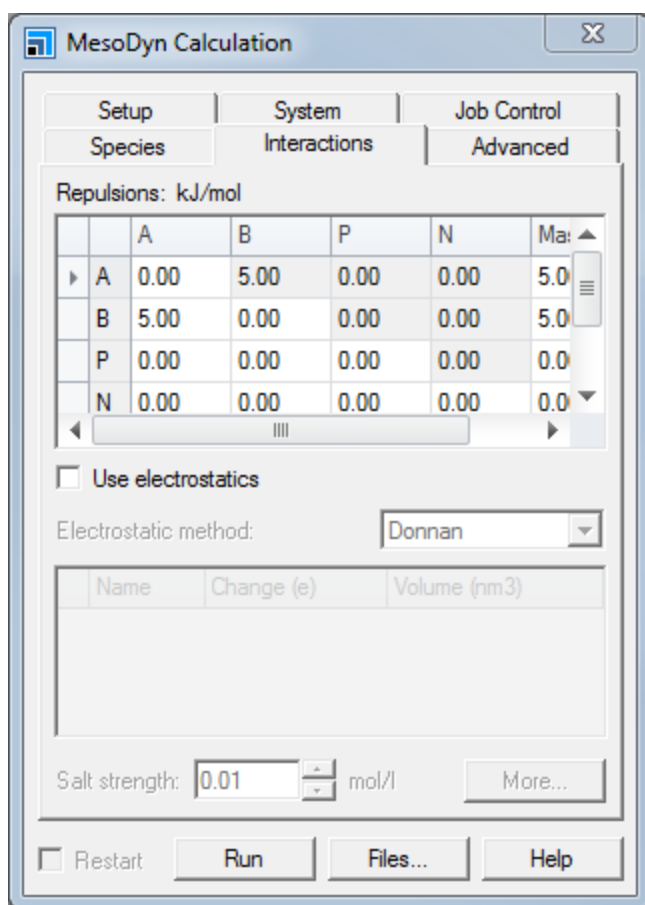
Select the **Species** tab and replace the A 4 B 4 topology with **P 1 A 3 B 3 N 1**.

A message prompts you to add the unknown beads to the **Bead types** table. Click the **Yes** button for both the P and N beads.

The interactions of P and A, and B and N, must be identical so the system behaves like a true diblock.

Select the **Interactions** tab.

The first calculation will use no charges.



MesoDyn Calculation dialog - Interactions tab with A, B, P and N beads defined

Complete the **Repulsions** grid as follows:

	A	B	P	N
A	0.0	5.0	0.0	5.0
B	5.0	0.0	5.0	0.0
P	0.0	5.0	0.0	5.0
N	5.0	0.0	5.0	0.0

On the **Job Control** tab uncheck the **Automatic** checkbox and enter **no_electrostatics** as the **Job description**. Click the **Run** button.


When the job is complete you will run the same system again, but this time including a charge on the terminal beads of the diblock.

On the **Interactions** tab check the **Use electrostatics** checkbox and ensure that **Donnan** is selected as the **Electrostatic method**. Assign a **Charge** of **0.5** to bead **P**, and **-0.5** to bead **N**.

On the **Job Control** tab, change the **Job description** to **with_electrostatics** and click the **Run** button.

Wait for the job to complete. The job takes significantly longer when charges are specified.

When the job is completed, compare the structures side by side. It is useful to color the P and A fields green, and the B and N fields red.

Click the **Volumetric Selection** button  on the **Volume Visualization** toolbar to open the Volumetric Selection dialog. Select the **A Density** field so that it is highlighted in blue on the dialog.

Right-click in **no_electrostatics MesoDyn Dynamics\no_electrostatics.mtd** and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Field** tab change the color of the **A Density** field to **green**. On the **Volumetric Selection** dialog select the **P Density** field and change its color to **green** also.

Repeat these steps for the **B** and **N** density fields, changing their color to **red**.

Repeat this procedure to similarly color the density fields in **with_electrostatics MesoDyn Dynamic/with_electrostatics.mtd**.

The comparison of this view for the case with and without electrostatics may not be entirely convincing. A more dramatic effect is noted in the order parameters and free energy graphs.

In the **Project Explorer**, locate the MesoDyn results folders for these two calculations. Each folder should contain two graphs called `FreeEnergy.xcd` and `OrderParameters.xcd`. Double-click on the chart documents in the Project Explorer.

Comparing the **OrderParameter** graphs from the two simulations clearly shows that the non-charged system is more strongly segregated.

The obvious conclusion is that the oppositely charged end-groups are interpenetrating the lamellae leading to a more diffuse phase boundary and potentially a more complex morphology.

3. To vary other parameters

If numerical stability problems occur when using charges, techniques similar to those used in pseudo-dynamics may be tried:

Time step - Reducing the time step is often the best way to increase the numerical stability of a calculation. The *Time step* parameter is found on the *Setup* tab.

Compressibility - The compressibility, which more accurately would be described as the incompressibility of the fluid, may be altered to improve numerical stability. The *Compressibility* parameter is found on the *Advanced* tab.

Solver tolerance - It may be necessary to use a value for solver tolerance that is lower than the specified default value. In general, a value leading to 5-20 iterations per time step should be used. The *Solver tolerance* parameter is found on the *Advanced* tab.

Max. iterations - Increasing the maximum number of iterations may improve numerical stability but should be used as a last resort. The *Max. iterations* parameter is found on the *Advanced* tab.

Max. line searches - Similarly the number of line searches should only be increased if all else fails. The *Max. line searches* parameter is found on the *Advanced* tab.

Noise parameter - A lower value implies more noise. Increasing the noise, by decreasing this value, may allow the system to escape from numerical traps. The *Noise* parameter is found on the *Advanced* tab.

Salt strength - For charged systems the salt strength is used to screen the charges, and must be large for the Donnan approximation to be valid. Increasing the value from the default may aid numerical stability. The *Salt strength* parameter is found on the *Interactions* tab.

You can delete the files generated during this tutorial.

This is the end of the tutorial.

Using pseudodynamics

Purpose: To introduce the use of using the potential-field only solve space. To highlight best operating practices for successful implementation.

Modules: Materials Visualizer, MesoDyn

Time: 🕒

Prerequisites: None

Background

The significant computational demands of MesoDyn create a pressing need for shortcuts. The heart of the dynamics algorithm is the update of the potential fields at given time step, followed by a corresponding update of density fields at the next half time step. The updating of one field as a result of the other's new value is the rate determining step of the simulation.

Fraaije's group examined the possibility of updating only the potential fields and creating density fields solely upon user-request ([Maurits, 1998](#)). The algorithm was proved to give results identical to the full algorithm but with a 10-fold increase in the number of time steps that could be performed in the same amount of CPU time. It was, however, noted that the system became less stable numerically, leading to a necessary reduction in dynamics time step of around 50%. Nevertheless a 5-fold reduction in CPU requirements is most welcome.

Introduction

This tutorial demonstrates setting up a simulation with the fast pseudo-dynamics option selected, and the consequent changes that are made to other input options in order to best guarantee numerical stability and results accuracy. You will view results in the form of 2D and 3D graphics

This tutorial covers:

- [Getting started](#)
- [To set up a MesoDyn calculation with fast pseudo-dynamics](#)
- [To vary other parameters](#)
- [Best practices for using pseudo-dynamics](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started


Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MD_pseudodyn** as the project name, click the **OK** button.

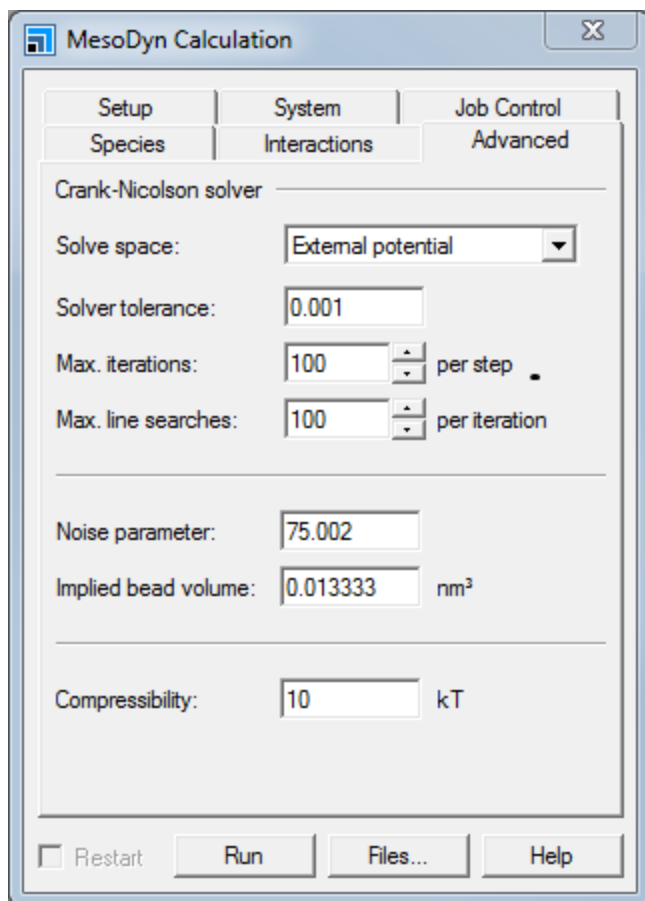
The new project is created with *MD_pseudodyn* listed in the Project Explorer.

2. To set up a MesoDyn calculation with fast pseudo-dynamics

To select the fast pseudo-dynamics option it is necessary to use an external potential for the solve space.

Click the MesoDyn button  on the **Modules** toolbar and select **Calculation** to open the MesoDyn Calculation dialog.

On the **Advanced** tab change the **Solve space** to **External potential**.



MesoDyn Calculation dialog - Advanced tab

You will change several parameters in order to improve numerical stability in the pseudo-dynamics calculation. It is advisable to reduce the time step to about half of its default value, and to double the run length.

On the **Setup** tab change the **Time step** to **25 ns**. Set **Number of steps** to **200**, and click the **Run** button.

Wait for the job to finish. Typically a calculation of this type takes about 75% as long as a traditional mixed density/potential integration scheme. While this may not seem particularly impressive, a comparison of the evolution of the system shows that the pseudo-dynamic run has progressed much further.

For comparison, run the system again, with the traditional potential and density field solver option. Double the time step and halve the number of steps, returning them to their default values.

On the **Setup** tab change the **Time step** to **50 ns**, and the **Number of steps** to **100**.

Return the Solve space to its original value.

On the **Advanced** tab and change the **Solve space** to **Mixed - density & potential**. Click the **Run** button, do not use the *Restart* option.

When the job has completed, compare the two sets of results. Visual inspection reveals little - both structures show broadly similar structures. However, comparison of the order parameter graphs shows that the pseudo-dynamics has moved the simulation considerably further than the standard solver option.

3. To vary other parameters

If numerical instabilities occur, try adjusting the following parameters.

Compressibility - The compressibility, which more accurately would be described as the incompressibility of the fluid, may be altered to improve numerical stability. Use lower values for compressibility when using pseudo-dynamics. The *Compressibility* parameter is found on the *Advanced* tab.

Solver tolerance - It may be necessary to use a value for solver tolerance that is lower than the specified default value. In general, a value leading to 5-20 iterations per time step should be used. The *Solver tolerance* parameter is found on the *Advanced* tab.

Max. iterations - Increasing the maximum number of iterations may improve numerical stability but should be used as a last resort. The *Max. iterations* parameter is found on the *Advanced* tab.

Noise parameter - A lower value implies more noise. Increasing the noise, and thus decreasing the value, may allow the system to escape from numerical traps. The *Noise* parameter is found on the *Advanced* tab.

4. Best practices for using pseudo-dynamics.

It is best to use the pseudo-dynamics in the equilibration stages of a simulation. This rapid algorithm allows a speedy approach to an equilibrium morphology. When the free energy and order parameter begin to asymptotically approach their equilibrium values, it is advisable to restart the job with the full potential and density field solver space.

This is the end of the tutorial.

References

Maurits, N. *Mathematical modeling of complex systems*, Ph.D. thesis, Rijksuniversiteit Groningen: Groningen (September 1998).

Morphology tutorials

The following tutorials illustrate how to use Morphology's capabilities.

- [Morphology prediction for Pigment Red](#)
- [Calculating morphology using Crystal Graph](#)

Morphology prediction for Pigment Red

Purpose: Illustrates how to predict crystal morphology from the atomic structure of a crystal using Morphology

Modules: Materials Visualizer, Morphology, Forcite, COMPASS

Time: 🕒 🕒

Prerequisites: Using the Crystal Builder Visualizer Tutorial

Background

Morphology allows you to predict crystal morphology from the atomic structure of a crystal. The bulk shape of crystals is critically important to many industrial processes. There are numerous examples of processes in the chemical and pharmaceutical industries where crystal shape is an important factor, including:

- Dissolution rate of chemicals and biological availability of drugs
- Handling, packaging, and storage of crystalline products
- Slurry handling, caking, and filtration during processing
- Milling, grinding, fragmentation, and dusting
- Density and texture optimization
- Wax and scale formation in petrochemicals

The relationship between the crystal morphology and the internal arrangement of atoms in the crystal is therefore of great interest to chemists, chemical engineers, and process engineers. Rationalization of this relationship allows the prediction of crystal shape, the development of tailor-made additives, and the control of solvent and impurity effects. Morphology's application areas include pharmaceuticals, agrochemicals, food sciences, petrochemicals, cements, and commodity and specialty chemicals.

Introduction

This tutorial demonstrates that computational chemistry methods offer a powerful means of deriving the morphology of a molecular crystal and allow you to examine the molecular landscape of crystal faces using graphic visualization.

Pigment Red (a diphenyl derivative of 1,4-diketopyrrolo(3,4-c)pyrrole, DPP) is a high quality heterocyclic pigment, offering good heat stability, high coloring strength and hiding power, and excellent light and weather fastness. It can be produced as transparent or opaque color by controlling the particle size during manufacture.

In order to optimize certain physico-chemical properties, such as shade, it is thought that it may be beneficial to change the morphology of the crystal from a plate-like habit to a more isometric shape.

In this tutorial, the crystal morphology for Pigment Red will be determined using the Morphology module.

This tutorial covers:

- [Getting started](#)
- [To load and optimize the crystal structure of Pigment Red](#)
- [To set up and run Morphology](#)
- [To analyze the Morphology results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.


Open the **New Project** dialog and enter **Pigment Red** as the project name, click the **OK** button.

The new project is created with *Pigment Red* listed in the Project Explorer.

2. To load and optimize the crystal structure of Pigment Red

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Structures\molecular-crystals\pigments\pigment_red.msi**, click the **Open** button.

Now you will optimize the crystal structure of Pigment Red using Forcite and the COMPASS forcefield, first just minimizing the molecules, then including the cell.

On the **Modules** toolbar, click the **Forcite** button  and choose **Calculation** from the dropdown list to open the Forcite Calculation dialog. On the **Setup** tab select **Geometry Optimization** from the **Task** dropdown list and set the **Quality** to **Medium**.

On the **Energy** tab of the Forcite Calculation dialog set the **Forcefield** to **COMPASS**. Set both the **Summation method** values to **Ewald**.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click the **More...** button to open the Forcite Job Control Options dialog. Make sure that the **Live updates** checkboxes for **structure**, **graphs**, and **textual results** are all checked and close the dialog.

Click the **Run** button.

A new folder called `pigment_red Forcite GeomOpt` is created in the Project Explorer. The calculation should take less than a minute to complete. When the calculation has finished, the minimized structure is saved in the `pigment_red.xsd` document in the new folder and is also displayed in the Materials Visualizer. Now you will include the cell parameters in a second minimization.

Ensure that the optimized structure is the active document. On the **Setup** tab of the Forcite Calculation dialog click the **More...** button to open the Forcite Geometry Optimization dialog. Check the **Optimize cell** checkbox and close the dialog.

Click the **Run** button and close the dialog.

Compare the cell parameters of the minimized structure with those of the experimental structure to make sure that none of them have been changed significantly, this indicates that the forcefield is adequate for the structure.


Note: Before you start a Morphology calculation, it is very important to select an appropriate energy expression and verify that it is able to describe the crystal geometry as well as the configurations of the molecules forming the crystal. Secondly, the geometry of the input crystal structure must be optimized using the same energy expression. This should include optimization of the cell parameters.

Tip: The COMPASS forcefield has been parameterized with non-zero forcefield charges and employs the bond increment approach. Since charge assignments are part of the parameters stored in the forcefield definition, you should normally accept the default option to use forcefield-assigned charges instead of assigning specific charges manually.

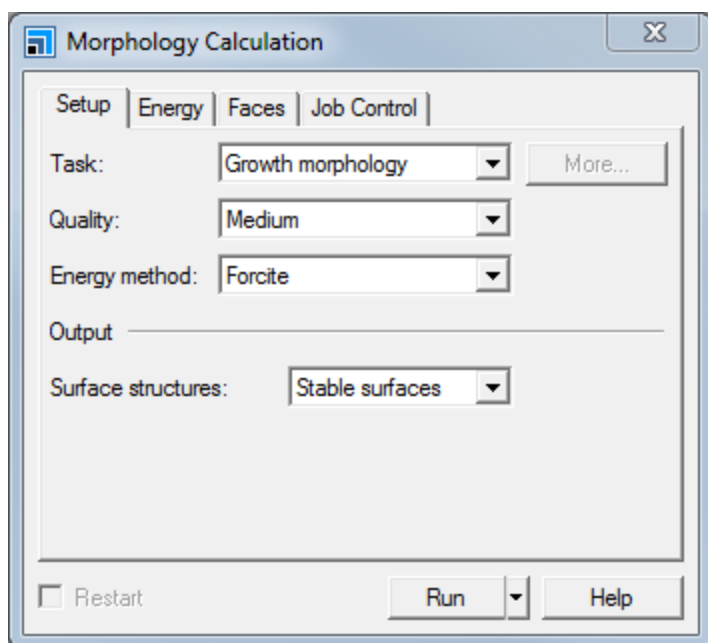
3. To set up and run Morphology

In this section, you will calculate the crystal morphology of Pigment Red by applying the growth morphology method in Morphology. The growth morphology algorithm assumes that the growth rate of a crystal face is proportional to its attachment energy (the potential energy released on attachment of a growth slice to a growing crystal surface in a vacuum). This method attempts to simulate crystal habits obtained under non-equilibrium growth conditions.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **pigment_red.xsd** in the **pigment_red Forcite GeomOpt/pigment_red Forcite GeomOpt** folder.

Click the **Morphology** button  and choose **Calculation** from the dropdown list to open the Morphology Calculation dialog.

On the **Setup** tab, change the **Task** to **Growth morphology**. Set the **Quality** to **Medium** and the **Energy method** to **Forcite**.



Morphology Calculation dialog, Setup tab

The *Quality* option offers a fast, single-click method of choosing the full set of parameters that control the simulation speed and accuracy. In a real-life situation, you should generally use the [Fine](#) or [Ultra-fine](#) settings. In this tutorial, you will set the *Quality* level to [Medium](#) so that the calculation does not take too long.

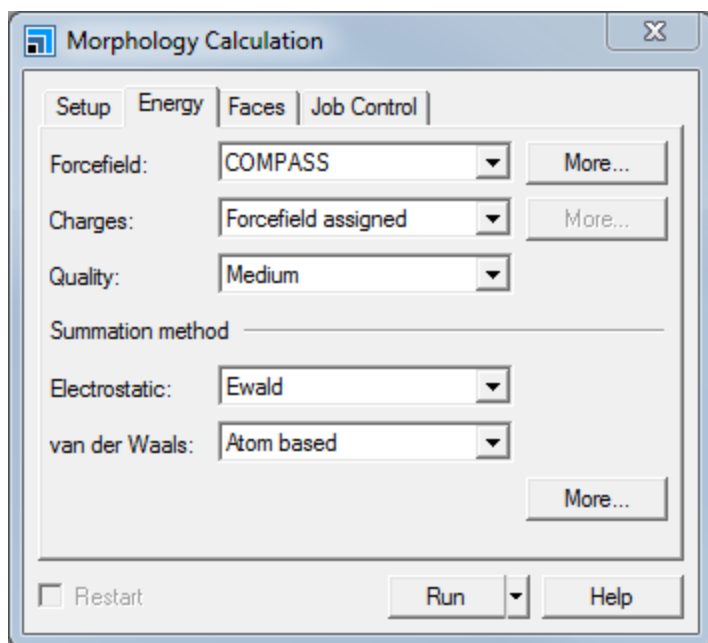
The *Energy method* control allows you to select the source of the energy expression to be used for the Morphology calculations. The [Forcite](#) option uses the Forcite energy server to compute interaction energies according to the settings on the *Energy* tab.

On the **Setup** tab, make sure that **Surface structures** is set to **Stable surfaces**.

This option sets the parameters determining which surfaces will be reported and whether surface structure documents will be produced for the reported surfaces as part of growth morphology and equilibrium morphology calculations. The [Stable surfaces](#) option reports data only for the most stable surface for each face and generates surface structure documents for the reported surfaces.

On the **Energy** tab, change the **Forcefield** to **COMPASS**.

The *Quality* is set to [Medium](#), as specified on the *Setup* tab earlier.

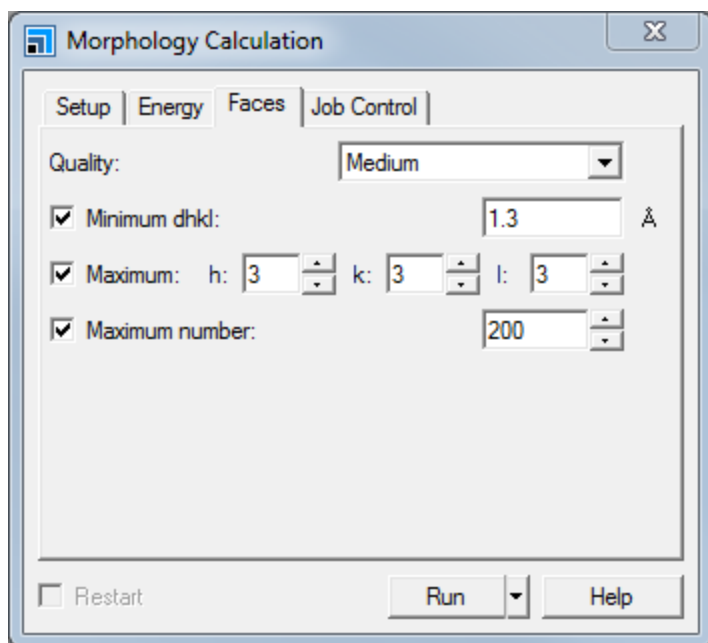


Morphology Calculation dialog, Energy tab

Note: For forcefields that include their own charges, such as COMPASS, cvff, and pcff, the default is to use the [Forcefield assigned](#) charges. For the other forcefields, such as Dreiding and Universal, the default is set to [Use current](#) charges assigned to the input model. In these cases, you must ensure that exactly the same charges are used for all Morphology runs and that they are the same as those in the optimized crystal structure used as the input.

Note: The *Quality* settings here and on the *Faces* tab propagate from the quality level selected for the overall calculation on the *Setup* tab. As a result, altering these other *Quality* settings will cause the quality level of the overall calculation to be set to [Customized](#).

On the **Faces** tab, make sure that the **Quality** is set to **Medium**.



Morphology Calculation dialog, Faces tab

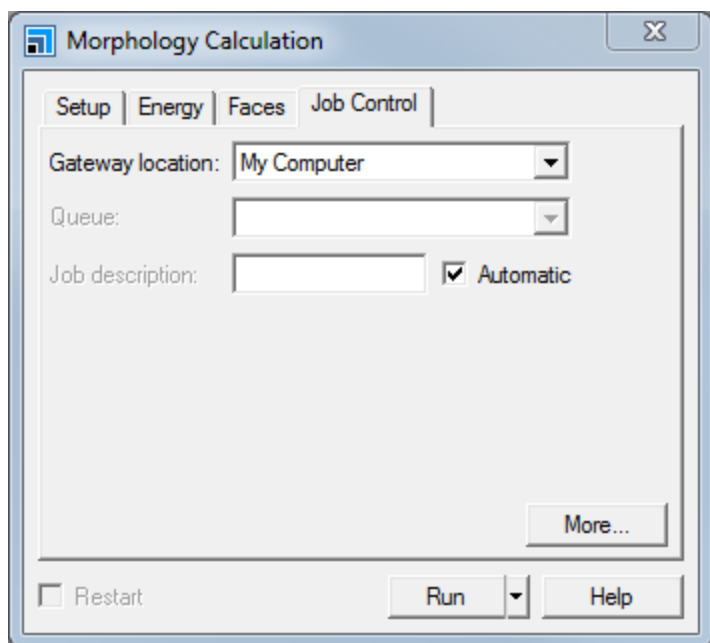
Note: Typically, increasing the *Quality* setting for a calculation will increase the computation time. It is usually sufficient to use a **Coarse** or **Medium** setting to ensure that all of the growth faces that build the crystal habit are included in the calculation.

The *Quality* setting controls the extent of the list of growth faces that will be produced by a Morphology calculation. Face list generation is controlled by three variables:

- *Minimum dhkl* - the minimum interplanar spacing for faces appearing on the face list.
- *Maximum h, k, l* - the absolute values of the Miller indices of faces appearing on the face list must be less than or equal to these specified values.
- *Maximum number* - the maximum number of faces to appear on the face list. Face list generation will cease when this number of faces have been added to the face list, even if faces that satisfy the other criteria still remain to be added.

Note: According to the Donnay-Harker rules, only higher orders of some Miller indices may appear on the morphology surface. In such cases, if the original Miller index satisfies the *Maximum h, k, l* criteria, the relevant higher order Miller index will be added to the list, even if the higher order index violates these criteria.

On the **Job Control** tab, select **My Computer** as the **Gateway location**.



Morphology Calculation dialog, Job Control tab

Click the **Run** button on the Morphology Calculation dialog and close the dialog and the **pigment_red.xsd** 3D Viewer.

The Job Explorer informs you about the progress of the calculation. After some time, a text document, **Status.txt**, may be displayed. This document is updated regularly as the job progresses. **Status.txt** informs you about:

- The task that is currently being performed, for example a growth morphology calculation.
- The total number of growth faces and the number of processed faces.
- Properties for a list of the most recent processed growth faces, including Miller indices, multiplicity, D_{hkl} , attachment energy, and center-to-plane distance.

Once the calculation starts, a new folder called **pigment_red Mph Growth** is created in the Project Explorer. The parameter settings for this job are automatically saved in a file called **pigment_red - Calculation**. A second text file, **pigment_red.txt**, is created in the new folder, but not opened in the Materials Visualizer. Initially, **pigment_red.txt** contains all of the calculation parameters. It is then updated if any non-fatal errors occur during the calculation.

You should wait until the job finishes before proceeding.

4. To analyze the Morphology results

In this section, you will analyze the output from the Morphology run.

Once the calculation is finished, two documents are displayed automatically. The first one is a Morphology report file, **pigment_red.txt**, which contains the values of all the settings used as input for the calculation, and a short summary of the calculation results.

Note: It is important to check this file for warnings about unstable surfaces. If unstable surfaces are found, the calculation will continue with the next face. In most cases, unstable surfaces are a result of the crystal structure not being optimized using the current energy settings. It is recommended that you optimize the geometry of the crystal structure as part of the structure preparation step, using the same energy settings as those used for the Morphology calculation.

You should not find any warning messages in this particular report file.

Close **pigment_red.txt**.

The main output of a Morphology calculation is a 3D Atomistic document (called the crystal habit document), **pigment_red.xsd**, containing the unit cell of the input crystal structure overlaid with a projection of the calculated crystal habit, and a study table document, **pigment_red.std**, providing a detailed list of properties for each growth face. **pigment_red.xsd** is automatically displayed in the Materials Visualizer once the calculation is finished. **pigment_red.std** is shown as part of the project in the Project Explorer.

You will examine the crystal habit document first.

Close **Status.txt** and make **pigment_red.xsd** the active document. Examine the habit document using the tools on the **3D Viewer** toolbar.

You can control the relative scaling of the habit data with respect to the atomistic data, since these two sets of data are defined in different coordinate systems.

Right-click in **pigment_red.xsd** and choose **Display Style** from the shortcut menu to open the Display Style dialog.

On the **Habit** tab, change the **Habit size** to **0.500**, then press the **TAB** key. Repeat this for a **Habit size** of **1.000**. Alternatively, use the spin controls to change the relative scaling of the two objects.

The larger the *Habit size* setting, the larger the size of the calculated crystal habit relative to the input crystal structure.

Move the **Transparency** slider from left to right before setting it back to the default midpoint position.

The transparency of the habit facets changes from completely opaque (solid) when the slider bar is in its leftmost position to fully transparent (invisible) when in its rightmost position.

Uncheck the **Show facets** checkbox and then check it again.

This option allows you to switch on and off display of the facets of the crystal habit. Selecting one or more facets and then unchecking the *Show facets* checkbox enables you to switch off the display of particular facets.

To make the crystal habit easier to see, you can switch off the display of the crystal structure.

On the **Lattice** tab, change the **Style** to **None** in the **Display style** section. **Close** the Display Style dialog.

The crystal habit representation contains two important types of objects - growth faces and habit facets:

- Growth faces - represent all slow growing crystal faces that have been included in the Morphology calculation. They are placed at a distances from the growth origin equivalent to the calculated center-to-plane distances. Growth faces are represented as arrows normal to the respective planes, with their bases on the planes. By default, growth faces are not displayed.
- Habit facets - form the external shape of the crystal. The habit is built from growth faces that enclose the smallest volume around the growth origin. Each habit facet is associated with a growth face. However, the reverse is not necessarily true. Habit facets are represented as solid planes and are visible by default.

Right-click in **pigment_red.xsd** and choose **Label** from the shortcut menu to open the Label dialog.

Select **Habit Facet** from the **Object type** dropdown list and choose **FacetMillerIndex** from the **Properties** list. Click the **Apply** button and **close** the dialog.

The habit facets are now labeled with their Miller indices.

Open the **Morphology Calculation** dialog. On the **Setup** tab, change the **Task** to **Report habit properties**. Click the **Run** button and close the dialog.

A grid document, **pigment_red.xgd**, summarizing important habit properties in tabular form, is created in the **Pigment_red Mph Growth** folder. The grid document contains three different tabs:

- **Summary** - contains important habit properties, including the point group, aspect ratio (the ratio between the longest and the shortest diameter), surface area, volume, number of symmetrically unique facets, and the total number of facets of the habit.
- **Facets** - lists all the symmetrically unique facets of the habit and reports the Miller indices representing one of the symmetry-related facets, the symmetry multiplicity of the facet, the center-to-plane distance, the area and percentage area of a single facet, and the total area and total percentage area of all symmetry-related facets.
- **Angles** - lists the interplanar angles between facets.

Tip: This grid document can be exported as a **.csv** file that can be opened in spreadsheet applications such as Microsoft Excel.

Looking at the calculated crystal morphology of Pigment Red, you will notice the slowest growing (0 0 1) face accounts for more than 70% of the crystal surface. The aspect ratio suggests a plate-like morphology. Inhibition of the growth of the fast growing (0 1 0) and (1 -1 0) faces might lead to a more isometric crystal morphology.

Close **pigment_red.xgd**, click the **Yes** button when prompted to save the file.

Make **pigment_red.xsd** the active document. Select the **(0 1 0)** face of the habit. Open the **Display Style** dialog.

On the **Habit** tab, click on the **Facet color** chooser and select a color from the palette on the Color dialog and click the **OK** button. Click once in **pigment_red.xsd** to deselect everything.

Repeat the same procedure for the **(1 -1 0)** face of the habit.

Note: Symmetry is not respected when coloring growth faces, making it possible to color symmetry-related faces individually.

Hold down the **SHIFT** key and click on the **(0 1 0)** face and then the **(1 -1 0)** face of the habit.

The (0 1 0) and (1 -1 0) faces are colored yellow, indicating that they are selected.

On the **Habit** tab of the Display Style dialog, check the **Show growth faces** checkbox.

The (0 1 0) and (1 -1 0) growth faces are represented as arrows normal to the growth planes, with their bases on the planes.

Set the **Arrow size** in the **Display style** section to **0.35** and close the dialog.

The *Size* setting controls the relative size of the arrows representing the growth faces and has a default value of **0.10**.

Note: The *Show facets*, *Show growth faces*, and *Size* controls all respect the symmetry of the system. So, if one facet or growth face has its visibility altered by these controls, all the symmetrically equivalent facets or growth faces will be affected in the same way.

Deselect all the faces by clicking on the background, then select one of the growth face arrows. Hold down the **SHIFT** and **ALT** keys and right-click. Drag the mouse from right to left, then upward to change the center-to-plane distance (growth rate).

As you move the object, the habit will be automatically updated. If you move a habit facet and increase the center-to-plane distance to a point where it stops being part of the habit, the facet object disappears. Similarly, if you reduce the center-to-plane distance (growth rate) of a growth face such that it becomes part of the habit, a habit facet will automatically be created and associated with the growth face.

Continue to manipulate the center-to-plane distances for the (0 1 0) and (1 -1 0) faces until you obtain a more isometric morphology. Now you should find the new center-to-plane distances for the growth faces in the modified crystal habit.

Open the **Morphology Calculation** dialog. On the **Setup** tab, set the **Task** to **Report habit properties**. Click the **Run** and close the dialog.

A new grid file, `pigment_red (2).xgd`, is created in the `pigment_red Mph Growth` folder.

Close `pigment_red.xsd` and click the **No** button when prompted to save the file.

In the Project Explorer, double-click on `pigment_red.xgd` in the `pigment_red Mph Growth` folder. Select **Window | Tile Vertically** from the menu bar so that you can see both of the grid documents.

On the **Facets** tabs, compare the **Distance** for (0 1 0) and (1 -1 0) in `pigment_red.xgd` and `pigment_red (2).xgd`.

Repeat the same procedure for other growth faces of interest. After examining the crystal habit document, you will now analyze the surface properties for each growth plane in the study table document.

Select **File | Save Project** from the menu bar and then **Window | Close All**. In the Project Explorer, double-click on `pigment_red.std` in the `pigment_red Mph Growth` folder.

The study table provides a detailed tabular view of properties for each growth face, as calculated during the Morphology run, including Miller indices, multiplicity, interplanar spacing, surface area, atomistic surface structures, attachment energy (*E_{att}*) and its non-bond components, center-to-plane distance, total facet area, and percentage total facet area.

In addition to making simple changes to the crystal habit document to study the dependence of the morphology on growth rate interactively, you can achieve the same effect by manually editing the center-to-plane distances in the study table.

Select column **F** by clicking on the column header. Hold down the **SHIFT** key, and select columns **G**, **H**, and **I**. Right-click on the header of one of the selected columns in **pigment_red.std** and choose **Hide** from the shortcut menu.

You can now see the Miller indices, atomistic surface structures, and the center-to-plane distances for each growth face in one view.

Double-click on the **Distance** corresponding to the (0 1 0) face and change it to **10**, then press the **TAB** key. Repeat the same procedure for the (1 -1 0) face.

Select column **A** by clicking on the column header. Hold down the **CTRL** key and click on the header of column **J**.

Open the **Morphology Calculation** dialog, change the **Task** to **Generate habit**. Click the **Run** button and close the dialog.

You should get a more isometric crystal habit.

Tip: The study table infrastructure provides extensive functionality that enables you to sort, filter, process, and plot data, and to calculate additional properties.

Make the new **pigment_red.xsd** the active document and select **File | Save As...** from the menu bar to open the Save As dialog. Enter **pigment_red_isometric** and click the **Save** button.

Select **Window | Close All** from the menu bar. Click the **No to All** button when prompted to save the changes.

The atomistic surface models are embedded in the study table and can be viewed independently. You will examine the (0 1 0) surface.



In the Project Explorer, double-click on **pigment_red.std** to open the study table. Double-click on **Surface (0 1 0)** in column **E** to display a Study Table Detail View of the (0 1 0) surface.

You can now examine the surface in detail. At this stage, it would be useful to increase the thickness of the surface model.

Select **Build | Surfaces | Recleave Surface** from the menu bar to display the Recleave Surface dialog. On the **Surface Box** tab, increase the **Thickness** to **3.0** in the **Fractional** column. Close the dialog.

The surface is recleaved.

Note: The recleave functionality cleaves the new surface from the crystal structure document **pigment_red.xsd** situated in the results folder of the Morphology calculation. If you turned off [lattice visibility](#) in the crystal habit document to better investigate the habit, you will need to turn it on again, otherwise, all the objects in the surface structure will be invisible. You can make the lattice visible again by resetting the *Style* to **Default** on the *Lattice* tab of the Display Style dialog.

Copy the entire document by clicking the **Copy** button . In the Project Explorer, right-click on the project **Pigment Red** and choose **New | 3D Atomistic Document** from the shortcut menu. Paste the structure into the empty document using the **Paste** button . In the Project Explorer, right-click on **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Change the name of the document to **pigment_red_010.xsd**.

Close **pigment_red Detail View: E2 (Surface (0 1 0))**.

A dialog is displayed asking if you want to commit the edits made to the study table.

Click the **No** button when prompted to save the changes.

Repeat the same procedure for **pigment_red.std**, then select **File | Save Project** from the menu bar.

Note: If you modify any surface and commit the change to the study table, the changes will be permanent.

An additive can interact with the fast growing (0 1 0) faces, acting as a growth inhibitor for these faces. Slowing down the growth rate of the (0 1 0) faces could result in the Pigment Red crystals developing a more isometric morphology. The attachment energy of the growth face is needed for comparison to such a calculation.

Open **pigment_red.std** and find the value of **Eatt(Total)** in column **F** for the (0 1 0) face.

Interactions between the Pigment Red (0 1 0) surface and the inhibitor can be studied through dynamics simulation as described in the [Modeling inhibitor adsorption onto a Pigment Red crystal face](#) Adsorption Locator tutorial.

This is the end of the tutorial.

Calculating morphology using Crystal Graph

Purpose: Illustrates how to use crystal graph to identify interactions between molecular fragments in a crystal.

Modules: Materials Visualizer, Morphology, COMPASS

Time: 🕒 🕒

Prerequisites: [Morphology prediction for Pigment Red](#)

Introduction

Pigment Red (a diphenyl derivative of 1,4-diketopyrrolo(3,4-c)pyrrole, DPP) is a high quality heterocyclic pigment, offering good heat stability, high coloring strength and hiding power, and excellent light and weather fastness. It can be produced as transparent or opaque color by controlling the particle size during manufacture.

In this tutorial instead of performing an energy calculation as part of the Morphology calculation, you will use the Crystal Graph functionality to identify interactions between molecular fragments in a crystal. The bond energies for all these interactions can then be calculated and used as input for growth morphology or equilibrium morphology calculations to determine the habit of the crystal.

The Hartman-Perdok theory ([Hartman-Perdok, 1955](#); [Bennema, 1996](#); [Grimbergen et al., 1998](#)) starts from the concept that crystals are stable because of the ability of the molecular fragments to form strong attractive intermolecular interactions. A crystal graph describes interactions between molecular fragments in a crystal structure. This enables you to explore the effect of intermolecular interaction strength on crystal morphology.

This tutorial covers:

- [Getting started](#)
- [To set up and run Crystal Graph](#)
- [To analyze the Crystal Graph results](#)
- [To calculate morphology using the Crystal Graph outputs](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Pigment Red CG** as the project name, click the **OK** button.

The new project is created with *Pigment Red CG* listed in the Project Explorer. Now you will import the input file you will be studying.


In the Project Explorer, right-click on the project root and select **Import...** to open the Import Document dialog. Navigate to the location where you saved the **Pigment Red** project in [Morphology prediction for Pigment Red](#). Open **Pigment Red Files\Documents\pigment_red Forcite GeomOpt\pigment_red Mph Growth\pigment_red.xsd** and click the **OK** button.

Right-click on **pigment_red.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Enter **pigment_red_input** as the name and press the **ENTER** key.

You will save the project.

Select **File | Save Project** from the menu bar.

2. To set up and run Crystal Graph

Click the **Morphology** button  on the toolbar and choose **Crystal Graph** from the dropdown list to open the Crystal Graph Calculation dialog.

On the **Setup** tab, set the **Forcefield** to **COMPASS**, the **Charges** to **Forcefield assigned**, and the **Quality** to **Medium**.

Note: It is important that you use the same energy settings for the Crystal Graph calculation as you used to optimize the crystal structure. So, the energy settings are linked to the energy settings on the Morphology Calculation dialog.

Make sure that the **Assign molecules automatically** checkbox is checked.

Enabling this option means that all the atoms in the crystal structure will be automatically assigned to molecules.

Tip: Alternatively, to define molecules manually, use the tools on the **Molecules** tab of the Crystal Graph Calculation dialog to group manually selected atoms in the crystal structure into molecules.

Note: When you choose to automatically assign molecules, all the atoms in a covalently bonded fragment will be assigned as a molecule, while individual atoms in, for example, an ionic structure will be assigned as separate molecules. At present, these are the only two possibilities that will be recognized.

When you are manually assigning molecules, the only recognizable selection is either an entire covalently bonded fragment or individual atoms that do not have any covalent bonds to other atoms, for example elemental metals. You cannot create a molecule from part of a molecular fragment or from multiple atoms or fragments that are held together by non-covalent bonding, such as ionic or hydrogen bonding.

Select the **Maximum unit cell separation** option.

This option specifies the maximum molecular center-to-center distances along each lattice vector for molecular interactions in multiples of the unit cell dimensions. Interactions that extend over distances greater than the specified values are not considered in the Crystal Graph calculation.

Alternatively, you can select the *Maximum molecular separation* option to specify the maximum distance allowable between the nearest two atoms in the interacting molecules. In this tutorial, you will use the default spatial range of *Maximum unit cell separation*.

On the **Setup** tab, make sure that the **Apply initial energy filter** checkbox is checked.

The energy filter applies an energy cutoff to exclude the weakest interactions. The default value of -0.596 kcal mol⁻¹ represents the thermal energy at room temperature, that is, interactions with energies weaker than this value will not be stable at room temperature.

Click the **Create** button and close the dialog.

You should wait until the calculation is finished before proceeding.

3. To analyze the Crystal Graph results

In this section, you will analyze the outputs from the Crystal Graph run.

Once the calculation is finished, a crystal graph is displayed in the `pigment_red_input.xsd` document, overlaid on the unit cell view. You can control the way in which the molecular interactions in a crystal graph are rendered and colored.

Make `pigment_red_input.xsd` the active document and select **File | Save As...** from the menu bar to open the Save As dialog. Enter `pigment_red_CG` as the **File name** and click the **Save** button.

Right-click in the `pigment_red_CG.xsd` 3D Viewer and choose **Display Style** from the shortcut menu to open the Display Style dialog. On the **Molecule Interaction** tab, change the **Display style** setting from **Dashed line** to **Line**.

All the molecular interactions are now rendered as solid lines, rather than the default display style of dashed lines. You can control the relative line width of the interactions.

Change the **Line width** to **1.00**.

You may wish to color the interactions according to their bond energies.

In the **Coloring** section, select the **Color by energy** option.

In the current selection, the strongest interactions are colored blue and the weakest colored red. The colors are smoothly graduated between these two extremes for interactions with intermediate bond energies.

Note: The interaction coloring will not be updated dynamically if the energies are re-evaluated. In order for the interaction coloring to reflect current property values correctly, it is recommended that you recolor the molecule interactions whenever any changes to their bond energies have been made.

In `pigment_red_CG.xsd`, select one of the interactions colored in blue. Right-click in the 3D Viewer and choose **Label** from the shortcut menu to display the Label dialog.

Set the **Object type** to **Energy**. Select **PotentialEnergy** from the **Properties** list and click the **Apply** button.

Repeat the same procedure for one of the interactions colored in red.

The two interactions are now labeled with their potential energy.

Next, you will look at the molecular fragments in the crystal.

Click once in **pigment_red_CG.xsd** to deselect everything. On the Label dialog, click the **Remove All** button and **close** the dialog.

Select the **Molecule** tab on the Display Style dialog, change the **Display style** from **None** to **Polyhedron**, and then **Ellipsoid**.

When the *Polyhedron* display style is selected, all the molecules are rendered as polyhedra. The vertices of the polyhedra are defined by the locations of the atoms contained within each molecule. When *Ellipsoid* is selected, the molecules are rendered as ellipsoids covering the approximate extent of the atoms contained in each molecule.

Click the **Color** chooser to display the Color dialog and select a color from the palette. Click the **OK** button.

All the molecule objects are now colored in the chosen color. To make the crystal graph easier to see, you can switch off the display of the molecules.

On the **Molecule** tab of the Display Style dialog, change the **Display style** back to **None** and **close** the dialog.

It is common for a Crystal Graph calculation to produce a large number of interactions. You can filter the interactions according to energy so that you can disregard the less significant interactions and focus only on those that appear to have the greatest influence on the crystal morphology.

Open the **Crystal Graph Calculation** dialog. On the **Analysis** tab, move the **Weakest** slider in the **Energy filter** section from its rightmost position one notch to the left. It is also possible to enter a specific value in the text box.

The weakest energy is now set to about $-3.9 \text{ kcal mol}^{-1}$. All the interactions with energies that fall outside the defined range are selected in the crystal graph.

Click the **Apply** button on the Crystal Graph Calculation dialog.

All the selected interactions with energies that fall outside the defined range are deleted from the crystal graph.

Select **Edit | Undo Apply Crystal Graph Criteria** from the menu bar.

The crystal graph is now restored to its original state with the weakest energy filter set to about $-0.9 \text{ kcal mol}^{-1}$.

On the **Analysis** tab of the Crystal Graph Calculation dialog, move the **Weakest** slider in the **Energy filter** section from its rightmost position one notch to the left.

When graph augmentation is applied, all the interactions that fail the energy filter, but which are different from every other interaction sharing the same molecule by more than 45° , are restored to the crystal graph. A specific set of interactions is selected and deselected in **pigment_red_CG.xsd** according to the energy filter setting, as well as the crystal graph augmentation setting.

Note: When augmentation is applied, Crystal Graph will try to restore interactions that fall outside the defined energy filter range, starting with the strongest rejected interaction and continuing with the second strongest, until no more interactions can be added that conform to the specified angle constraint.

The crystal graph augmentation method is intended to ensure that sufficient interactions exist to define a suitable habit when used in an appropriate Morphology calculation.

With the **Perform graph augmentation by directional criterion** checkbox checked, click the **Apply** button.

Fewer interactions are deleted from the crystal graph as compared to the same operation without graph augmentation applied.

Select **Edit | Undo Apply Crystal Graph Criteria** from the menu bar.

Click the **Export crystal graph as grid document** button on the Crystal Graph Calculation dialog and **close** the dialog.

A grid document, `pigment_red_CG.xgd`, listing all the interactions in the crystal graph, along with their lengths and bond energies, is created in the Project Explorer.

Note: Interactions that have been filtered out or manually deleted from a crystal graph are removed permanently and will not be listed in the grid document.

The grid document contains the following columns:

- *Molecule1, Molecule2* - list the atomic compositions of the molecules, along with the symmetry transformations that uniquely identify each individual molecule.
- *Unit Cell of Molecule2* - reports the coordinates, in unit cell lengths, of the unit cell containing Molecule2 in relation to that containing Molecule1, which is taken to be located at the origin.
- *Multiplicity* - reports the symmetry multiplicity.
- *Center-Center Length* - reports the length, in Å, of the interaction, that is the distance between the centers of the two molecules.
- *Energy* - reports the bond energy, in kcal mol⁻¹, of the interaction.

Note: Crystal Graph considers molecular interactions which span unit cells to operate bidirectionally and reports them as such, so that in the case of two isolated molecules in different unit cells, both the interaction Molecule1···Molecule2 and its inverse, Molecule2···Molecule1, would be reported, even though their lengths and bond energies are identical. This ensures that all interactions 'entering' a unit cell are matched by a similar interaction 'leaving' the unit cell, as in the visual representation of the crystal graph.

Note: A crystal graph is associated with the crystal structure from which it was derived. Modifying the atomic arrangement of the crystal structure, by moving or deleting atoms, will invalidate the crystal graph.

Tip: This grid document can be exported as a `.csv` file that can be opened in spreadsheet applications such as Microsoft Excel.

4. To calculate morphology using the Crystal Graph outputs

In this section, you will calculate the growth morphology of Pigment Red by using the orientation and bond energies of the interactions reported in the crystal graph as input.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **pigment_red_CG.xsd**.

Open the **Morphology Calculation** dialog. On the **Setup** tab, make sure that the **Task** is set to **Growth morphology** and the **Quality** to **Medium**. Change the **Energy method** to **Crystal Graph**.

The **Energy** tab of the Morphology Calculation dialog is automatically disabled when **Crystal Graph** is selected as the **Energy method**. Morphology calculates the attachment energies using the bond energies of the interactions reported in the currently active crystal graph document. Since the number of energy calculations required is reduced, a shorter calculation time can be expected.

On the **Faces** tab, set the **Quality** to **Medium**. Click the **Run** button and **close** the dialog.

Close **pigment_red_CG.xsd**.

Once the calculation starts, a new folder called **pigment_red_CG Mph Growth** is created in the Project Explorer. You should wait until the job finishes before proceeding.

You will examine the results of the calculation, starting from the text output file **pigment_red_CG.txt**. You should not find any warning messages in this particular report file.

Scroll through **pigment_red_CG.txt**. When you are satisfied that no errors or warnings are reported in this document, close the text document.

Make **pigment_red_CG Mph Growth\pigment_red_CG.xsd** the active document and examine the habit document using the tools on the **3D Viewer** toolbar.

Next, you will explore the effect of the intermolecular interaction strength on the crystal morphology.

Open **pigment_red_CG.xsd** and select one of the interactions highlighted in red.

Select **View | Explorers | Properties Explorer** from the menu bar. Choose **Energy** from the **Filter** dropdown list. Double-click on **PotentialEnergy** to display the Edit PotentialEnergy dialog. Enter **-10** and click the **OK** button. Click in the 3D Viewer to deselect the molecular interaction.

The potential energy for this interaction is now set to **-10 kcal mol⁻¹**. The same potential energy value is automatically applied to all its symmetry images.

Open the **Morphology Calculation** dialog. Click the **Run** button and close the dialog.

Close the **pigment_red_CG.xsd** document and click the **No** button when prompted to save the changes.

When the calculation is complete, you will examine the crystal habit document. Increasing the bond strength for these weak interactions improves the stability of the growth planes constructed from them. Stable growth planes are more likely to have smaller center-to-plane distances, so a more isometric morphology is anticipated, in agreement with the Hartman-Perdok theory.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **pigment_red_CG Mph Growth\pigment_red_CG.xsd**.

Next, you will import the crystal morphology obtained using the Forcite energy method in [Morphology prediction for Pigment Red](#) and compare it with the morphology obtained using the Crystal Graph method.

In the Project Explorer, right-click on the project root and select **Import...** to open the Import Document dialog. Navigate to the location where you saved the **Pigment Red** project in [Morphology prediction for Pigment Red](#). Open **Pigment Red Files\Documents\pigment_red Forcite GeomOpt\pigment_red Forcite GeomOpt\pigment_red Mph Growth\pigment_red.xsd** and click the **OK** button. You should also import the **pigment_red.xgd** grid document from the same location.

Right-click on **pigment_red.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Enter **pigment_red_forcite** as the name and press the **ENTER** key. Repeat this to rename **pigment_red.xgd** as **pigment_red_forcite.xgd**.

You will hide the facets, lattice, and molecules from both predicted morphologies to leave just the crystal shape, to ease comparison.

With the focus on **pigment_red_CG Mph Growth\pigment_red_CG.xsd**, right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog.

On the **Lattice** tab, change the **Style** from Default to **None** in the **Display style** section.


On the **Habit** tab, uncheck the **Show facets** checkbox. Set the **Edge color** to green. Repeat these steps for **pigment_red_forcite.xsd** but set the **Edge color** to red.

You can overlay the two documents by inserting them into a 3D Atomistic Collection document.

In the Project Explorer, right-click on the project root **Pigment Red CG** and select **New | 3D Atomistic Collection Document** from the shortcut menu.

In the Project Explorer, right-click on **3D Atomistic Collection.xod** and select **Rename** from the shortcut menu. Change the name of the new collection document to **morphology_overlay.xod**.

A collection document allows you to display multiple structures in the same 3D space, while keeping them isolated in all other respects; for instance, there can be no physical interaction between systems in a collection document.

In the Project Explorer, hold down the **CTRL** key and select **pigment_red_CG Mph Growth\pigment_red_CG.xsd** and **pigment_red_forcite.xsd**. Right-click on one of the selected files and choose **Insert Into** from the shortcut menu. Click the **3D Viewer Reset View** button .

The two habits are overlaid in the collection document. If there is a size discrepancy between the habits, you can change this using the Display Style dialog.

Open the **Display Style** dialog and select the **Habit** tab. Right-click in **morphology_overlay.xod** and select **Physical Systems** from the shortcut menu.

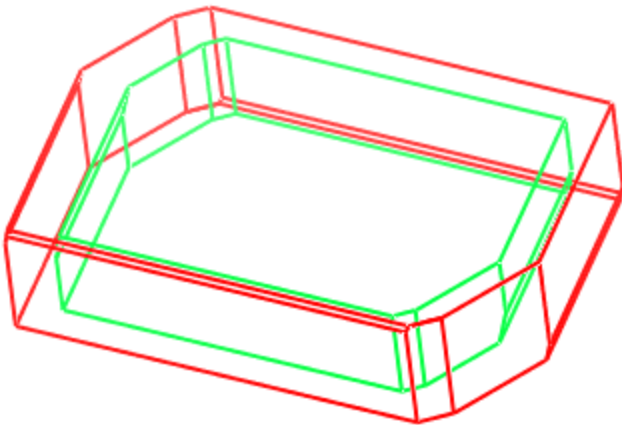
This opens the Physical Systems dialog which enables you to select and work with multiple systems in a collection document.

On the Physical Systems dialog, select **pigment_red_forcite** followed by **pigment_red_CG**.

The *Habit size* value on the *Habit* tab of the Display Style dialog changes if you have different values set for the two structures. You should set the *Habit size* parameter to the same value for both structures.

Select **pigment_red_forcite** on the Physical Systems dialog. On the **Habit** tab of the Display Style dialog, set the **Habit size** to **0.6**. Repeat this process for **pigment_red_CG** and **close** the Physical Systems dialog.

The two crystal morphologies are now displayed in the same 3D space, colored in red and green. They are in excellent agreement with each other, as shown below.



Overlay of the morphology of Pigment Red obtained using the Forcite energy method (red) and the Crystal Graph energy method (green)

You may wish to examine the finer details of the two crystal morphologies.

Close **morphology_overlay.xod** and click the **Yes** button when prompted to save the file as part of the project.

In the Project Explorer, double-click on **pigment_red_CG Mph Growth\pigment_red_CG.xsd**.

Open the **Morphology Calculation** dialog and, on the **Setup** tab, set the **Task** to **Report habit properties**. Click the **Run** button and **close** the dialog.

A new grid file, **pigment_red_CG.xgd**, is created in the **pigment_red_CG Mph Growth** folder. You will compare this with the habit properties from the Forcite morphology calculation in the **pigment_red_forcite.xgd** document that you imported.

Close **pigment_red_CG.xsd** and click the **Yes** button when prompted to save the file as part of the project.

In the Project Explorer, double-click on **pigment_red_forcite.xgd** to make it the active document.

Select **Window | Tile Horizontally** from the menu bar.

The two grid documents are now titled horizontally.

There are six habit facets in the crystal morphology calculated by the Crystal Graph energy method and these are also identified by the Forcite energy method. However, two minor facets, (0 1 -1) (0.859% of the total surface area) and (1 1 -1) (0.003% of the total surface area), produced by Forcite are not present in the crystal morphology obtained using the Crystal Graph energy method.

The observation is not unexpected. The Crystal Graph energy method only considers bond energies for the interactions between molecular fragments in a crystal structure. As a result, the energy evaluation is less accurate than a full energy evaluation using the Forcite energy method. In addition, Ewald summation can be used with the Forcite energy method. This is extremely important if individual molecules have a net charge, such as in ionic systems, or for a morphology consisting of planes having a dipole moment. In such cases, without Ewald summations, the calculation will not converge properly because the interaction radius will often contain a non-zero net charge, leading to arbitrary energy oscillations as a function of interaction radius. For non-ionic systems, you must decide whether the increased accuracy obtained by using Ewald summations justifies the greater computation time.

In the example presented here, the two energy methods provide results that are in excellent agreement.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Hartman, P.; Perdok, W. *Acta Crystallogr.*, **8**, 521 (1955).

Bennema, P. J. *Cryst. Growth*, **166**, 17 (1996).

Grimbergen, R. F. P.; Bennema, P.; Meekes H. *Acta Crystallogr., Sect. A*, **54** 491 (1998).

ONETEP tutorials

The following tutorials illustrate how to utilize ONETEP's capabilities.

LiF density of states (DOS) with ONETEP and CASTEP

Purpose: Introduces how to use the ONETEP module in Materials Studio. Special attention is paid to the comparison with CASTEP results.

Modules: Materials Visualizer, ONETEP and CASTEP

Time: 🕒🕒🕒

Prerequisites: None

Background

Lithium fluoride is a white, inorganic, crystalline, ionic, solid salt under standard conditions. It transmits ultraviolet radiation more efficiently than any other known substance. Uses include specialized UV optics and as a material used to record gamma and neutron exposure in thermoluminescent dosimeters. Lithium fluoride also has a very high electrical resistance due to its wide band gap. Griceite is the name for very rare mineralogical form of LiF.

Lithium fluoride (highly enriched in the common isotope lithium-7) forms the basic constituent of the preferred fluoride salt mixture used in liquid-fluoride nuclear reactors. Typically lithium fluoride is mixed with beryllium fluoride to form a base solvent, into which fluorides of uranium and thorium are introduced. Lithium fluoride is exceptionally chemically stable and LiF/BeF₂ mixtures have low melting points and the best neutronic properties of fluoride salt combinations appropriate for reactor use.

In this tutorial you will use ONETEP and CASTEP to study the electronic structure of lithium fluoride and to obtain the corresponding density of states (DOS) charts.

The following steps will be covered here:

- [Getting started](#)
- [To prepare the structure](#)
- [To run the ONETEP calculation](#)
- [To run the CASTEP calculation](#)
- [To compare the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Note: The calculations in this tutorial are demanding in terms of CPU time and memory requirements. It is likely that you would need a Linux server with at least 2 GB of available memory in order to complete the tutorial. Error messages in ONETEP or CASTEP output files containing "Out of RAM" or similar statements indicate that the memory on the server is not sufficient. The output files from both the ONETEP and CASTEP calculations described in this tutorial are provided in the Examples/Projects/ONETEP/LiF Files/Documents directory of your Materials Studio installation.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **LiF_DOS** as the project name, click the **OK** button.

The new project is created with *LiF_DOS* listed in the Project Explorer.

2. To prepare the structure

The first thing you need to do is to prepare the structure of the lithium fluoride crystal.

Select **File | New...** from the menu bar to open the New Document dialog. Select **3D Atomistic** from the options and click the **OK** button.

Select **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog. On the **Space Group** tab enter **FM-3M** for **Enter group**. On the **Lattice Parameters** tab enter **4.03** as the **a** length in Å. Click the **Build** button.

A new window with the crystal lattice will be opened. Now you need to add the Li and F atoms.

Select **Build | Add Atoms** from the menu bar to open the Add Atoms dialog. Select **Li** as **Element** and click the **Add** button.

Enter for **F** as the **Element** and set **a** to **0.5**, click the **Add** button and close the dialog.

The unit cell you have just created contains 8 atoms only. For this tutorial you will perform a calculation on a larger system, so you need to build a $2 \times 2 \times 2$ supercell.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Enter **2** for the values of **A**, **B** and **C**. Click the **Create Supercell** button and close the dialog.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. On the Atom tab select **Ball and stick** and close the dialog.

Rename the document **LiF.xsd**.

The final LiF structure containing 64 atoms is depicted in Figure 1.

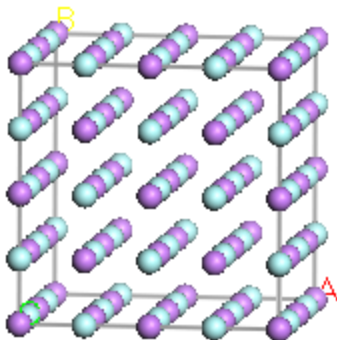



Figure 1. LiF structure

3. To run the ONETEP calculation

The next step is to setup the ONETEP calculation.

With **LiF.xsd** as the active document, click the **ONETEP** button  on the **Modules** toolbar and select **Calculation** to open the ONETEP Calculation dialog.

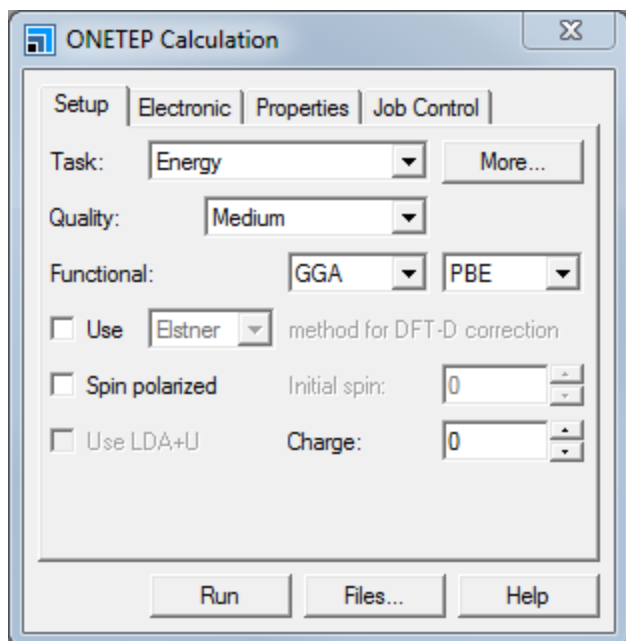


Figure 2. ONETEP Calculation dialog, Setup tab.

On the **Setup** tab select **Energy** as the **Task** and **Medium** for the **Quality**. Choose **GGA-PBE** from the **Functional** dropdown list.

On the **Properties** tab check the **Population analysis** checkbox.

To obtain results in a reasonable amount of time, you will change the Li and F radii, this should not be done for production calculations.

On the **Electronic** tab click the **More...** button to open the **ONETEP Electronic Options** dialog. Choose the **Basis Set** tab, change the Li and F radius values to **3.3 Å** and close the dialog.

To complete the ONETEP calculation in a reasonable amount of time you need to run the calculation in parallel.

On the ONETEP Calculation dialog select the **Job Control** tab. Enter the number of cores on which you want to run the calculation in the **Run in parallel on** textbox.


Now you are ready to run the calculation.

Click the **Run** button and close the dialog.

Tip: While the job is running, you can proceed to [step 4](#).

Depending on your hardware, this calculation may take around 30 minutes to complete. The results of the calculation will be stored in the **LiF ONETEP Energy** folder. The **LiF.onetep** file is the output of the calculation and includes the SCF progress, the final converged energy, the population analysis

results and a summary of orbitals and occupancies. To visualize the DOS or the orbitals you need to use the ONETEP Analysis dialog. The output of this calculation is provided in the `Examples/Projects/ONETEP/LiF Files/Documents` directory in the LiF ONETEP Energy folder.

When the calculation has completed open the final **LiF.xsd** document. Click the **ONETEP** button  on the **Modules** toolbar and select **Analysis** to open the ONETEP Analysis dialog.

Select **Density of states** from the list and click the **View** button. A new window with a chart of the DOS is displayed.

The final DOS graph is depicted in Figure 3 below.

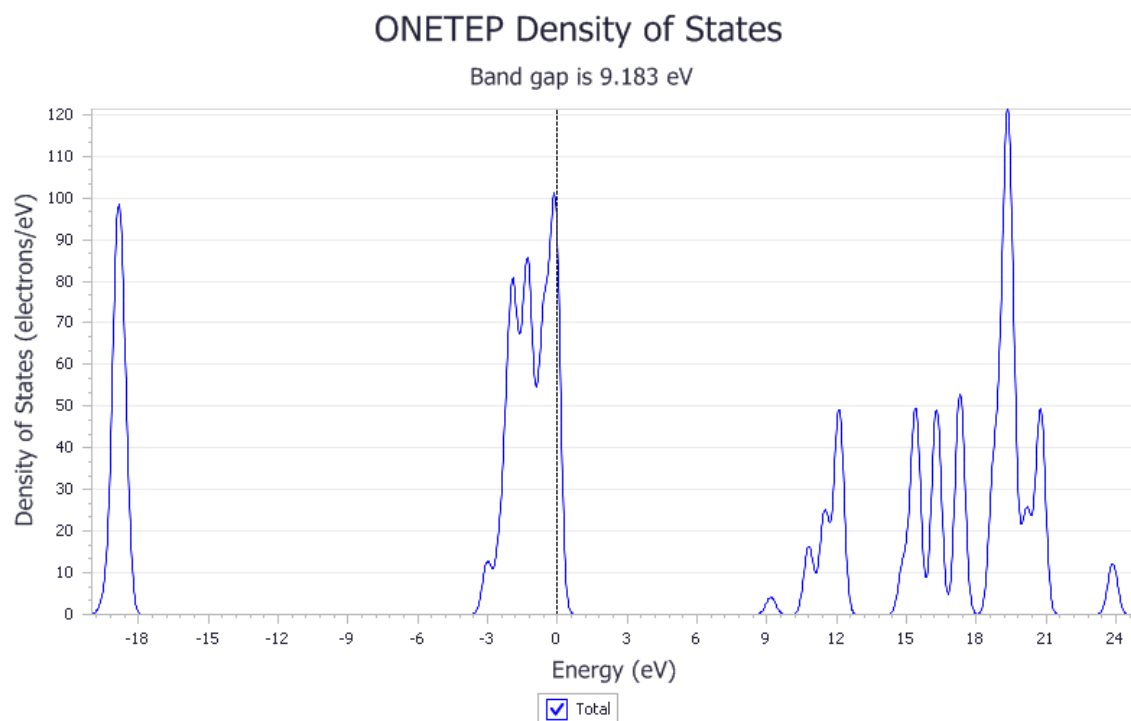



Figure 3. ONETEP DOS for a LiF crystal containing 64 atoms.

You can proceed in a similar way to display other properties (orbitals, potentials, and so on) if they have been requested during the energy calculation.

4. To run the CASTEP calculation

You will now proceed to setup the CASTEP calculation. To obtain similar results with both modules you will run a CASTEP calculation with a single k-point (Gamma point) and the same norm conserving pseudopotentials.

With the original **LiF.xsd** document as the active document, click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** to open the CASTEP Calculation dialog.

On the **Setup** tab select **Energy** as the **Task** and **GGA-PBE** as the **Functional**. Uncheck the **Metal** checkbox as the compound is definitely dielectric. On the **Electronic** tab select **Gamma** as the **k-point set** and set the **Pseudopotentials** to **Norm conserving**. Click the **More...** button to open the CASTEP Electronic Options dialog. Choose the **Potentials** tab and select **Reciprocal space** for **Pseudopotential representation**. Close the dialog.

To be able to get information about the conduction band you need to set up the number of empty bands used in the DOS CASTEP calculation. 20 empty bands will be enough to get the first conduction band for LiF.

On the **Properties** tab of the CASTEP Calculation dialog check the **Density of states** checkbox and change the number of **Empty bands** to **20**. Select **Gamma** from the **k-point set** dropdown list. Uncheck the **Population analysis** checkbox.

Before running the calculation you just need to define the number of processors where you want to run the calculation.

On the **Job Control** tab enter the number of cores on which you want to run the calculation in the **Run in parallel on** textbox.

Now you are ready to run the calculation.

Click the **Run** button.

Click the **No** button on the warning dialog so that the calculation proceeds using P1 symmetry.

Close the CASTEP Calculation dialog.

The results of the calculation will be stored in the LiF CASTEP Energy folder. Depending on your hardware, this calculation may take around 2 minutes to complete. The output of this calculation is provided in the Examples/Projects/ONETEP/LiF Files/Documents directory in the LiF CASTEP Energy folder. To visualize the DOS you need to use the CASTEP Analysis dialog.

When the calculation is complete, open the **LiF CASTEP Energy/LiF.xsd** document, select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog.

Select **Density of states** from the list and click the **View** button. A new chart of the DOS will be displayed.

The final CASTEP DOS graph is depicted in Figure 4 below.

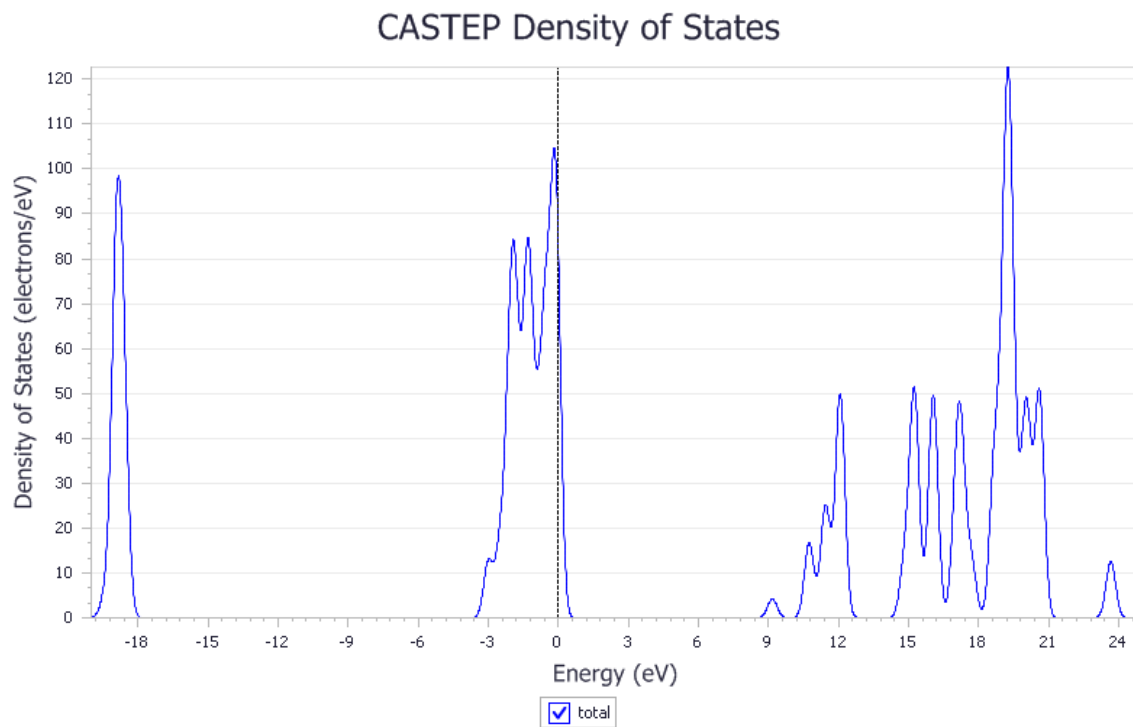


Figure 4. CASTEP DOS for a LiF crystal containing 64 atoms.

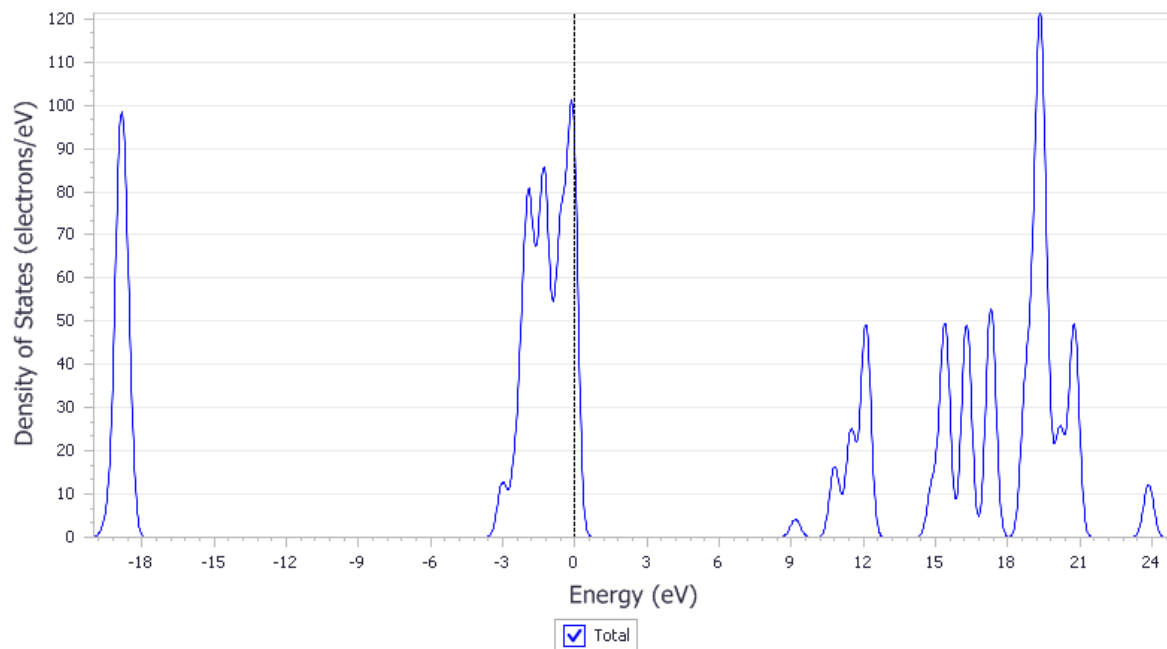
5. To compare the results

If you check the final energies obtained with ONETEP and CASTEP you will see that those are of the same order of magnitude (-21519.25 eV with ONETEP and -21522.11 eV with CASTEP), the DOS results are also very similar.

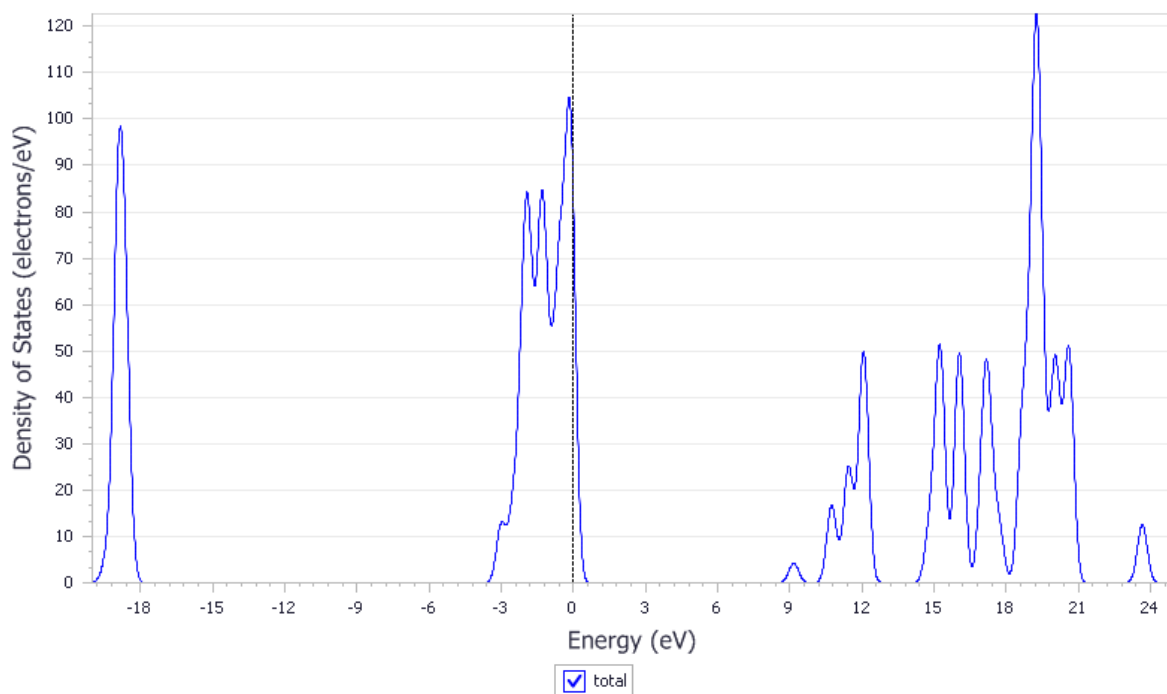
Note: The energy reported in the ONETEP LiF output file (.onetep) is reported in Hartree, -790.82 Ha corresponds to -21519.25 eV.

ONETEP Density of States

Band gap is 9.183 eV



CASTEP Density of States



This is the end of the tutorial.

Polymorph tutorials

The following tutorials illustrate how to utilize Polymorph's capabilities.

- [Predicting the Crystal Structure of 3-oxabicyclo\(3.2.0\)hepta-1,4-diene](#)
- [Predicting a polymorphic form of a potential anti-cancer drug - conformational analysis](#)
- [Predicting a polymorphic form of a potential anti-cancer drug](#)
- [Using Materials Studio to edit a forcefield](#)

Predicting the crystal structure of 3-oxabicyclo(3.2.0)hepta-1,4-diene

Purpose: Illustrates how to predict possible crystal packing arrangements based on molecular structure using Polymorph.

Modules: Materials Visualizer, DMol³, Polymorph, Reflex

Time: 🕒🕒🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Pharmaceuticals, agrochemicals, pigments, dyes, specialty chemicals, and explosives are all, at some stage during the manufacturing process, organic crystalline materials. Polymorphism affects these products during downstream development and formulation because the crystal form determines many of the properties of the material, including:

- Shelf life
- Vapor pressure
- Solubility
- Bioavailability
- Morphology
- Density
- Shock sensitivity

It is vital that researchers involved in crystalline product formulation select the polymorph with the correct properties and are able to anticipate problems such as competing crystallization of undesirable polymorphs. In order to do this, it is first necessary to establish the most likely polymorphic forms. Knowledge of polymorphic forms is also important for patenting and registration purposes.

It is often impossible or impractical to use single crystal X-ray diffraction, the standard experimental procedure for elucidating the structure of a molecular crystal. Thus, computational techniques that predict crystal structures without experimental data are of great value.

Polymorph uses forcefield technology to propose stable packing arrangements. This method keeps the molecular geometry fixed during the Monte Carlo simulation and only allows full optimization during the energy minimization stage. Therefore, when dealing with flexible molecules, parallel calculations must be performed for each stable molecular conformation of the compound under investigation.

Introduction

Possible crystal structures of 3-oxabicyclo(3.2.0)hepta-1,4-diene (OHD) will be determined using Polymorph. The molecule was used in a blind test organized by the Cambridge Crystallographic Data Centre (CCDC) to assess the performance of currently available methods for crystal structure prediction [1](#).

The success rate of crystal structure prediction depends critically on the accuracy of the forcefield employed. In this tutorial, you will use the Dreiding forcefield, which proved to be suitable for crystal structure prediction when it is used in conjunction with atomic charges calculated by high level ab initio calculations.

This tutorial covers:

- [Getting started](#)
- [To build and optimize the molecule with DMol³ and calculating ESP-fitted charges](#)
- [To set up and run Polymorph](#)
- [To analyze the results using a study table](#)
- [To compare the results with a known OHD crystal structure](#)
- [To identify the best match with an experimental powder pattern](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

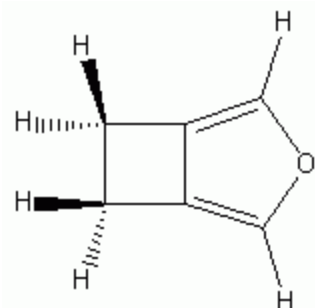
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **OHD** as the project name, click the **OK** button.

The new project is created with *OHD* listed in the Project Explorer.


2. To build and optimize the molecule with DMol³ and calculating ESP-fitted charges

In the Project Explorer, right-click on **OHD** and select **New | 3D Atomistic Document** from the shortcut menu. Change the name of the new structure document to **OHD-mol**. Use the Sketch tools to sketch an OHD molecule (shown below) and then clean the structure by pressing the **Clean** button



Molecular structure of OHD

Now you will optimize the molecule with DMol³ and calculate the ESP-fitted charges.

On the **Modules** toolbar, click on the **DMol³** arrow  and select **Calculation** from the dropdown list to open the DMol3 Calculation dialog.

On the **Setup** tab, select **Geometry Optimization** from the **Task** dropdown list. Select **GGA** and **PBE** from the **Functional** dropdown lists. Leave the Quality set to Medium.

On the **Electronic** tab, set the **Basis set** to **DNP**.

On the **Properties** tab, check the **Electrostatics** and **Population analysis** checkboxes. When **Electrostatics** is selected, check the **Electrostatic potential** checkbox. When **Population analysis** is selected, check the **ESP charges** checkbox.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click the **Run** button and close the dialog.

A new folder, called **OHD-mol DMol3 GeomOpt**, is created in the Project Explorer. The progress of the job is presented in the form of chart and text documents. The calculation may take some time, depending on the speed of the processor in your computer. You should wait until the job finishes before proceeding.

Next, you should analyze the DMol³ results and extract information on the ESP-fitted charges.

In the Project Explorer, double-click on **OHD-mol.outmol** in the **OHD-mol DMol3 GeomOpt** folder. Press the **CTRL + F** keys and search for **ESP-fitted charges**.

You will reach a part of the document that looks like this:

```
ESP-fitted charges      :
  n Elem   chg   vdW(in) vdW(ex)
  1  O    -0.121  1.72   3.22
  2  C    -0.188  2.00   3.50
  3  C     0.058  2.00   3.50
  4  C     0.058  2.00   3.50
  5  C    -0.188  2.00   3.50
  6  C    -0.220  2.00   3.50
  7  C    -0.220  2.00   3.50
  8  H     0.184  1.30   2.80
  9  H     0.184  1.30   2.80
 10 H     0.113  1.30   2.80
 11 H     0.113  1.30   2.80
 12 H     0.113  1.30   2.80
 13 H     0.113  1.30   2.80
```

Note: The actual ESP charge values might be slightly different to these due to the differences in the initial drawn structure and optimization level.

The ESP-fitted charges for each atom, as calculated by DMol³, are listed. You will now assign all these charges to the fully optimized structure of OHD.

In the Project Explorer, double-click on **OHD-mol.xsd** in the **OHD-mol DMol3 GeomOpt** folder. Select **Modules | DMol3 | Analysis** from the menu bar to open the DMol3 Analysis dialog. Select **Population analysis** and change the **charges to structure** setting to **ESP**. Click the **Assign** button and close the dialog.

The ESP-fitted charges generated by DMol³ do not sum to exactly zero because of truncation errors. So, before proceeding, you should modify the charges slightly so that they do add up to zero.

Select **Modify | Charges** from the menu bar to open the Charges dialog. On the **Edit** tab, select **Set total charge to** and specify a value of **0.0**. Click the **Assign** button and close the dialog.

Now display the charges on each atom.

Right-click in the **OHD-mol.xsd** 3D Viewer and select **Label** from the shortcut menu to open the Label dialog. Select **Charge** from the **Properties** list box and click the **Apply** button.


When you have examined the charges, click the **Remove All** button to remove the charges from the display, and close the dialog.

3. To set up and run Polymorph

In this section, you will use Polymorph to predict various possible crystal packing arrangements for OHD. OHD is a rigid molecule, so no conformation analysis is necessary.

According to the Cambridge Structural Database (CSD), about 90% of all organic and organometallic crystal structures are covered by the 17 most frequent space groups. Without prior knowledge of the crystal symmetry (for example, from an indexable powder pattern), you will have to run the calculations for at least five of the most common space groups.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **OHD-mol DMol3 GeomOpt\OHD-mol.xsd**.

Click the **Polymorph** arrow  on the **Modules** toolbar and select **Calculation** from the dropdown list to open the Polymorph Calculation dialog. On the **Setup** tab, click the **Assign automatically** button. Select **Fine** from the **Quality** dropdown list.

In this tutorial, you will run a Polymorph prediction sequence. You could do this by running each step in the sequence separately or all of them in a single consecutive calculation. The Polymorph prediction sequence consists of four steps: packing (Monte Carlo simulation), pre-clustering, optimization, and clustering. The entire sequence can take hours or even days, during which time Polymorph:

- Runs a Monte Carlo simulation to generate thousands of potential crystal structures for OHD in the selected space group(s)
- Runs a pre-clustering analysis to group the crystals into clusters of similar structures
- Minimizes each cluster to get a set of optimized structures
- Runs a second clustering analysis to check whether any of the optimized structures converge to the same energy minima

The crystal structures generated by Monte Carlo simulations are sorted into groups of similar structures in the pre-clustering step. Similarity is defined by the geometric tolerances set on the control panel. The pre-clustering step reduces the total number of structures before the next stage of the calculation: optimization. Since optimization is the most computationally expensive step, pre-clustering can help

speed up the calculation significantly. However, there is a risk of losing possible solutions at the pre-clustering stage. The number of structures retained depends on the tolerances and the maximum number of clusters you set. Since the crystal structures generated by the Monte Carlo simulation are not optimized before the pre-clustering, the measure of similarity is not very precise. By default, the pre-clustering step is not included, so that no structures are discarded. In this tutorial, you will include this step in order to speed up the calculation.

On the **Setup** tab of the Polymorph Calculation dialog, set the **Task** to **Prediction**. Click the **More...** button to open the Polymorph Prediction dialog.

Check both **Clustering** checkboxes and click the **More...** button for **Packing** to open the Polymorph Packing dialog.

The *Quality* is set to **Fine**, as specified on the *Setup* tab of the Polymorph Calculation dialog.

In total, there are seven parameters for the Monte Carlo temperature cycles including: the *Cooling Factor* (accessed from the *Space Groups* tab, as indicated below), the *Heating factor*, the *Maximum number of steps*, the number of *Steps to accept before cooling*, the *Minimum move factor*, the *Maximum temperature*, and the *Minimum temperature*. By changing the *Quality* from **Coarse** to **Ultra-fine**, you increase both the probability of generating all relevant crystal packing arrangements and the total amount of CPU time required.

Each parameter set is optimized, so, ideally, you should select a set of parameters rather than try to set individual parameters manually. In a real-life situation, you should generally use the **Medium**, **Fine**, or **Ultra-fine** search levels. In this tutorial, leave the search level set to **Fine**.

Make sure you can see the **Setup** tab of the Polymorph Calculation dialog. On the Polymorph Packing dialog, change the **Quality** setting to **Coarse**, then to **Medium**, and then back to **Fine**.

As you change the *Quality* setting for the packing task, the overall quality setting on the *Setup* tab of the Polymorph Calculation dialog changes automatically from **Fine** to **Customized**, and finally returns to **Fine**.

Close the Polymorph Packing dialog.

If you wish, you can observe the effect on the global *Quality* parameter of modifying other settings by repeating the same procedure for the Polymorph Clustering and Polymorph Geometry Optimization dialogs.

The clustering procedure depends on several parameters. Again, it is advisable to select one of four predefined parameter sets, rather than to choose individual parameters manually (except, in certain cases, for the maximum number of clusters).

On the Polymorph Prediction dialog click the **More...** button for **Clustering** to open the Polymorph Clustering dialog.

In the **Cluster generation** section, change the **Maximum clusters** to **2000**. Close the Polymorph Clustering dialog.

Increasing the quality reduces the likelihood of clustering different structures together and consequently increases the number of clusters that are produced. In a real-life calculation, you must make sure that the correct crystal structure is not lost in the clustering process. The search level should therefore be set to **Fine** or **Ultra-fine**.

The geometry optimization procedure also depends on several parameters. Once again, it is advisable to select one of the four predefined parameter sets, rather than to choose individual parameters manually. In a real-life calculation, the search level should be set to **Medium** or **Fine**. You can also choose to set the maximum number of iterations, whether to apply external pressure, or whether to optimize the atomic coordinates only or to include the cell parameters as well. It is advisable to use the *Optimize cell* option. In this tutorial, you should use the default settings.

Tip: By default, the geometry of each unique structure is optimized with respect to all degrees of freedom. However, rigid body constraints can be applied where the relative distances between a group of atoms are fixed. Rigid body constraints are useful in preventing the geometry optimizer from exploring unrealistic regions of configuration space. Defining rigid bodies tends to reduce the number of degrees of freedom needed to describe the configuration of a system, hence calculations are often sped up. To use rigid body optimization, check the *Keep motion groups rigid* checkbox on the Polymorph Geometry Optimization dialog.

Note: Different polymorphic crystal structures usually differ by only a fraction of a kcal/mol in energy. It is therefore recommended that you optimize all degrees of freedom of the crystal, including the cell parameters. All atoms should be movable. You should use exactly the same energy expression for all geometry optimization runs that you wish to compare.

Close the Polymorph Prediction dialog.

Next, you will choose the Dreiding forcefield and use the ESP charges obtained with DMol³ earlier.

On the **Energy** tab of the Polymorph Calculation dialog, select **Dreiding** as the **Forcefield** and select **Use current** from the **Charges** dropdown list.

Polymorph can search all space groups. However, by default, it searches only the five most common space groups. The crystal structure of OHD is in space group PBCA. So, to speed up the tutorial, you are going to search in only the two orthorhombic space groups, P212121 and PBCA. Typically, you would have to include all of the other common space groups in the search.

A cooling factor can be set independently for each space group. In this tutorial, you will use the default value of **0.001** for both space groups.

On the **Space Groups** tab of the Polymorph Calculation dialog, check the checkboxes for the space groups **P212121** and **PBCA** and uncheck all the others.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Uncheck the **Automatic** checkbox and enter **OHD-Fine** as the **Job description**. Click the **Run** button and close the Polymorph Calculation dialog.

The Job Explorer informs you about the progress of the calculation. After some time, two new windows appear: a text document, *Status.txt*, and a chart document. These documents are updated regularly as the job progresses.

The text document displays information about:

1. The task that is currently being performed, for example *Polymorph Packing* or *Polymorph Geometry Optimization* (you will not see *Polymorph Clustering* - the calculation finishes quite rapidly).
2. The space group in which the search is currently being performed. The search follows the order listed on the *Space Groups* tab.
 - For Polymorph packing: space group, current step number, current crystal structure acceptance, temperature, total energy for the current crystal structure (including the contributions of the H-bond, van der Waals, and electrostatics energies), and the density of the current crystal structure.
 - For Polymorph geometry optimization: space group, total number of frames, current frame number, optimization convergence, total energy for the current crystal structure, total non-bond energy (including a breakdown of the H-bond, van der Waals, and electrostatics contributions), and total bonded energy (including a breakdown of the bond, angle, torsion, inversion, and cross-terms contributions).

The chart document varies depending on the current step of the prediction sequence and the space group. During Polymorph packing, a chart document called OHD-Fine [*space group name*] Ener-Dens.xcd is created, which shows the density and energy information for each potential crystal structure found so far. During Polymorph geometry optimization, a chart document called OHD-Fine [*space group name*] Energy.xcd is created, which shows the energy for each optimized crystal structure.

Once the calculation starts, a new folder called OHD-Fine PMP Predict is created in the Project Explorer. The parameter settings for this job are automatically saved in a file called OHD-Fine - Calculation.

In the new folder, four subfolders are created as the job progresses:

1. **Input** - contains the input molecular structure required for restart if the job is stopped for any reason.
2. **Packing** - includes four types of files for each space group: a trajectory file containing all the potential crystal structures generated by the Monte Carlo simulation, a chart document showing the acceptance ratio and temperature profile for the Monte Carlo simulation, a second chart document showing the density and energy for each potential crystal structure, and a text file showing the acceptance, temperature, energy, and density for all the structures generated.
3. **GeomOpt** - includes a trajectory file for each space group, containing the lowest energy structure for each cluster, and a chart document showing the energy for each optimized crystal structure.
4. **Pre-clustering** - includes a trajectory file for each space group that groups together similar crystal structures generated by the Monte Carlo process. Each cluster is represented by the structure that has the lowest lattice energy.

The whole process generates hundreds of crystal structures. Many of these are very similar and will minimize to the same crystal structure. It is useful to group together similar crystal structures and to represent each cluster by the structure with the lowest lattice energy. These results, which are the final results of the Polymorph Prediction sequence, are saved in the top level of the OHD-Fine PMP Predict folder. A trajectory file containing all non-redundant energy minima is created for each space group.

Note: The search in Polymorph relies on a Monte Carlo simulation which is a stochastic method. Therefore a single calculation may not guarantee that all low energy crystal structures in a given space group have been identified. To assess the completeness of the Polymorph search, the Polymorph prediction should be run more than once with the same settings. If separate runs with identical settings produce the same low energy crystal structures, the search can be considered complete. If different results are obtained, the search must be repeated until no new crystal structures can be found.

Now you will start a second Polymorph job using the same settings.

Select **File | Save Project** from the menu bar and **close** all of the open documents, apart from **OHD-mol.xsd** in the **OHD-mol DMol3 GeomOpt** folder.


Open the **Polymorph Calculation** dialog. On the **Job Control** tab, select **My Computer** as the **Gateway location** and enter **OHD-Fine 2** as the **Job description**. Click the **Run** button and close the dialog.

You should wait until the job finishes before proceeding.

4. To analyze the results using a study table

In this section, you will analyze the output from the Polymorph run.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Click on the **Polymorph** arrow  and select **Analysis** from the dropdown list to open the Insert Polymorph Results File dialog. Navigate to the **OHD-Fine PMP Predict** directory, hold down the **CTRL** key and select **OHD-Fine PBCA.xtd** and **OHD-Fine P212121.xtd**. Click the **Open** button.

Repeat the same procedure to navigate to the **OHD-Fine 2 PMP Predict** directory and insert the trajectories **OHD-Fine 2 PBCA.xtd** and **OHD-Fine 2 P212121.xtd** into the study table.

All of the frames in the four trajectory files are displayed in the study table. The study table provides you with detailed information about each potential polymorph, including crystal *Structures* (column A), *Frame number* (column B, the lower the frame number the lower the total energy for the structure), *Space group* (column C), *Cell Volume* (column D), *Density* (column E) and *Total energy* (column F), the contribution of *van der Waals* (column G) and *Electrostatic* (column H) energy to the non-bond energy, and the cell parameters (columns I-N).


The name of each structure has the format: *[job name] [space group name] - [frame number]*. By default, the structures are already sorted within each space group, according to their total energy values. The lowest energy frames are at the top of the table. To locate the global minimum structure, you can sort the study table across different space groups and/or obtained by different calculation runs.

Select **Tools | Sort Rows...** from the menu bar to open the Sort Rows dialog. Select **F : Total energy** from the **Sort by column** dropdown list, click the **Ascending** radio button, and click the **OK** button.

All the structures are now ranked by their total energy, with the lowest energy structures at the top of the table. In this tutorial either **OHD-Fine PBCA - 1** (which is the structure in frame 1 of the trajectory for space group PBCA) or **OHD-Fine 2 PBCA - 1**, which should have essentially the same total energy value, is the lowest energy structure. Since two separate runs were carried out using the same

settings here, any given low energy structure could likely be found more than once. A clustering analysis is therefore needed to remove the duplicates.

Select all the cells by clicking in the top left heading cell in the study table.

Click the **Models** button  on the **QSAR Models** toolbar. Click on the **Category** heading to sort by category and locate the **Crystallization** category, select the **Polymorph clustering** row. Click the **Run** button and close the dialog.

Note: Polymorph clustering can only be carried out for 3D crystal structures that either have the same asymmetric unit formula or at least contain the same cluster groups (same forcefield type, or element types, or names). However, it is not necessary for all the crystals to have the same space group symmetry. If the study table contains structure documents that do not conform to these restrictions, #N/A will be entered in the results column.

The outputs produced by the Polymorph clustering model include:

- cluster number
- Rank in cluster - Similarity ranking with respect to the reference structure in that particular cluster
- Similarity to cluster reference - Crystal similarity measure with respect to the reference structure in that particular cluster


OHD-Fine PBCA - 1 and OHD-Fine 2 PBCA - 1 were indeed classified into the same cluster - Cluster 1 with the crystal similarity measure value being 0. In other words, the same lowest energy structure was found twice. You should remove the duplicate crystal structures in any given cluster, and create a subset of the unique structures.

Open the **Sort Rows** dialog. Select **P : Rank in cluster (Polymorph Clustering)** from the **Sort by column** dropdown list and click the **Ascending** radio button. Select **O : Cluster number (Polymorph Clustering)** from the **Then by column** dropdown list and click the **Ascending** radio button. Click the **OK** button.

In the study table, click on row **1**. Hold down the **SHIFT** key, and click on the last row which has a value of **1** in column **P : Rank in cluster (Polymorph Clustering)**. Choose **Tools | Filter** from the menu bar.

The lowest energy representative of each cluster was filtered into a new sheet - Sheet 2. The structures in Sheet 2 are already sorted according to their total energy values. You can examine the energy profiles for all the structures.

Note: Since the filtered structures can come from either Polymorph execution, the term OHD-Fine PBCA - 1 will be used to refer to the lowest energy structure regardless of the original trajectory in which it was located.

In the study table, select column **F (Total energy)** by clicking on the column heading. Click on the **Quick Plot** button  on the **Study Table Viewer** toolbar.

The lattice energies of all the crystal structures are shown in a chart document. The most likely candidate for the experimentally observed crystal structure is the frame with the lowest lattice energy in the trajectory files.

Close the chart document and click the **No** button when prompted to save the document.

To find the most likely stable polymorphs, you can also sort the study table using different criteria; for example density, van der Waals energy, and so on.


Note: Structures with low lattice energies generally have relatively high densities. You should therefore examine the density profile.

Ensure that the study table document is active and open the **Sort Rows** dialog. Change the **Sort by column** setting to **E : Density**, select **Descending**. Click the **OK** button.

Now, all the structures are sorted by density. The structure OHD-Fine PBCA - 1 should have a high density value and, consequently, should appear near the top of the table.

After you have finished examining the density chart, you should sort the table by total energy once more. You may also wish to generate a density-energy plot.

Open the **Sort Rows** dialog. Change the **Sort by column** setting back to **F : Total energy**, select **Ascending**, and click the **OK** button.

In the study table, click on the heading of column **E** and then, holding down the **SHIFT** key, click on the heading of column **F**. Click the **Quick Plot** button .

By default, the leftmost of the two columns selected is plotted on the x-axis and the other column is plotted on the y-axis.

The density-energy plot also shows that the lowest energy structures normally have higher densities.

Close the chart document and click the **No** button when prompted to save it.

Note: To distinguish different crystal structures, it is usually sufficient to compare their total energies and densities.

Now create a subset of the five lowest energy structures and examine them in greater details.

In the study table, click on the **Sheet 2** tab. Click on row **1**, hold down the **SHIFT** key, then click on row **5** to select the top five structures. Choose **Tools | Filter** from the menu bar.

The five structures are placed in a new sheet. You should examine each of the structures carefully. Start with the lowest energy structure, OHD-Fine PBCA - 1.

In column **A**, right-click on the first structure, **OHD-Fine PBCA - 1**, and choose **View** from the shortcut menu.

The crystal structure of OHD-Fine PBCA - 1 is displayed.

Click the **3D Viewer Rotation Mode** button  and rotate the structure.

To make the crystal structure clearer, you can switch off the display of the motion groups.


Hold down the **ALT** key and double-click on a motion group.


All the motion groups should now be selected.

In the Properties Explorer, ensure that the **Filter** is set to **Motion Group**. Double-click on the **IsVisible** property to open the Edit IsVisible dialog. Select **No / False** and click the **OK** button. Press the **CTRL + D** keys to deselect the motion groups.

Examine the crystal structure.

Note: An asterisk is now appended to the name of the file. This indicates that the structure has been modified and is no longer the same as the one saved in the trajectory file.

Press the **CTRL + A** keys to select the entire contents of the document and click the **Copy** button  to copy the selection.

In the Project Explorer, right-click on the project **OHD** and choose **New | 3D Atomistic Document** from the shortcut menu. Click the **Paste** button  to paste the structure into the empty document. In the Project Explorer, right-click on **3D Atomistic.xsd** and select **Rename**, change the name of the document to **OHD-PBCA-frame1.xsd**.

Close the **Polymorph Analysis Detail View : A1 OHD-Fine PBCA - 1** and click the **No** button, so that the changes are not saved.

Repeat these steps to extract the other 4 lowest energy frames from the trajectory file and save them as 3D Atomistic documents.


Select **File | Save Project** from the menu bar and close all of the open documents, apart from **Polymorph Analysis.std**.

5. To compare the results with a known OHD crystal structure

Frequently, Polymorph is used to find the crystal structure of a compound for which the crystal structures of other polymorphic forms have already been determined experimentally. In such cases, it is common to assess the reliability of the Polymorph prediction procedure by verifying that the experimentally observed crystal structures are among the generated crystal structures with lowest lattice energies. The agreement between the experimental structure and the calculated structures can be determined using the same similarity measure that is used for clustering.

In this tutorial, you will compare the calculated crystal structures with one of the known crystal structures of OHD.


Load the experimental crystal structure for comparison.

In the Project Explorer, select the project **OHD**. Click the **Import** button  to open the Import Document dialog. Navigate to **\Examples\Polymorph\Structures** and import the file **ohd_pm1.msi**.

Make **Polymorph Analysis.std** the active document, click on the **Sheet 2** tab, and select all the cells by clicking in the top left heading cell in the study table.

Click the **Models** button .

This opens the Models dialog which dialog allows you to choose a list of properties to be calculated. The results are automatically added to the study table. You are going to use the *Crystal Similarity Measure* model to compare the experimentally determined crystal structure with all the structures calculated by Polymorph.

Click on the **Category** heading to sort by category and locate the **Crystallization** category. Select the **Crystal similarity** row and click the **Edit Model** button .

This opens the Model Editor - Crystal Similarity Measure dialog.

On the **Inputs** tab, click in the **Value** cell for **Reference crystal** and select **ohd-pm1.xsd** from the dropdown list.

On the **Outputs** tab, check the **Calculate** checkbox for **Crystal similarity** and click the **Save** button. Close the Model Editor - Crystal Similarity Measure dialog.

Click the **Run** button on the Models dialog, and close the dialog.


A new column called *Crystal Similarity Measure* is created in the study table.


With **Polymorph Analysis.std** as the active document, select **Tools | Sort Rows...** from the menu bar to open the Sort Rows dialog. Change the **Sort by column** setting to **R : Crystal Similarity Measure**, select **Ascending**. Click the **OK** button.

Now all the structures are sorted by their similarity to the experimental structure. The similarity measure is based on interatomic distances and it may be that the structure with the lowest similarity measure is not necessarily the one that corresponds best to the experimentally observed polymorph. In the present case, OHD-Fine PBCA - 1, should be among the first 30 structures in the list.

The choice of unit cell may not necessarily be the same for the experimental crystal structure and the predicted crystal structures. So, to compare the crystal structures visually, you should overlay the experimental crystal structure with the predicted structures, looking at the molecular arrangement, rather than the size and shape of the unit cell.

Tip: Calculating hydrogen bonding patterns can help identify similar structures. However, in the present case, there is no hydrogen bonding in the structure.


Minimize the study table by clicking the  icon. In the Project Explorer, double-click on **OHD-PBCA-frame1.xsd** to open it in a 3D Viewer.

Make **ohd-pm1.xsd** the active document. Click the **Copy** button  to copy the entire unit cell. In the Project Explorer, right-click on the project **OHD** and select **New | 3D Atomistic Collection Document** from the menu bar. Selecting **Edit | Paste** from the menu bar to paste the unit cell into the empty document.

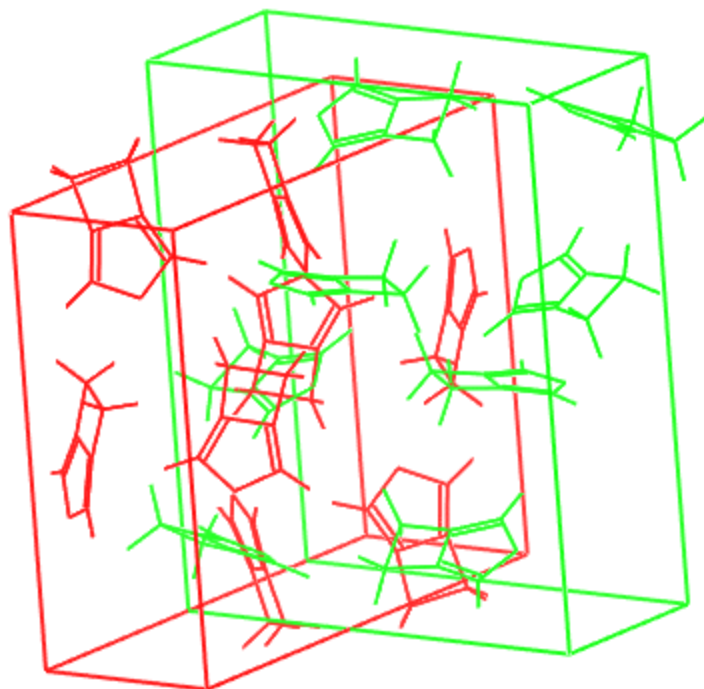
Rename **3D Atomistic Collection.xod** to **overlay.xod**.

Right-click in **overlay.xod** and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Atom** tab, select **Custom** in the **Coloring** section. Choose red using the **Color** chooser and click the **OK** button. On the **Lattice** tab, set the **Color** to red as well.

Now make **OHD-PBCA-frame1.xsd** the active document. **Copy** the structure and **Paste** it into **overlay.xod**. Change the **Atom** and **Lattice** colors to **green** using the Display Style dialog.

Expand the **overlay.xod** window by clicking the  icon. Click once in the 3D Viewer to deselect everything.

The experimental crystal structure and the lowest energy frame from the Polymorph run are now displayed in the same 3D space, colored red and green, respectively.

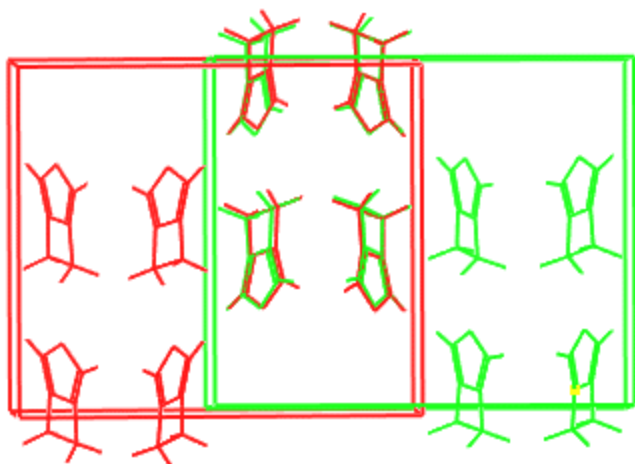


Overlay of the experimental structure of OHD (red) and the lowest energy frame (green) from the Polymorph run

Select the lowest energy frame by clicking on the green unit cell in **overlay.xod**. To translate this unit cell independently, hold down the **SHIFT** and **ALT** keys and the right mouse button while dragging the mouse. To rotate this unit cell independently, hold down the **SHIFT** key and the right mouse button while dragging the mouse.

Tip: If you have a three-button mouse or a mouse with a wheel, you can translate a selection by pressing the center mouse button or wheel and the *SHIFT* key while dragging the mouse.

Position the green (calculated) unit cell so as to maximize the overlaps with the red (experimental) unit cell. You should find that matching up the unit cells as closely as possible produces a view like that shown below.



Experimental structure of OHD (red) and the lowest energy frame (green) from the Polymorph run aligned for maximum overlap

You can see that the packing arrangements for the two overlaid structures are essentially the same, although the unit cell choice is different. Repeat these steps to compare other frames with the experimental structure.

Alternatively, you can automatically align the molecular fragments to produce the best overall fit between the two crystal structures.

Make **overlay.xod** the active document. Select **File | Save As...** from the menu bar to open the Save As dialog. Enter the filename **overlay2** and click the **Save** button.

Double-click on one of the atoms in **red** to select the **experimental structure**. Select **View | Explorers | Properties Explorer** from the menu bar and choose **Physical System** from the **Filter** dropdown list. Double-click on the **Name** field, and type in **experiment** in the text box. Click the **OK** button.

Repeat the same procedure to define **Physical System** for **the lowest energy frame** to be **predicted**.

Select **File | Save** from the menu bar.

Note: Each structure or group of atoms in a collection document is known as a physical system. Physical systems are defined when the atoms or structures they contain are initially brought into the collection document. The introduction of the physical system into the data hierarchy in 3D Atomistic Collection documents means that you can, for example, color atoms according to the physical system to which they belong.

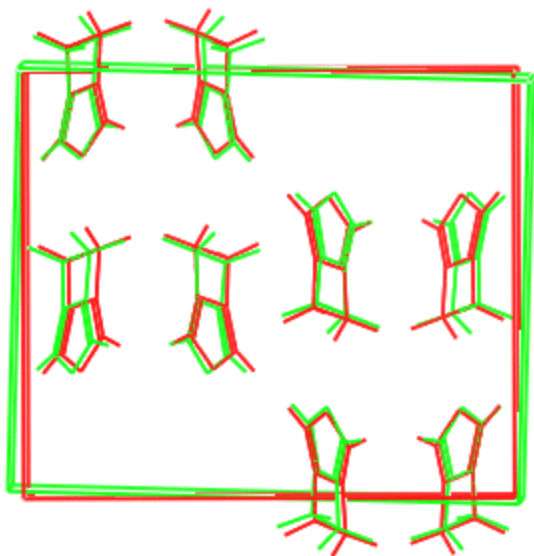
Physical systems do not interact; this allows atoms in different physical systems to be in close proximity without affecting each other. As a result, you can, for example, calculate hydrogen bonds for a structure in a particular physical system without atoms and molecules in other physical systems influencing the calculation.

Right-click in the 3D Viewer and choose **Physical Systems** from the shortcut menu to open the Physical Systems dialog.

Select the **predicted** systems, hold down the **SHIFT** key and select **experiment**.

Select **Tools | Superpose Structures** from the menu bar to open the Superpose Structures dialog. On the **Alignment** tab, click the **Consensus** radio button and select **Field** as the **Fit method**. Ensure the output checkboxes for **Update original structures** and **Output to study table** are checked. Click the **Superpose** button and close the Superpose Structures and Physical Systems dialogs.

A new study table document called *Similarity.std* is created in the Project Explorer. The similarity between the two structures is **0.989**. The closer the similarity value is to 1, the more similar the two structures are. The superposed structures are shown below.



Experimental structure of OHD (red) and the lowest energy frame (green) from the Polymorph run aligned for maximum overlap

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.


6. To identify the best match with an experimental powder pattern


Polymorph can be used for structure determination in cases where an experimental powder diffraction pattern is available but is of insufficient quality for structure determination. By comparing the

experimental pattern to simulated diffraction patterns for all of the crystal structures found by Polymorph, the correct crystal structure can be identified.

You can use the Powder Comparison model for this task.

Unit cell parameters calculated with Polymorph will typically differ by a few percent from experimental lattice parameters, resulting in a mismatch of calculated and experimental diffraction peaks. To improve the overlap between the peak positions, it is important to broaden the experimental peak profile by convolution with a Gaussian function and to use the same Gaussian function for the calculation of the simulated powder patterns. Additionally, the background has to be subtracted from the experimental powder pattern.

In the Project Explorer, select the project **OHD** and click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the file types dropdown list for the **File name**. Navigate to the **Examples\Reflex\Experimental Data** folder and select the file **ohd.xcd**. Click the **Open** button.

Click on the **Reflex** arrow  on the **Modules** toolbar and select **Pattern Processing** from the dropdown list to open the Reflex Pattern Processing dialog.



On the **Pattern Preparation** tab, in the **Background** section, increase the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document, **ohd (Background Removed) .xcd**, is created, in which the background has been subtracted from the powder pattern. You should now smooth the powder diffraction pattern. The best choice of Gaussian width for smoothing depends on the noise level and the peak width, and has to be found empirically.

Select the **Pattern Processing** tab on the Reflex Pattern Processing dialog. In the **Smoothing** section, set the **Gaussian width** to **1.0**. Click the **Smooth** button and close the dialog.

A new chart document, **ohd (Background Removed) (Smoothed) .xcd**, is created, containing the smoothed powder diffraction pattern.

Make **Polymorph Analysis.std** the active document and choose sheet **1**, select all the cells by clicking in the top left heading cell in the study table.

Click the **Models** button  to open the Models dialog. Locate **Crystallization** in the **Category** column. Click on the row for **Figure of merit** and click the **Edit Model** button .

On the **Inputs** tab of the Model Editor - Powder Comparison dialog, click on the **Value** for **Experimental data** and select **ohd (Background Removed) (Smoothed).xcd** from the dropdown list. Set the **Profile FWHM W** to **1**.

On the **Outputs** tab, check the **Calculate** checkboxes for **Rp**, **Rwp**, and **CMACS**, then click the **Save** button. Close the Model Editor - Powder Comparison dialog.

Click the **Run** button and close the Models dialog.

In the study table, three new columns have been added: *Rwp (Powder Comparison)*, *Rp (Powder Comparison)*, and *CMACS (Powder Comparison)*. These different measures describe the level of agreement between the powder patterns. Low numbers indicate good agreements.

Ensure that the **Polymorph Analysis.std** study table is the active document and select **Tools | Sort Rows...** from the menu bar to open the Sort Rows dialog. Change the **Sort by column** setting to **S : Rp (Powder Comparison)**, select **Ascending**, and click the **OK** button.

Repeat the same procedure to sort the table by column *T*.

In both cases, the structure in frame 1 of the trajectory for space group PBCA, corresponds best with the experimental powder diffraction pattern. The same structure also has the lowest lattice energy, thus, you have confirmed that the structure in frame 1 of the trajectory for space group PBCA, matches the experimental crystal structure.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Lommerse, J. P. M.; Motherwell, W. D. S.; Ammon, H. L.; Dunitz, J. D.; Gavezzotti, A.; Hofmann, D. W. M.; Leusen, F. J. J.; Mooij, W. T. M.; Price, S. L.; Schweizer, B.; Schmidt, M. U.; van Eijck, B. P.; Verwer, P.; Williams, D. E. "A test of crystal structure prediction of small organic molecules", *Acta Crystallogr., Sect. B*, **56**, 697-714 (2000).

Predicting a polymorphic form of a potential anti-cancer drug - conformational analysis

Purpose: Illustrates how to set up a molecular structure for a subsequent Polymorph calculation.

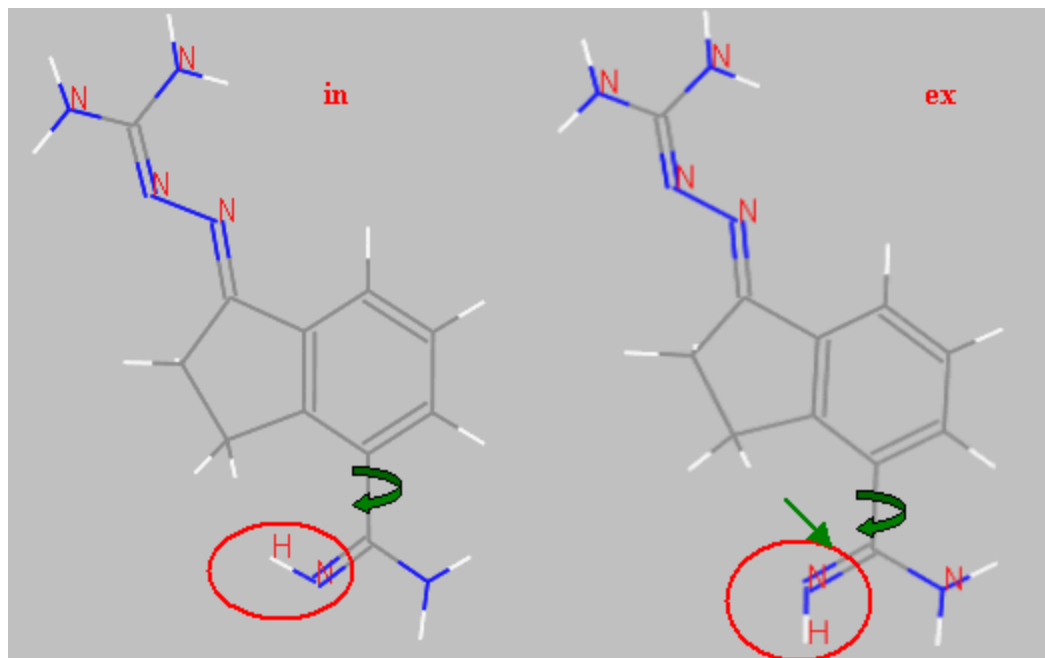
Modules: Materials Visualizer, Conformers, DMol³

Time: 🕒 🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Polymorph uses forcefield technology to propose stable packing arrangements. This method keeps the molecular geometry fixed during the Monte Carlo simulation, allowing full optimization only during the energy minimization stage. Therefore, when dealing with flexible molecules, parallel calculations must be performed for each stable molecular conformation of the compound under investigation.



The two conformers of the hydrogen atom in the terminal imide group

The ESP charges are calculated from the full electrostatic potential of the molecule. See Fitting atomic point charges to the electrostatic potential (ESP) for more details. Partial atomic charges, such as ESP charges, depend on the conformation of the molecule under consideration. Therefore they need to be recalculated for each conformer.

This tutorial shows how to perform a conformational analysis of 4-Amidino-indanone guanyl-hydrazone (AIGH) using Conformers, and how to calculate ESP-fitted charges using DMol³. AIGH was recently suggested by scientists of Novartis as a new selective inhibitor of S-adenosyl-methionine decarboxylase, which is an anti-cancer drug (Stanek et al., [1993](#)). This example is a typical case for polymorphism of pharmaceutical compounds. Two anhydrous polymorphs are known to exist, but only one crystal structure has been determined experimentally, as suitable single crystals of the other polymorph could

not be grown. Karfunkel (Karfunkel et al., [1996](#)) describes how his group used Polymorph to determine the unknown polymorphic form on the basis of ab initio packing calculations.

Introduction

The molecular conformation of AIGH differs in the rotation of the terminal amine and imide groups around the C-C bond connecting them to the ring fragment. Also, the hydrogen for the imide group can adopt one of two orientations: "*in*", where the hydrogen is pointing toward the ring; or "*ex*", where the hydrogen is pointing away from the ring.

The Conformers module is designed specifically to enable the searching of conformational space of a molecule. You can search by random, boltzmann jump, or systematic search methods. In this tutorial, you will perform two systematic searches of the C-C bond.

This tutorial covers:

- [Getting started](#)
- [To prepare the AIGH molecule](#)
- [To generate the conformers](#)
- [To calculate ESP-fitted charges using DMol³](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

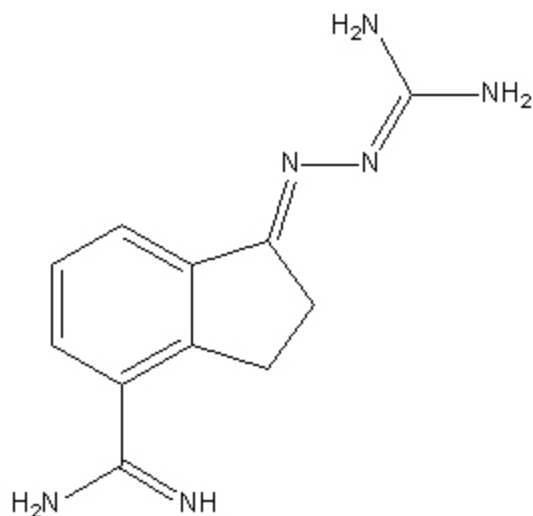
Open the **New Project** dialog and enter **AIGH_conf** as the project name, click the **OK** button.

The new project is created with *AIGH_conf* listed in the Project Explorer. Now you will import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Polymorph\Structures** folder and double-click on **AIGH-mol.xsd**.


2. To prepare the AIGH molecule

You will create two copies of the input molecule, one with the C=N torsion angle in the "*in*" position and the other with the torsion angle in the "*ex*" position.



The molecular structure of AIGH


There are many different ways to make a copy of the document in Materials Studio. In this example, you will add the C-C torsion angle, save the document, modify the "in/ex" torsion angle, and save it as a different name.

Click on the **Measure/Change** arrow  on the **Sketch** toolbar, and select **Torsion** from the dropdown list. Click on the C-C single bond, identified by the curly arrow in the [sketch](#) of the *in* conformer.

You can now rename the structure as AIGH-mol_in.xsd.

In the **Project Explorer**, right-click on **AIGH-mol.xsd** and select **Rename** from the shortcut menu, enter **AIGH-mol_in.xsd** and press **ENTER**. Choose **File | Save Project** from the menu bar.

Modify the structure to change the imide group to the [ex position](#).

Click on the **C=N double bond** to add another torsion, identified by the straight arrow in the [sketch](#) of the *ex* conformer. Click the **3D Viewer Selection Mode**  button and left click the torsion that you just created. Select **View | Explorers | Properties Explorer** from the menu bar.

The value in the *Filter* dropdown list should be **Torsion**. If it is **Bond**, the bond, and not the torsion, is selected. Click on the torsion in the structure.

In the **Properties Explorer**, double-click on **Angle**, and enter a value of **180**. Click the **OK** button.

The torsion angle is now 180°. You should save the structure as the *ex* version and remove the C=N torsion angle.

Select **File | Save As...** from the menu bar. Enter the filename **AIGH-mol_ex.xsd**. With the torsion still selected, press the **DELETE** key. Select **File | Save Project** from the menu bar.

You have created both the *in* and *ex* conformers, which will be used as the input files for the conformational search.

3. To generate the conformers

In this section, you will use the Conformers module to perform a conformational analysis independently for the *in* and *ex* structures.

Note: This section will only deal with the parts of Conformers that are applicable to this tutorial. For a more detailed introduction, please complete the dedicated Conformers tutorial.

In addition to the difference in the hydrogen orientation for the imide group, an examination of the molecular structure suggests the molecular conformation differs in a rotation of the terminal amine and imide groups around the C-C bond connecting them to the ring structure. To find the most stable conformers, you can set up a systematic search for the torsion angle.

Change the focus back to **AIGH-mol_in.xsd**. On the **Modules** toolbar, click the **Conformers** button



and choose **Calculation** from the dropdown list.

This opens the Conformers Calculation dialog. The first step is to setup the torsion angle that you want to rotate.

Click the **Torsions...** button.

This opens the Conformers Torsions dialog. Any torsion monitors that are defined on the molecule are displayed. If you have no torsions, you can use the Find functionality to search for rotatable torsions. However, you should already have the C-C torsion defined so you just need to set the # Steps. In this example, you want to minimize the structure every 1 degree whilst keeping the torsion that you are changing fixed.

Change the # **Steps** to **360**. Check the **Restrained** checkbox and close the dialog.

On the Conformers Calculation dialog, the Estimated conformers should be 360.

You are going to optimize the conformers as they are generated. The default optimization values are set to coarse but this can lead to some conformers not optimizing and giving odd torsion-energy plots. For this system, you should set the optimization convergence criteria to ultra-fine.

On the **Search** tab of the Conformers Calculation dialog, check the **Optimize geometry** checkbox and click the **More...** button to open the Conformers Geometry Optimization dialog. In the **Convergence tolerance** section, change the **Quality** to **Ultra-fine**. Close the dialog.

You now have to set the forcefield preferences.

On the **Energy** tab of the Conformers Calculation dialog, change the **Forcefield** to **pcff**.

Click the **More...** button for the **Summation method** to open the Conformers Non-Bond Options dialog. Change the **Truncation** to **None** and close the dialog.

The non-bond options treat the Van der Waals and Coulomb interactions. By nature, these are long range interactions and are computationally expensive so a truncation method is generally used as their effects decrease with distance. For this case, you are treating the non-bond interactions with no-cutoff so they are calculated for all the atoms to give you very accurate non-bond energies.


You are now ready to run the calculation. This may take a few minutes to calculate.

Click the **Run** button and close the Conformers Calculation dialog.

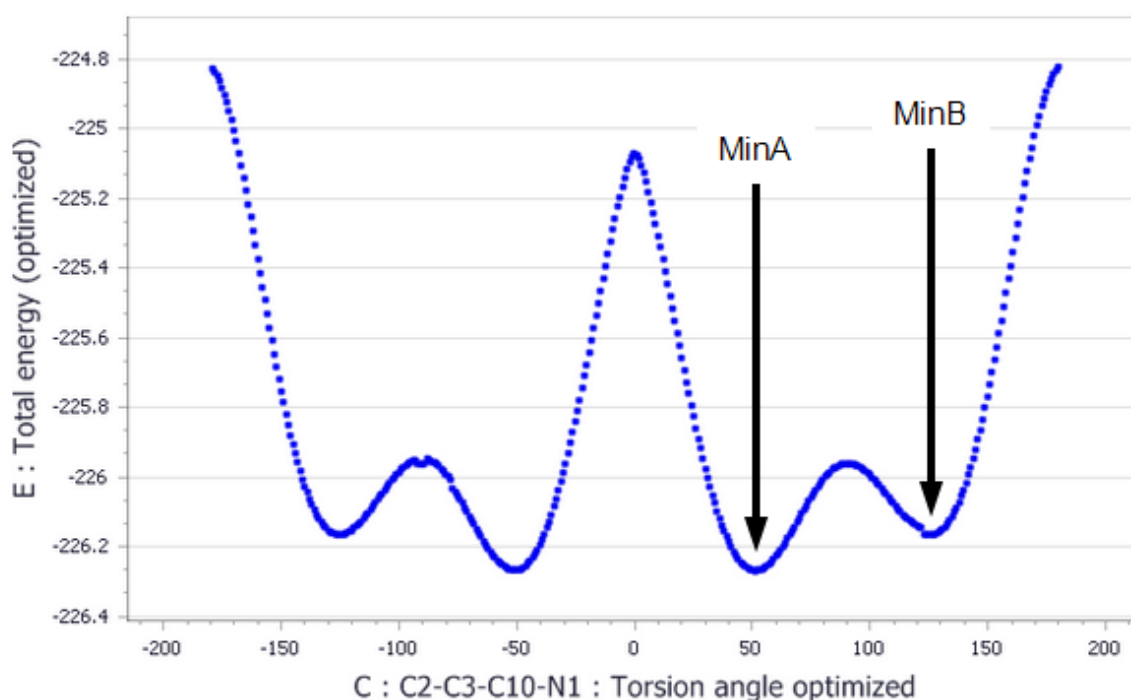
A new folder, called AIGH-mol_in Conformers Calculation is created. When the calculation completes, this will contain several documents but the one of interest is the study table as this holds the structures and energies.

When the calculation completes, select **File | Save Project** followed by **Window | Close All** from the menu bar. Re-open **AIGH-mol_in.std**.

The study table contains the structure, the optimized structures, the torsion angle that was varied, the energy of the unoptimized structure and the energy of the optimized structure. You will focus on the optimized energy and structure.

Select columns **C** and **E** and click the **Quick Plot** button .

The following chart is generated:



Energy profile for the *in* conformer

From the energy profile you can see that there are four energy minima for this system. The energy profile is almost symmetrical, so the conformers at $+50^\circ$ and -50° will give the same results from the polymorph search. You need to find the conformers at MinA and MinB on the chart.

Finding the lowest energy conformer can be achieved by sorting the study table by energy.

Select column **E** in the study table and click the **Sort Ascending** button.

You will see that the two lowest energy structures are at $+50^\circ$ and -50° and the energy difference between them is minimal. The lowest energy conformer is AIGH-mol_in-182 optimized. This is the conformer at Min A on the chart. To find the lowest energy conformer at Min B, you should select the points on the chart, and then examine the study table.

Change focus back to **AIGH-mol_in Scatter Plot.xcd**. Draw a rectangle around the points at the bottom of the energy well in Min B.

Using the selection tools to select the points on the chart means that they will also be selected in the study table. As the rows in the study table are sorted by their energy, you just have to locate the row nearest to the top that is highlighted and this will be the minimum energy structure in the energy well.

In the Project Explorer, double-click on **AIGH-mol_in.std**. Scroll up and down the study table to find the selected row that is closest to the top of the table.

This should be AIGH-mol_in-257 optimized. You can now create two new xsd documents to hold this. You can use copy and paste to do this or you can use the collection document.

Select column **B** and click the **Sort Ascending** button. Scroll down and **select** the cell in column B containing **AIGH-mol_in-257 optimized**. Scroll up and hold down the **CTRL** key and select **AIGH-mol_in-182 optimized**. With your mouse over the selected cell, **right-click** and select **Extract To Collection** from the shortcut menu.

A new collection document is displayed with the two molecules overlaid. You can now extract these into .xsd documents.

Right-click in **Extracted from AIGH-mol_in.xod** and select **Extract to Atomistic Documents** from the shortcut menu.

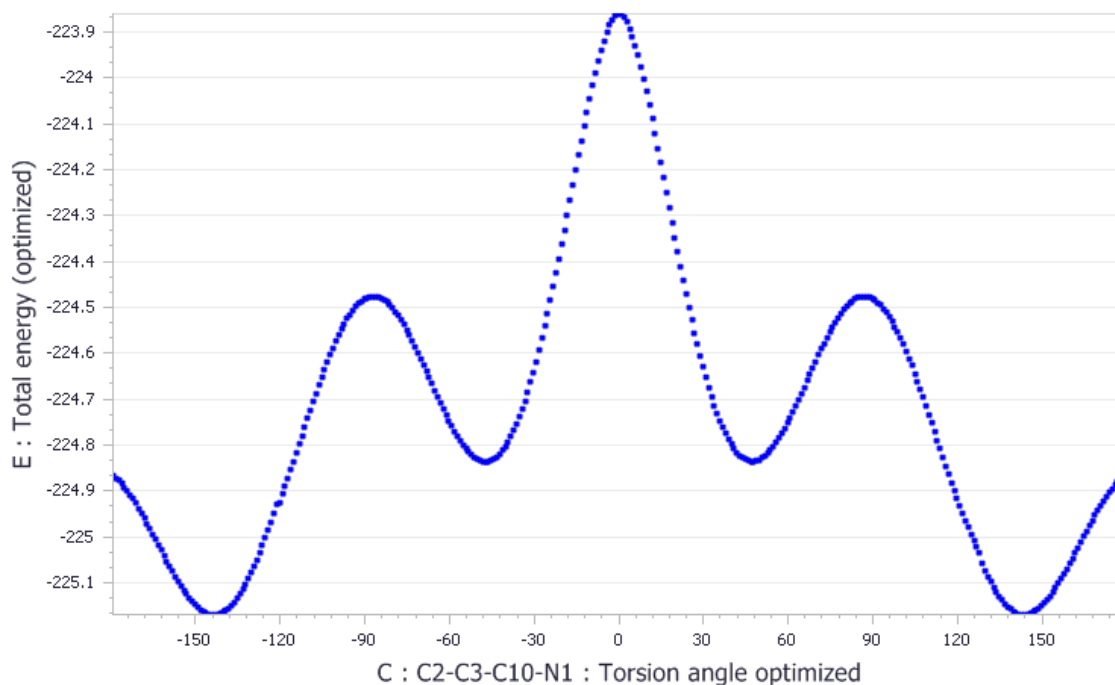
In the Project explorer, two new atomistic documents are created. You can now rename these to reflect their place in the energy profile.

Rename **AIGH-mol_in-257 optimized.xsd** to **AIGH-mol_in_MinB.xsd**. Rename **AIGH-mol_in-182 optimized.xsd** to **AIGH-mol_in_MinA.xsd**.

You will use these documents in the next section. However, you should repeat the above Conformers calculation for AIGH-mol_ex.xsd.

Change the focus to **AIGH-mol_ex.xsd**. Repeat the steps from the start of [section 3](#) again on this document.

You should find that you will have to reset the torsion angle for the new document but the energy setup will remain the same. Again, you can extract the frames for the two minima for further calculation. The energy profile should look similar to the one below.




Energy profile for the ex conformer

4. To calculate ESP-fitted charges using DMol³

Now you will calculate the ESP-fitted charges with DMol³. To maintain the conformation from the Conformer calculations, only a single point energy calculation will be carried out here.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**. Re-open **AIGH-mol_in_MinA.xsd**.

On the Modules toolbar, click on the **DMol³**  button and choose **Calculation** from the dropdown list. On the **Setup** tab, change the **Task** to **Energy**. Set the **Quality** to **Fine**. Select **GGA** and **PBE** from the **Functional** dropdown list.


On the **Properties** tab, check **Population analysis** and then, with this option highlighted, also check **ESP charges**. Click the **Run** button.

A new folder, called **AIGH_in_MinA DMol3 Energy**, is created in the Project Explorer. The progress of the job during the computation is presented in the form of chart and text documents. The calculation may take some time, depending on the speed of the processor in your computer. You should wait until the job finishes before proceeding.

Tip: To speed up the calculation, you can set the **Quality** to **Medium**. However, you must ensure that you choose the **DNP** basis set on the **Electronic** tab. The charges obtained from these two sets of settings are comparable.

Next you should analyze the DMol³ results and extract information on the ESP-fitted charges.

In the **Project Explorer**, double-click on **AIGH-mol_in_MinA DMol3 Energy\AIGH-mol_in_MinA.xsd**.

Click the **DMol³**  button and choose **Analysis** to open the DMol3 Analysis dialog. Select **Population analysis** from the **DMol3 Analysis** dialog. Choose **ESP** and click the **Assign ESP charges to structure** button. Close the dialog.

The ESP fitted charges are assigned to the molecule.

Right-click on the **AIGH-mol_in_MinA.xsd** document and choose **Label** from the shortcut menu. On the **Label** dialog, select **Charge** from the **Properties** and click the **Apply** button.

Once you finish examining the charges, click the **Remove All** button on the **Label** dialog to remove the charges from the display. Close the dialog.

You have now generated your first conformer ready for the polymorph calculation run.

Repeat section 5 to calculate the ESP-fitted charges for the other three conformer molecules you have generated.

Tip: You should only have to re-open the DMol3 Calculation dialog and click the **Run** button as the settings will be the same.

You can now use these four conformers of AIGH as inputs to Polymorph simulations.

This is the end of the tutorial.

References

Stanek, J., Caravatti, G., Frei, J., Furet, P., Mett, H., Schneider, P., Regenass, U., *J. Med. Chem.*, **36**, 2168 (1993).

Karfunkel, H.R., Wu, Z.J., Burkhard, A., Rihs, G., Sinnreich, D., Bürger, H.M., Stanek, J., *Acta Cryst.*, **B52**, 555 (1996).

Predicting a polymorphic form of a potential anti-cancer drug

Purpose: Illustrates how to predict possible crystal packing arrangements based on molecular structures using Polymorph

Modules: Materials Visualizer, Polymorph

Time: 🕒🕒🕒

Prerequisites: [Predicting a polymorphic form of a potential anti-cancer drug - Conformational analysis](#)

Introduction

This tutorial shows how to perform a polymorph search on 4-amidinoindanone guanylhydrazone (AIGH). Four possible conformations for the AIGH molecule were obtained in the [Predicting a polymorphic form of a potential anti-cancer drug - Conformational analysis](#) tutorial. In case you have not completed this tutorial, the necessary results files are provided as part of the Polymorph installation for you to import.

You will use Polymorph to predict various crystal packing arrangements for all four conformers independently. Only one of the four conformations will lead to successful prediction of the polymorphs of AIGH.

This tutorial covers:

- [Getting started](#)
- [To set up and run Polymorph](#)
- [To analyze the results using a study table](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **AIGH** as the project name, click the **OK** button.


The new project is created with *AIGH* listed in the Project Explorer. In this tutorial, you will use Polymorph to predict crystal packing arrangements for one of the low energy conformers obtained from the previous tutorial.

Click the **Import** button  to open the Import Document dialog. Navigate to the project folder in which you saved the four results of the previous tutorial. Select the file **AIGH-mol_in_MinA.xsd** and click the **Open** button. Rename the file **aigh_in_minA.xsd**.

Alternatively, navigate to **Examples/Polymorph/Results** and select the file **aigh_in_129.xsd**. Click the **Open** button, then rename the file **aigh_in_minA.xsd**.

2. To set up and run Polymorph

According to the Cambridge Structural Database (CSD), about 90% of all organic and organometallic crystal structures are covered by the 17 most frequent space groups. Without prior knowledge of the crystal symmetry (for example from an indexable powder pattern), you will have to run the calculations in a minimum of the 5 most common space groups, or better still, in the 17 most common ones.

Make **aign_in_minA.xsd** the active document. Click the **Polymorph** button  on the toolbar and choose **Calculation** from the dropdown list to open the Polymorph Calculation dialog. On the **Setup** tab, if the motion group is not defined click the **Assign automatically** button. Change the **Quality** to **Fine**.

In this tutorial, you will run a Polymorph prediction sequence. You could do this by running each step in the sequence separately or all of them in a single consecutive calculation. The Polymorph prediction sequence consists of four steps, namely: packing (Monte Carlo simulation), pre-clustering, optimization, and clustering. The entire sequence can take hours or even days, during which time:

- A fast and reliable Monte Carlo simulated annealing process searches the lattice energy hypersurface for probable crystal packing alternatives for the AIGH molecule, typically generating thousands of possible structures.
- Optionally, these potential structures are clustered into unique groups based on packing similarity.
- The geometry of each unique structure is optimized with respect to all degrees of freedom.
- The optimized structures are clustered again to remove duplicates. The final structures are ranked according to lattice energy.

On the **Setup** tab of the Polymorph Calculation dialog, set the **Task** to **Prediction**. Click the **More...** button to open the Polymorph Prediction dialog.

Check both the **Clustering** checkboxes and close the dialog.

Next, you will choose the Dreiding forcefield and use the ESP charges obtained with DMol³ earlier.

On the **Energy** tab of the Polymorph Calculation dialog, select **Dreiding** as the **Forcefield** and set the **Charges** to **Use current**.

Polymorph can search all space groups. However, by default, it searches only the five most common space groups (these are the ones in the list). To speed up this demonstration of the technique, you are setting the Polymorph Predictor to search just one space group, P-1. In a real case, you would have to include all other common space groups.

On the **Space Groups** tab of the Polymorph Calculation dialog, check the **Use** checkbox for the space group **P-1** and uncheck all the others.


On the **Job Control** tab, select **My Computer** as the **Gateway location**. Uncheck the **Automatic** checkbox and enter **aign_in_minA** as the **Job description**. Click the **Run** button and close the dialog.

The Polymorph Prediction calculation is now running and you will get regular updates about the progress of the job. You should wait until the job finishes before proceeding.

3. To analyze the results using a study table

In this section, you will analyze the output from the Polymorph run.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Click the **Polymorph** button  and choose **Analysis** to open the Insert Polymorph Results File dialog. Navigate to the **aigh_in_minA PMP Predict** directory and select **aigh_in_minA P-1.xtd**. Click the **Open** button.

All of the frames in the trajectory file are now displayed in a study table named **Polymorph Analysis.std**. The study table provides you with detailed information about each potential polymorph, including crystal *Structures* (column *A*), *Frame* number (column *B*, the lower the frame number the lower the total energy for the structure), *Space group* (column *C*), *Cell Volume* (column *D*), *Density* (column *E*) and *Total energy* (column *F*), the contribution of *van der Waals* (column *G*), *Electrostatic* (column *H*), and *H-bond energy* (column *I*) to the non-bond energy, and the cell parameters (columns *J-O*).

The name of each structure has the format: *[job name] [space group name] - [frame number]*. By default, the structures are already sorted, within each space group, according to their total energy values. The lowest energy frames are at the top of the table.

To find the most likely stable polymorphs, you can now sort the study table using different criteria, for example total energy, density, and so on.

Select **Tools | Sort Rows...** from the menu bar to open the Sort Rows dialog. Change the **Sort by column** setting to **F : Total energy**, select **Ascending**, and click the **OK** button.

All the structures are now ranked by their total energy, with the lowest energy structures at the top of the table. In this tutorial, **aigh_in_minA P-1 - 1** (which is the structure in frame 1 of the trajectory for space group P-1), is the lowest energy structure. You can also examine the energy profiles for the other structures.

You could also sort the table by density (column *E*). You should generate a density energy plot.


In the study table, click on the heading of column **E** and then, holding down the **SHIFT** key, on the heading of column **F**. Click the **Quick Plot** button .

The density-energy plot also shows that the lowest energy structures normally have higher densities.


You can now examine each possible polymorph. Start with the lowest energy structure, that in frame 1 of the trajectory.

Make **Polymorph Analysis.std** the active document. In column **A**, right-click on the first structure, **aigh_in_minA P-1 - 1**, and choose **View** from the shortcut menu.

The crystal structure of **aigh_in_minA P-1 - 1** is displayed.

Copy the entire document by pressing the **Copy** button  on the toolbar.

In the Project Explorer, right-click on the project **AIGH** and choose **New | 3D Atomistic Document**.

Paste the structure into the empty document using the **Paste** tool . In the Project Explorer, right-click on **3D Atomistic.xsd** and select **Rename** to change the name of the document to **aigh_in_minA_frame1.xsd**.

Right-click anywhere in the **aigh_in_minA_frame1.xsd** 3D Viewer and choose **Display Style** from the shortcut menu to open the Display Style dialog. On **Lattice** tab, select **Default** from the **Style** dropdown list. Set the **Max** value for **A** to **2**. **Close** the dialog.


To make the crystal structure clearer, you can switch off the display of the motion groups.

Hold down the **ALT** key and double-click on a motion group.

All the motion groups should now be selected.

In the Properties Explorer, double-click on **IsVisible** to open the Edit IsVisible dialog. Choose **No / False** and click the **OK** button. Press the **CTRL + D** keys to deselect the motion groups.

Now you will examine the hydrogen bonding patterns in the structure.

Click the **Calculate Hydrogen Bonds** arrow  and select **Monitor Hydrogen Bonding** from the dropdown list.

The hydrogen bonds are drawn as pale blue dotted lines. You can also check for close contacts in the packing arrangement.

Select **Build | Close Contacts** from the menu bar to open the Close Contact Calculation dialog. Click the **Calculate** button and close the dialog.

The close contacts are drawn as purple dotted lines in the crystal structure. There are no undesirable close contacts in this structure. All the hydrogen bonds are classified as close contacts, but are not undesirable.

To remove the display of the close contacts, hold down the **ALT** key and double-click on one of the purple dotted lines to select all the close contacts. Right-click on the structure and select **Delete** from the shortcut menu.

Open the **Display Style** dialog. On the **Lattice** tab, set the **Max** value for **A** to **1**.

Select all the hydrogen bonds, open the **Edit IsVisible** dialog. Choose **No / False** and click the **OK** button.

This is the predicted structure with the lowest calculated lattice energy (for 0 K) in space group P-1.

In the Polymorph Predictor sequence, you were only considering one low energy conformation of AIGH. To get reliable results, you have to compare the results of the other conformations.

You also need to take into account the fact that the calculations were performed in a single space group. Without prior knowledge of the crystal symmetry (for example, from an indexable powder pattern), you should run the calculations in a minimum of the 5 most common space groups, or better still, in the 17 most common ones.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

QMERA tutorials

The following tutorials illustrate how to utilize QMERA's capabilities.

- [QM/MM calculation of the SW1 defect formation energy for a carbon nanotube](#)
- [QM/MM geometry optimization of a Ru\(H\)₂\(diphosphine\)\(diamine\) complex](#)

QM/MM calculation of the SW1 defect formation energy for a carbon nanotube

Purpose: Introduces how to use the QMERA module in Materials Studio. Special attention is paid to preparing the system and which type of embedding scheme to use.

Modules: Materials Visualizer, QMERA

Time: 🕒🕒🕒

Prerequisites: None

Background

The Stone-Wales (SW) defect is a common defect on carbon nanotubes that is thought to have important implications for their mechanical properties (see [Andzelm et al., 2006](#)). The 90° rotation of two carbon atoms around the midpoint of the C-C bond transforms four hexagons into two pentagons and two heptagons. This substructure is known as Stone-Wales defect. In this tutorial you will calculate the formation energy of a nonchiral SW defect (SW1).

The following steps will be covered here:

- [Getting started](#)
- [QM region definition](#)
- [QMERA calculation](#)
- [Analysis of results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Stone-Wales** as the project name, click the **OK** button.

The new project is created with *Stone-Wales* listed in the Project Explorer.

2. Structure preparation

The first thing you need to do is prepare the structure of the single-walled nanotube (SWNT).

Select **Build | Build Nanostructure | Single-Wall Nanotube** from the menu bar. Change the **N** and **M** indices to **8** and **0** respectively.

This corresponds to a nanotube of 6.26 Å diameter.

Uncheck the **Periodic nanotube** box and change the number of **Repeat units** to **7**, this gives a nanotube length of 29.82 Å. Select **Both ends** from the **Hydrogen termination** dropdown list. Click the **Build** button and **close** the dialog.

Now you have to create the defect in the middle of the nanotube.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Click the **Stick** radio button and close the dialog.

Press the **LEFT** arrow key twice to rotate the nanotube so that you can see its full length horizontally.

The Z axis should be pointing to the left and the Y axis should be pointing up, on the axis orientation display, see [Figure 1](#).

Select two carbon atoms which are near the center of the nanotube wall and which are connected by a horizontal bond and then select the remainder of benzene rings at each end of the bond.

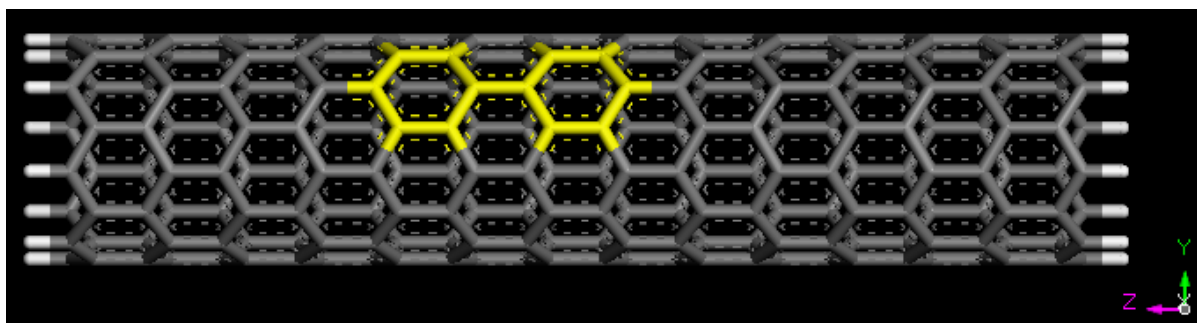



Figure 1. SWNT with two central carbon atoms and their pendant benzene rings selected.

Click on the arrow for the **3D Viewer Recenter**  from the toolbar and select **View Onto** from the dropdown list. Click anywhere in the 3D Viewer to deselect everything and **reselect** the central two carbon atoms.

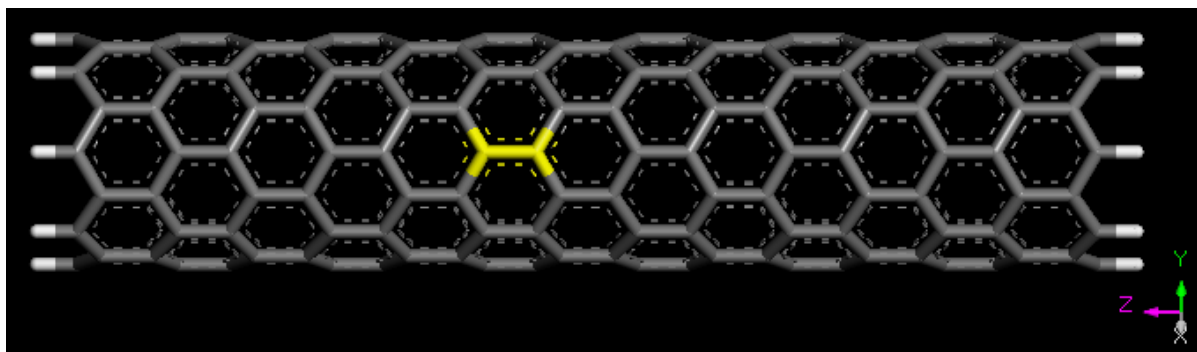




Figure 2. SWNT viewed from above, with two central carbon atoms selected.

Select the **Movement tools**  from the toolbar, change the **Angle** to **90.0** and click the **Move Around Z**  button. Close the dialog.

This creates the defect by rotating the two carbon atoms 90° around the screen Z axis.

To view the appropriate connectivity select **Build | Bonds** from the menu bar to open the **Bond Calculation** dialog. Uncheck **Calculate bond type**, set the **Convert representation to** option to **Resonant**. Click the **Calculate** button and close the dialog.

Rename the SWNT .xsd document to **SW1.xsd**.

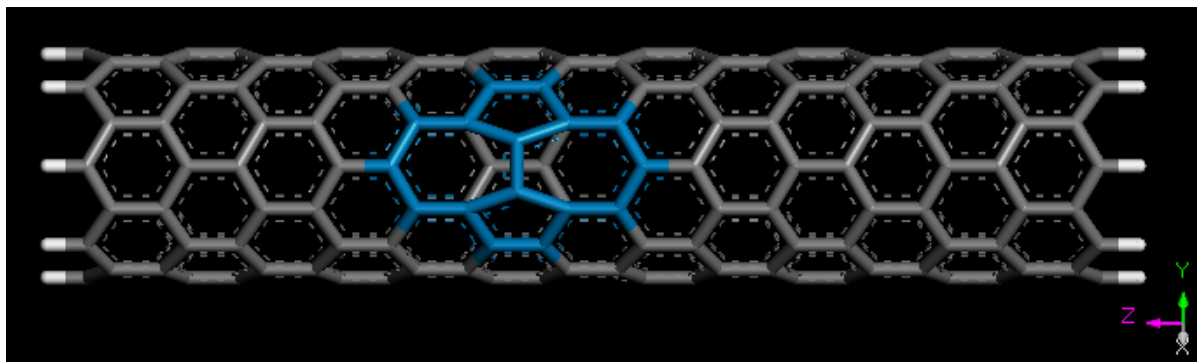



Figure 3. SW1 defect (highlighted here in blue) on an SWNT.

Tip: The input files can also be found in the *Examples* folder in the following location *Examples/Projects/QMERA/Stone-Wales Files/Documents*. The *SW1.xsd* file contains the defect structure and *SWNT.xsd* contains the defect-free nanotube.

3. QM region definition

The next step is to define the QM region that you want to use in the simulation. It is necessary to include full rings in the calculation to avoid possible clashes between hydrogen link atoms, and to leave enough space between the defect and the boundary QM-MM atoms. In this case you will include the defect plus a crown of full rings around it in the QM region (see Figure 4).

With the two carbon atoms central to the defect still selected, choose **Edit | Atom Selection** from the menu bar to open the Selection dialog. Select **Connected** from the **Select by Property** dropdown list and choose the **Add to the existing selection** radio button. Click the **Select** button four times and **close** the dialog. Hold down the **SHIFT** key and select the **four** carbons needed to complete the crown of six-membered rings.

Select  | **Calculation** from the modules toolbar to open the QMERA Calculation dialog. Click the **Add** button to add the selected atoms to the **QuantumAtoms** set.

Click anywhere in the 3D Viewer, the atoms in the set will be highlighted in purple.

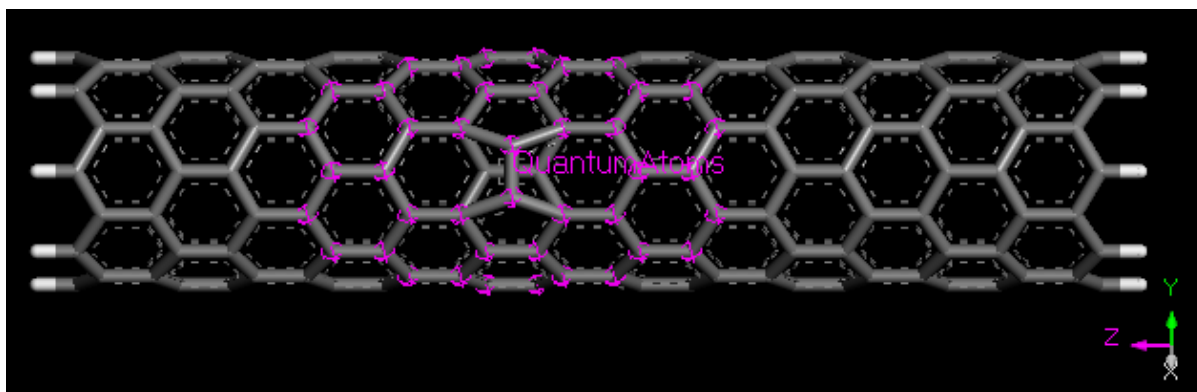


Figure 4. SW1 defect with the QuantumAtoms set defined.

If you want to visualize the hydrogen link atoms to be sure that there are no problems related to their position, you can use the *View* button on the QMERA Calculation dialog.

On the **Setup** tab of the **QMERA Calculation dialog** click the **View** button. A new window will open, double-click on the **LinkAtoms** label. Check that the position of the hydrogen link atoms makes sense and **close** the window. Click the **No** button on the dialog asking whether to save the document.

4. QMERA calculation

You are now ready to run the QMERA calculation. In this case the polarization effects are negligible and the charges of all atoms will be left as zero, which is compatible with the Dreiding forcefield. It is also sufficient to choose a mechanical embedding approach for the QM/MM calculation.

Note: By assigning charges to all atoms (for example using a charge equilibration method or using the charges from a forcefield) for this kind of embedding, the QM/MM electrostatic interaction is accounted for by the classical Coulomb interaction between all atoms. So the MM region charges do not enter the QM calculation. When non-zero charges are used, the net charges of the QM and MM regions must be integer values.

There are two different models available for mechanical embedding: QM-Pot and additive. You will use the QM-Pot model which uses a subtractive expression to calculate the total energy. Forcefield parameters are therefore required for all atoms of the system.

On the **Setup** tab of the **QMERA Calculation dialog** select **Geometry Optimization** as the **Task** and ensure that the **Quality** of the calculation is set to **Medium**.

In order to complete the tutorial more quickly, you could use the *Coarse* quality setting.

Click the **More...** button associated with the task, to open the **QMERA Geometry Optimization** dialog. Select **HDLC** as the **Method** and **close** the dialog.

The HDLC minimizer combines the use of highly decoupled delocalized internal coordinates with the linear scaling BFGS update of the Hessian (L-BFGS) method. This usually achieves faster convergence than normal BFGS or conjugate gradient methods for covalent systems of this size.

Click the **More...** button for the **QM server** to open the **QMERA DMol3 Parameters** dialog. Select **GGA** and **PBE** for the functional and **close** the dialog.

Click the **More...** button for the **MM server** to open the **QMERA GULP Parameters** dialog. Ensure that **Dreiding** is selected as the **Forcefield** and **Use current** is selected for **Charges**, **close** the dialog.

Select the **Options** tab of the **QMERA Calculation dialog**, ensure that **Mechanical** is selected as the **Embedding** scheme and **Model** is set to **QM-Pot**. Click the **Run** button.

GGA functionals provide a good description of the electronic subsystem and the PBE exchange-correlation functional has previously been identified as efficient for QM/MM calculations on nanotubes, see [Andzelm et al., 2006](#) for similar calculations.

Depending on your hardware, this calculation may take several hours to complete. If you wish to examine and analyze the results directly the output files are provided in the `Examples/Projects/QMERA/Stone-Wales Files/Documents/` directory in the `SW1 QMERA GeomOpt` and `SWNT QMERA GeomOpt` folders.

5. Analysis of results

The results of the calculation will be returned in a new folder called `SW1 QMERA GeomOpt`.

Open the **SW1.xsd** file in the `SW1 QMERA GeomOpt` folder to see the optimized geometry.

The final energy for this structure can be found in the `SW1.csout` file, the *QM/MM Energy* heading reports the corresponding energy in a.u., which is Hartree in this case.


Double-click on **SW1.csout** to open the energy file, press the **CTRL + F** keys and enter **Energy (subtractive)** into the Find dialog.

The end of the file is displayed. Scroll up a little and examine the **QM/MM Energy**.

To examine the relationship between the energy and the structure you can compare the energy chart with the trajectory. You will need to analyze the results to obtain the trajectory and chart documents, even if you already have some charts with intermediate updates.

Select **Modules | QMERA | Analysis** from the menu bar to open the QMERA Analysis dialog. Select **Energy evolution** and click the **View** button. **Close** the dialog.

The energy evolution either creates or opens two chart documents, called `SW1 Energies.xcd` and `SW1 Convergence.xcd`.

Make **SW1.xtd** the active document and, on the animation toolbar, click on the **Play**  button.

As the animation proceeds the seven-membered rings widen.

Stop the animation and open **SW1 Energies.xcd**.

Click on a point on the graph near the beginning of the optimization.

The 3D Viewer displays the structure at the corresponding step in the calculation. In this way you can examine the structure at specific energies during the calculation.

To obtain the formation energy for the SW1 defect you need to perform a QMERA calculation with the same settings for the defect free nanotube. To do this you should use a QM region of four fused C₆ rings and a surrounding crown. The resultant QM region will be similar to the one shown in Figure 4, except that the central C-C bond of the QM region in Figure 4 will be horizontal rather than vertical. The output files for this calculation are provided in the Examples/Projects/QMERA/Stone-Wales Files/Documents/SwNT QMERA GeomOpt/ folder.

Once you have both calculations you can calculate the formation energy of the SW1 defect as the difference in *QM/MM Energy*, converting from atomic units to eV according to:
1 a.u. (Hartree) = 27.2113845 eV.

You should obtain a value of around 2.1 eV.

This is the end of this tutorial.

Reference

Andzelm, J., Govind, N., Maiti, A., *Chem. Phys. Lett.*, **2006**, (421), 58-62.

QM/MM geometry optimization of a Ru(H)₂(diphosphine)(diamine) complex

Purpose: Introduces how to use the QMERA module in Materials Studio with special attention paid to which type of embedding scheme to use.

Modules: Materials Visualizer, QMERA

Time: 🕒🕒🕒

Prerequisites: None

Background

The preparation of enantiomerically pure alcohols is of high importance in drug design. A breakthrough in this field was the discovery, by Noyori and co-workers, of highly efficient ruthenium catalysts for the enantioselective hydrogenation of ketones (*R. Noyori, Angew. Chem., Int. Ed., 2002, 41, 2008*). Among the best catalysts for carbonyl hydrogenation are octahedral complexes where Ru(II) is coordinated by a chiral diphosphine and a chiral diamine.

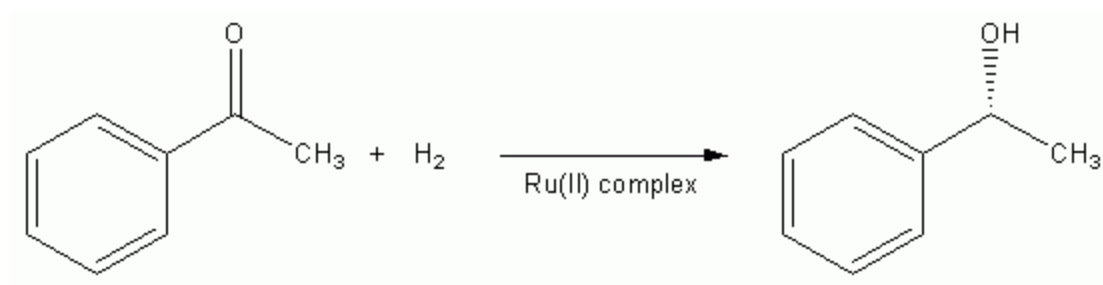


Figure 1. Conversion of a ketone to a chiral secondary alcohol.

In this tutorial you will use the QMERA module in Materials Studio to optimize the structure of a Ru(H)₂(diphosphine)(diamine) complex. You will use DMol³ to describe the QM region and the Dreiding forcefield to describe the MM region.

The following steps will be covered here:

- [Getting started](#)
- [Structure and QM/MM setup](#)
- [QMERA calculation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Ru_complex** as the project name, click the **OK** button.

The new project is created with *Ru_complex* listed in the Project Explorer.

2. Structure and QM/MM setup

The structure you will use is shown below:

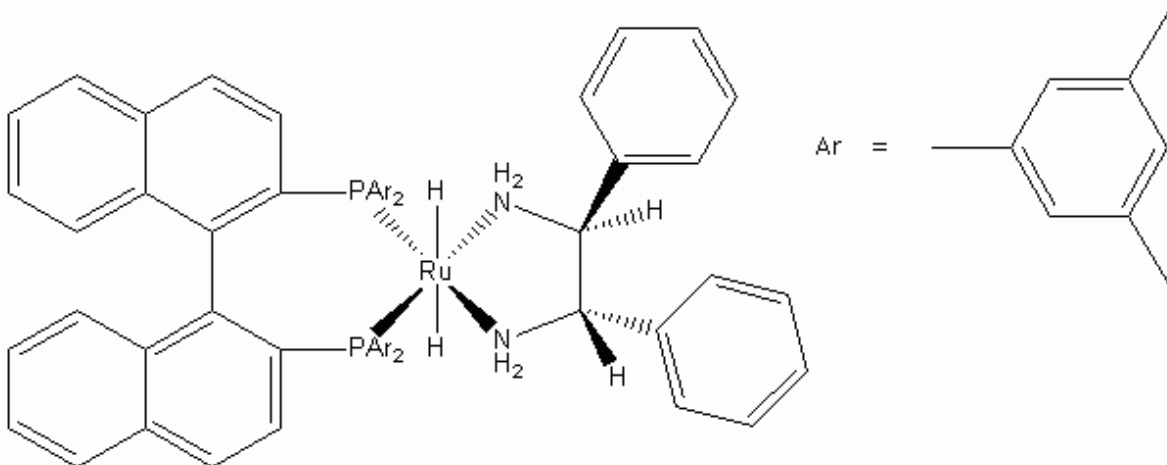


Figure 2. Ru(II) complex used as an asymmetric hydrogenation catalyst for ketones.

Select **File | Import...** from the menu bar and browse to **Examples\Projects\QMERA\Ru_complex Files\Documents\Ru_start.xsd**. Click the **Open** button.

Once you have the structure of the complex you can prepare the QMERA calculation. For this system you will include the polarization of the QM region due to the MM region. To this end, you will include the MM point charges in the SCF part of the QM calculation. This type of approach is called electrostatic embedding and it does not require forcefield parameters for the QM region, for either atom types or charges, because an additive expression is used to calculate the total energy of the system.

You need to define the QM region first. The atoms to include in the QM region are shown in Figure 3. The QM region includes the Ru center, the two hydrides (H), the two P atoms and the H₂NCHCHNH₂ diamine backbone.

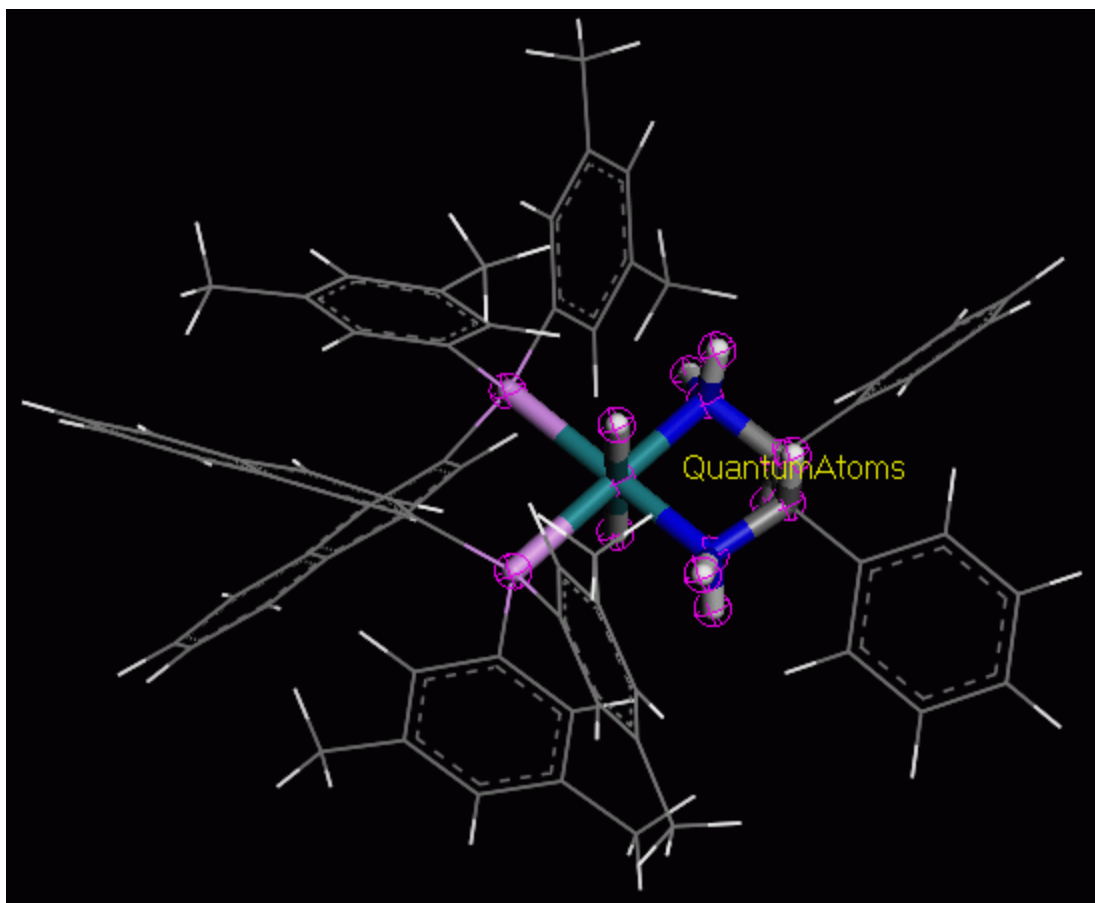




Figure 3. Ru(II) complex with the QM region indicated using stick representation.

Use the selection tool  to select the QM region indicated above. Select the **QMERA** module  from the Modules toolbar and choose **Calculation** to open the QMERA Calculation dialog. Click the **Add** button to add the selected atoms to the **QuantumAtoms** set.

Click anywhere in the 3D Viewer, the atoms in the set will be highlighted in purple.

If you want to visualize the hydrogen link atoms to be sure that there are no problems related to their position, you can use the *View* button in the QMERA Calculation dialog.

On the **Setup** tab of the QMERA Calculation dialog click the **View** button. A new window will open with the *LinkAtoms* selected. Check that the position of the hydrogen link atoms makes sense and **close** the window. Click the **No** button on the dialog which asks if you want to save this document.

You need to setup and modify the ligand charges. In electronic embedding methods, the basic requirement for the choice of charges is that net charge of the MM atoms must be integer. In this case this is achieved by using the QEq method to calculate separately the charges of each ligand bound to the QM region, under the constraint that the net charge must be zero.

Select **Modify | Charges** from the menu bar to open the Charges dialog. On the **Calculate** tab choose **QEq** as the **Method**. Select one of the MM ligand residues (for example a phenyl ring) and click the **Calculate** button. The ligand charges have been determined now. Repeat this procedure for all the other MM ligands.

Close the Charges dialog.

Note that the atoms in the QM region do not need to have charges assigned.

The prepared structure can also be imported from `Examples\Projects\QMERARu_complex Files\Documents\Ru_complex.xsd`.

You can now run the QMERA calculation.

3. QMERA calculation

On the **Setup** tab of the QMERA Calculation dialog, select **Geometry Optimization** as the **Task** and **Medium** for the **Quality** of the calculation. Click the **More...** button for the **Task** to open the QMERA Geometry Optimization dialog.

Select **HDLC** as the **Method** and **close** the dialog.

Click the **More...** button for the **QM server** to open QMERA DMol3 Parameters dialog. Select **GGA** and **PBE** for the **Functional** and **close** the dialog.

This Ru(II) complex has a zero net QM charge, the two hydride ligands act as electron donors (2×-1) to compensate for the metal's 2+ charge and no other QM atoms contribute charges (all other ligands coordinate the Ru center through dative bonding). So the DMol³ charge can remain at a value of zero for this system.

For the **MM server** click the **More...** button to open the QMERA GULP Parameters dialog. Select **Dreiding** as the **Forcefield** and **Use current** for the **Charges**, close the dialog.

On the QMERA Calculation dialog, click on the **Options** tab and select **Electronic** as the **Embedding** scheme and **Disperse boundary charge** as the **Model**. Click the **Run** button.

Depending on your hardware, this calculation may take several hours to complete. If you wish to examine and analyze the results directly the output files are provided in the `Examples\Projects\QMERARu_complex Files\Documents\ directory` in the `Ru_complex QMERA GeomOpt` folder.

After performing the calculation for the Ru(II) complex you can proceed to include the substrate (ketone) in the calculation. The ketone will belong to the QM region and as a consequence you do not need charges or atom types for that structure. You can draw the ketone in the same document as the Ru(II) complex and add it to the QM region using the *Add* button on the QMERA Calculation dialog.

The prepared structure for the complex and substrate can be found at `Examples\Projects\QMERARu_complex Files\Documents\Ru_complex+ketone_2.xsd`. If you wish to examine and analyze the results of the QM/MM calculation on the ketone system directly, the output files from the QMERA run can be found in the `Examples\Projects\QMERARu_complex Files\Documents\Ru_complex+ketone_2 QMERA GeomOpt` folder.

This is the end of this tutorial.

Reflex tutorials

The following tutorials illustrate how to utilize Reflex's capabilities.

- [Working with powder diffraction patterns](#)
- [Indexing powder patterns](#)
- [Indexing of 4-nitrophenylhexylurethane using X-Cell](#)
- [Indexing a flat unit cell with X-Cell](#)
- [Rietveld refinement of inorganics](#)
- [Rietveld refinement with energetic considerations](#)
- [Determining the degree of crystallinity of lactose monohydrate samples](#)

Working with powder diffraction patterns

Purpose: Introduces the Reflex tools for calculating and comparing theoretical and experimental powder diffraction patterns.

Modules: Materials Visualizer, Reflex

Time: 

Prerequisites: Project management Visualizer Tutorial

Background

Simulation and analysis of X-ray, electron, and neutron diffraction patterns in Materials Studio is handled by the Powder Diffraction tool in the Reflex module. Reflex supports real-time simulation during structure manipulation, allowing you to monitor the effects of structural changes on diffraction patterns. It can also be used to compare simulated and experimental data.

Introduction

This tutorial covers:

- [Getting started](#)
- [The Powder Diffraction tool](#)
- [To use different types of radiation](#)
- [To compare two similar structures](#)
- [To manipulate the graph](#)
- [To compare experimental data with simulated data](#)
- [To export study table data files](#)
- [To monitor changes in diffraction patterns](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.


1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Indigo** as the project name, click the **OK** button.

The new project is created with *Indigo* listed in the Project Explorer. Now you will import the input file you will be studying.

Crystal structures can be imported into Materials Studio in various file formats such as .cif and .PDB files. Two structure files have been provided containing different polymorphs of the dye indigo. This is the main constituent in the color of blue jeans.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Structures** folder and double-click on **indigo_a.xsd**.

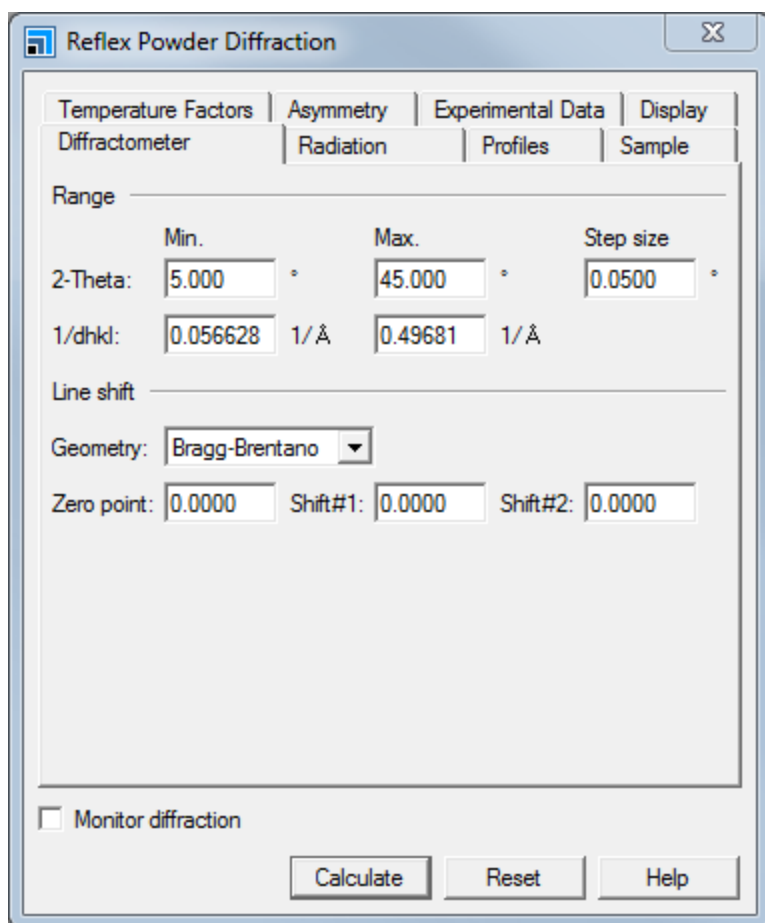
A unit cell containing six molecules is displayed in the 3D Viewer.

2. The Powder Diffraction tool

The Powder Diffraction tool is part of the Reflex module.

Click the **Reflex**  arrow on the **Modules** toolbar and select **Powder Diffraction**.

This opens the Reflex Powder Diffraction dialog.



Reflex Powder Diffraction dialog

The Reflex Powder Diffraction dialog consists of eight tabs containing all the settings you might need for the simulation and analysis of diffraction patterns.

The first step is to calculate a diffraction pattern.

Click the **Calculate** button on the Reflex Powder Diffraction dialog.

This creates a new chart document entitled `indigo_a.xcd`. This chart plots 2-theta values on the x-axis versus intensity values on the y-axis. Diffraction peaks are indicated by green markers.

3. To use different types of radiation

Different types of radiation can be used to generate powder diffraction patterns. You will now calculate powder patterns for the three different types of radiation available. The relevant parameters are on the *Radiation* tab.

On the **Reflex Powder Diffraction** dialog, select the **Radiation** tab.

This tab is split into four sections, relating to the three different types of radiation and monochromator options for X-ray diffraction. The default radiation type is X-ray and you used this to calculate your first pattern. In the X-ray radiation options section, you can choose which type of anode you would like to use as the source and if a polarization correction should be included. As you have already generated an X-ray powder diffraction pattern, you will now generate a neutron diffraction pattern.

Select **Neutron** radiation from the **Type** dropdown list.

The *Calculate* button is not active because the structure document is not in focus. To perform another calculation, you must make the 3D Atomistic document containing the indigo structure active.

Click on the 3D Viewer to make it active or double-click on `indigo_a.xsd` in the **Project Explorer**.

Now generate the powder pattern.

Click the **Calculate** button.

The chart document is updated with the diffraction pattern based on the new radiation source. You can repeat this for electron radiation.

Select **Electron** radiation from the **Type** dropdown list.

Remember to make the 3D Viewer active.

Make `indigo_a.xsd` the active document and click the **Calculate** button.

The chart document is updated again with the diffraction pattern for the new radiation source. Before continuing, return the radiation source to X-ray.

Set the radiation **Type** to **X-ray**.

4. To compare two similar structures

A second polymorph of indigo exists and its diffraction pattern can be compared with that for `indigo_a`.

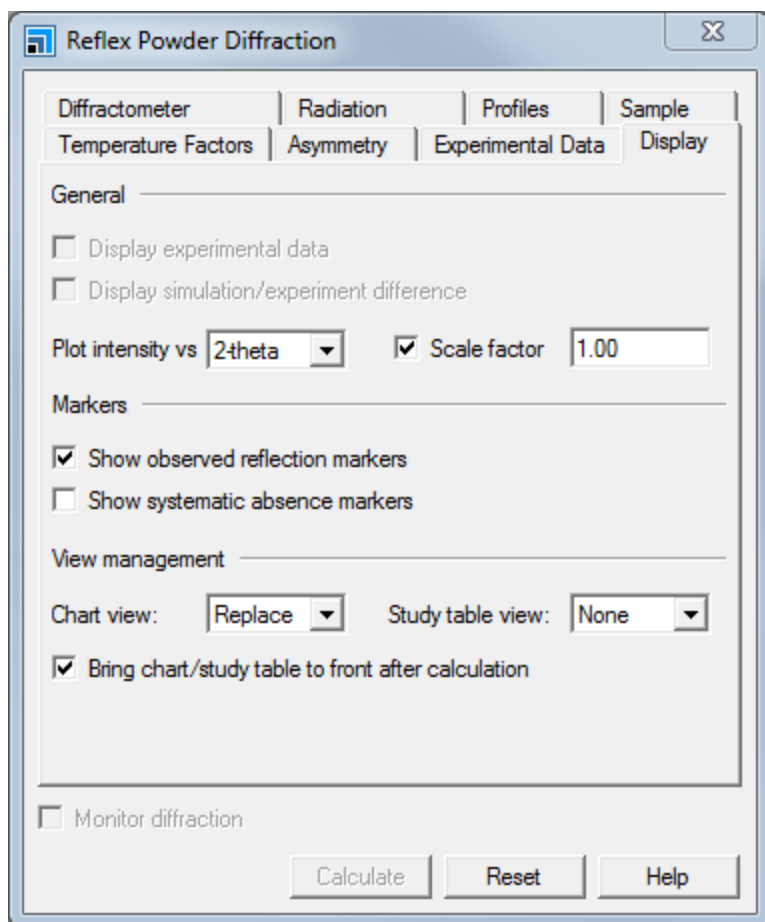
Import the crystal structure `Examples\Reflex\Structures\indigo_b.xsd`.

There are now two 3D Atomistic documents and one chart document open. You should load both sets of diffraction data into one chart document, so that you can compare them.

Make `indigo_a.xsd` the active document. Click the **Calculate** button on the Reflex Powder Diffraction dialog.

If you calculate the diffraction pattern for indigo_b now, the new graph will replace that of indigo_a, so you should first change the graph display options.

Select the **Display** tab on the Reflex Powder Diffraction dialog.



Reflex Powder Diffraction dialog, Display tab

The top section of the *Display* tab deals with the generation of graphs from experimental data. The second section controls the appearance of markers on the graph. The final section, entitled View management, allows you to specify the chart and study table options. The Study table view option allows you to output information directly to a spreadsheet style study table, as well as a graph.

The default Chart view option is *Replace* but you should change this so that the chart plots are added together.

Select **Add** from the **Chart view** dropdown list.


Now you can calculate the diffraction pattern for polymorph indigo_b.

Make **indigo_b.xsd** the active document and click the **Calculate** button.

A second line is added to the Chart Document. A legend is displayed at the bottom of the Chart Document indicating that the indigo_a data is plotted in blue and the indigo_b data is plotted in green.

5. To manipulate the graph

You can manipulate your view of the chart using the zoom and translate tools.

Select the **Zoom** tool  on the **Chart Viewer** toolbar. Left-click and hold in the **Chart Viewer** and move the mouse to the left and right and up and down.

Moving the mouse to the left and right compresses and expands the chart document horizontally. Moving the mouse up and down the screen expands and compresses the chart vertically.

Select the **Translation** tool . Click in the **Chart Viewer** and move the mouse around.

The *Translation* tool acts in the same way for the Chart Viewer as it does in the 3D Viewer. You can also translate using the scroll bars.

Click on the scroll bar on the bottom of the **Chart Viewer**. Scroll across the x-axis of the document.

You can reset the view of the chart by using either the *Reset View* button or pressing the HOME key on your keyboard, this applies to both Chart and 3D Viewers.


Click on the **Reset View** button  on the **Chart Viewer** toolbar.

Note: If you are using a mouse with a wheel, you can use the wheel to mimic the zoom function by simply moving the wheel up and down. You can also translate by holding down the wheel and moving your mouse around the screen.

If you wish to hide a data set from the chart you can do this by unchecking the corresponding checkbox in the legend.

In the chart legend uncheck the **Observed Reflections** checkbox.

The green observed peaks are removed from the chart. Now remove the current graph from the project.

Select **indigo_b.xcd** in the **Project Explorer** and click the **Delete** button . When a dialog opens asking if you are sure, click the **Yes** button.

Having removed the chart document, you should now save the project.

Select **File | Save Project** from the menu bar.

Finally, you should change the *Chart view* option back to *Replace*.

On the **Display** tab of the Reflex Powder Diffraction dialog, select **Replace** from the **Chart view** dropdown list.

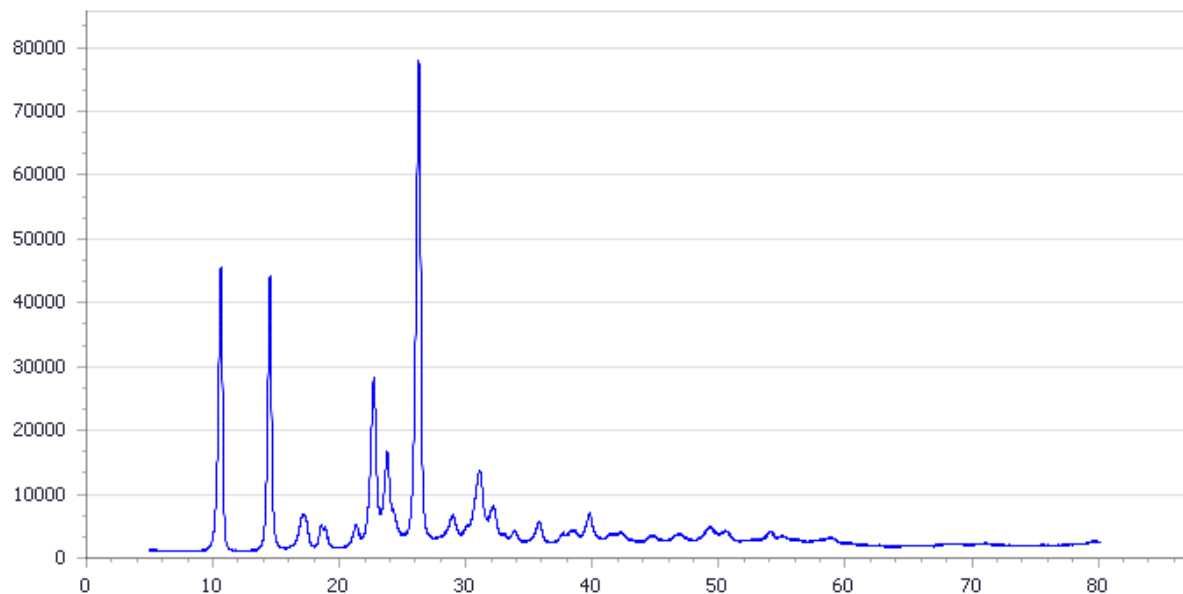
6. To compare experimental data with simulated data

An important feature of the Powder Diffraction tool is the ability to compare simulated diffraction patterns with those obtained experimentally. Materials Studio accepts many different experimental data formats but in this tutorial you will import data in the .3cam file format developed at Cambridge University.

Now import the experimental data, which was obtained using X-ray radiation.

Click on the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and open **indigo_1.3cam**.

The diffraction pattern is opened in a new Chart Viewer.



Select the *Experimental Data* tab, to display information about the experimental data file that you have imported.

On the Reflex Powder Diffraction dialog, select the **Experimental Data** tab and choose **indigo_1.xcd**. Click the **View** button.

The data consists of a filename, pattern, start and end values and step size. Now tell the program that you want to display the experimental data in your next chart.

On the **Display** tab check the **Display experimental data** checkbox.

The *Display difference plot* option is now active.

Check the **Display simulation/experiment difference** checkbox.

X-ray radiation was used to obtain the experimental results, so you must make sure that the simulated data are also based on X-rays.

On the **Radiation** tab, ensure that the radiation **Type** is set to **X-ray**.

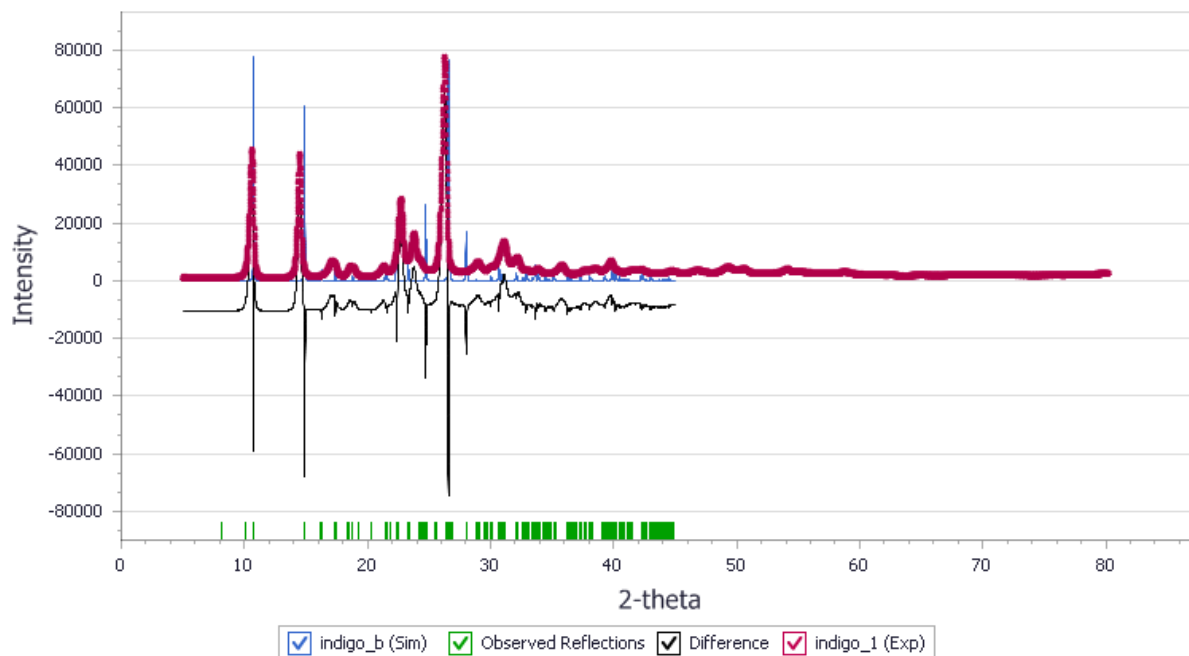
Before you display the plot, you must select the structure you would like to run the calculation on. This is done by making the required structure the active document.

Double-click on **indigo_b** in the **Project Explorer**.

Now generate the diffraction pattern for the **indigo_b** structure and compare it with the experimental data.

Click the **Calculate** button.

The generated plot should look similar to this.



The chart shows the experimental data in red, the simulated data in blue, and the difference between the two in black. Green observed check marks are also displayed.

You can see that the experimental data and the simulated data do not fit well. There are peaks in the experimental data that do not exist in the simulated data and vice versa. For example, there are simulated peaks at 2-theta values of approximately 25 and 28 that do not appear in the experimental pattern.

You will also notice that the experimental information range ends at 80.170, whereas the simulated data ends at 45. You can specify the range of the simulated data on the *Diffractometer* tab.

On the **Diffractometer** tab change the **2-Theta Max** value from 45 to **80.00**.

Now repeat the calculation with the wider 2-theta range.

Double-click on **indigo_b** in the **Project Explorer** and click the **Calculate** button on the Reflex Powder Diffraction dialog.

The chart is updated with the full range of the 2-theta values displayed.

Next compare the experimental data with the simulated pattern of the indigo_a polymorph.

Double-click on **indigo_a** in the **Project Explorer** and click the **Calculate** button on the Reflex Powder Diffraction dialog.

The new simulated diffraction pattern is in good agreement with the experimental data. There are no peaks that do not match up and the difference plot is much improved. This indicates that this is the polymorph identified experimentally.

You can improve the quality of the match by changing the sample crystallite size or the experimental resolution. Try reducing the crystallite size first and then the experimental resolution. The crystallite size can be specified using the L^* parameters.

On the **Sample** tab in the **Crystallite size** section, check the **Use in broadening calculation** checkbox. Change the values of L_a , L_b and L_c from **500** to **300**.

The crystallite size is the average size of the crystals in the powder. Generally, powders consist of different sizes of crystallites and these affect the broadness of the peaks in the experimental results. To improve the fit between the experimental results and the simulated results, you can change the simulated crystallite size.

Make **indigo_a** the active document and click the **Calculate** button.

Now change the experimental resolution on the *Profiles* tab.

On the **Profiles** tab change the **W** parameter to **0.24**.

Make **indigo_a** the active document and click the **Calculate** button.

The width of the simulated data peaks increases and the peaks above a 2-theta value of 35 match much better with the experimental data.

7. To export study table data files

It is also possible to export the diffraction data in study table form, that is as a spreadsheet. This is useful if you need the precise values of the peak intensities. The data can also be copied and pasted into most spreadsheet packages.

Select **File | Save Project** from the menu bar.

On the **Display** tab of the Reflex Powder Diffraction dialog, in the **View management** section, change the **Study table view** from **None** to **Replace**.

When you generate a powder diffraction pattern, you will also generate the spreadsheet style study table information to go with it.


Make **indigo_a** the active document and click the **Calculate** button.

The Chart Document is updated and a new Study table Document is displayed with several columns containing information about the calculations.

Note: The study table contains only the simulated data. It does not include the experimental data.

You can either leave this information in the Study Table (.std) file or you can copy and paste it into a spreadsheet package.

Before you continue, remove the Chart Document.

Select **indigo_a.xcd** in the **Project Explorer** and click the **Delete** button . When a dialog opens asking if you are sure, click the **Yes** button.

8. To monitor changes in diffraction patterns

The Monitor diffraction tool in Materials Studio allows you to make changes to a structure and watch the effects of those changes in real-time. These changes can include stretching or compressing bonds or changing the orientation of the molecules within the cell. In this section, you will monitor the changes in the diffraction pattern as you rotate the molecule in the cell and then as you stretch a bond in the indigo_a structure.

The first step is to close the other documents in the Visualizer.

Close the **indigo_b** 3D Viewer.

This does not remove the structure from the project but only from the Visualizer. Now set the Powder Diffraction options to monitor the diffraction.

Select the **Display** tab on the Reflex Powder Diffraction dialog and change the **Study table view** option to **None**. Ensure that **indigo_a.xsd** is the active document and check the **Monitor diffraction** checkbox.

The text at the bottom of the Powder Diffraction dialog changes to read Monitor diffraction: indigo_a. The chart document is displayed as normal. At this point, it is best to close the Powder Diffraction dialog as you are going to need room for visualization.

Close the **Reflex Powder Diffraction** dialog.

You can also move and resize the Chart and 3D Viewers so that you have a good view of both of these. Now select a fragment from the indigo_a structure to rotate.

Select any atom in one of the fragments, right-click and choose **Select Fragment** from the shortcut menu.

One of the structures in the cell is selected. Since the molecules in the cell are all related by symmetry, when you rotate one structure, you will automatically rotate the rest.

Hold down the **SHIFT** key and the right mouse button. Move the mouse.

As you rotate the fragment, the chart data changes because the relative positions of the groups have changed. You can also change the diffraction pattern by changing the bond lengths. Try stretching and moving one of the carbonyl oxygen atoms.

Click on one of the red oxygen atoms. Hold down **SHIFT + ALT**, right-click and drag the mouse.

Tip: If you have a three button mouse or a mouse with a wheel, you can translate the fragment by holding down **SHIFT** and the middle mouse button or wheel.

The oxygen is dragged as you move the mouse and the position and length of the bond changes. This has an immediate and observable effect on the diffraction pattern.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Indexing powder patterns

Purpose: Introduces the Powder Indexing tool and chart document manipulation enabling you to index powder patterns and determine cell parameters from experimental data.

Modules: Materials Visualizer, Reflex

Time: 🕒

Prerequisites: [Working with powder diffraction patterns](#)

Background

Certain compounds are difficult to crystallize. Often it is impossible to grow single crystals of such compounds of sufficient quality for X-ray analysis and subsequent structure solution. Instead, the crystallization experiments result in the formation of a crystalline powder. Such polycrystalline materials can be analyzed using powder diffractometry. A powder diffraction pattern is a 2D representation of the 3D crystal structure. The peak positions are related to the unit cell parameters, while the intensities of the peaks carry information about the space group and the arrangement of atoms in the unit cell.

Using modern software tools, crystal structures can now be solved routinely from powder diffraction data. In general, the determination of unit cell parameters from peak positions, a process known as indexing, is the first step toward determining the crystal structure.

Introduction

This tutorial shows how the Powder Indexing tool can be used to index powder diffraction patterns within Materials Studio. You will learn how to create peak lists for analysis and how to set up an indexing calculation.

Two powder patterns will be indexed, belonging to an organic and an inorganic compound. You will use different methods to establish a list of diffraction peaks.

This tutorial covers:

[Getting started](#)

[Indexing the powder pattern of an organic compound](#)

- To import the powder data
- To create a peak list
- To use the Marker tool on the Chart Viewer toolbar
- To recalculate the peak list
- To index the powder pattern

[Indexing the powder pattern of an inorganic compound](#)

- To import the data
- To remove the background noise
- To use a Study Table document to add markers
- To index the powder pattern
- To compare the indexing result to a crystal structure

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Getting started

Begin by creating a new project.


Open the **New Project** dialog and enter **Indexing** as the project name, click the **OK** button.

The new project is created with *Indexing* listed in the Project Explorer.


Indexing the powder pattern of an organic compound

1. To import the powder data

First create a folder for the powder pattern of cholamide dihydrate.

Right-click on the **Indexing** project root  in the Project Explorer and select **New | Folder**. Rename the folder **dihydrate**.


Next import the chart document containing the powder diffraction pattern into the dihydrate folder.

Click the **Import** button  to open the Import Document dialog. Select **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder. Locate and load the **dihydrate.xcd** file.

The powder pattern of cholamide dihydrate opens in a new Chart Viewer.

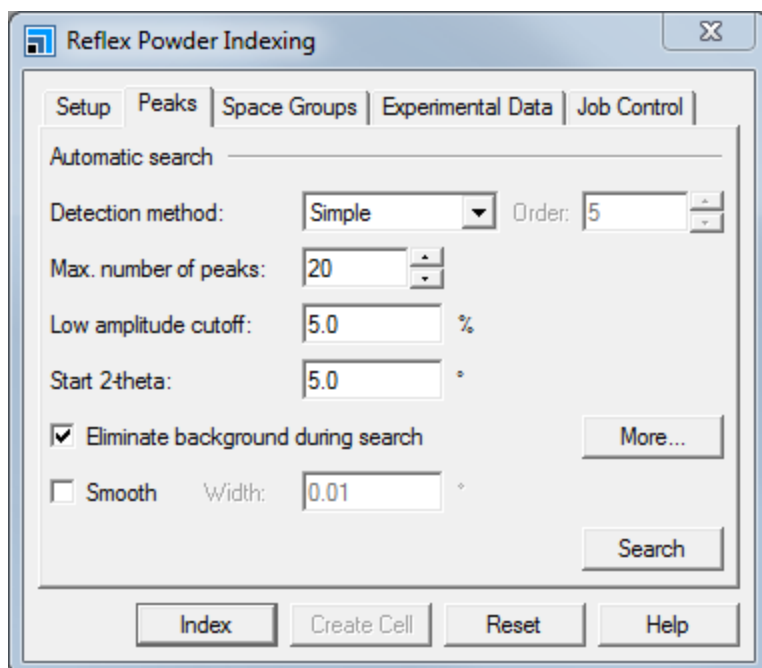
2. To create a peak list

Next identify the peaks that will be used to index the pattern. This is done initially using the automatic peak search functionality.

Click the **Reflex** arrow  on the **Modules** toolbar and select **Powder Indexing** from the dropdown list.

This opens the Reflex Powder Indexing dialog.

Select the **Peaks** tab.



Reflex Powder Indexing dialog, Peaks tab

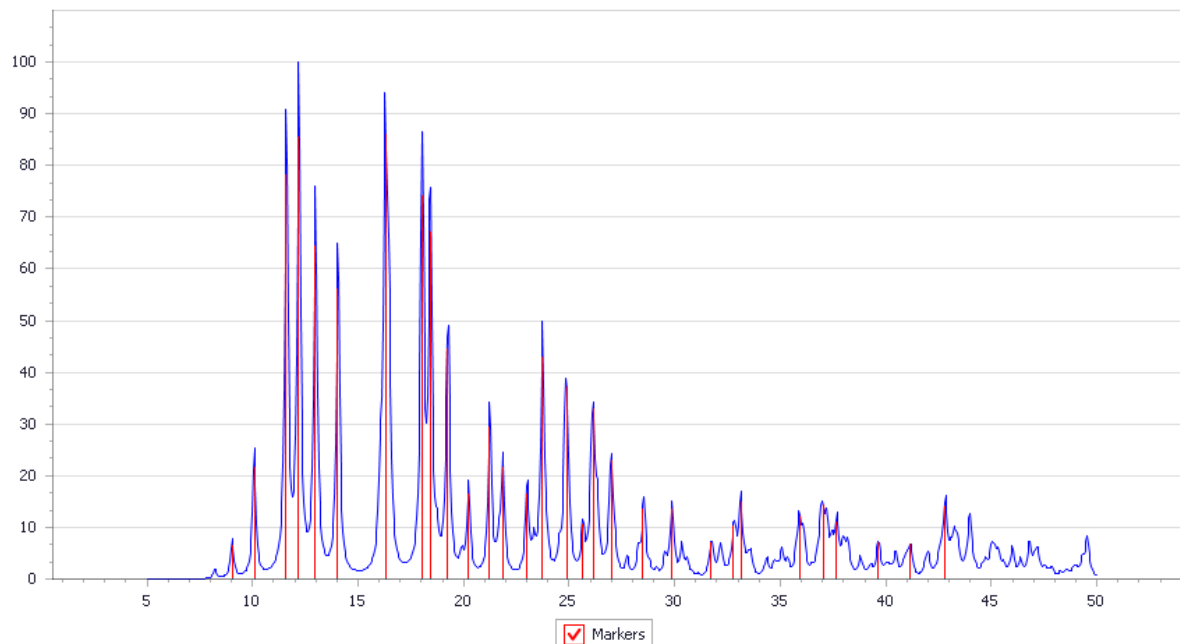
You can change the maximum number of peaks you wish the search algorithm to detect. The appropriate value for this parameter will vary between powder patterns, in this example you should use a value of 30.

Increase the **Max. number of peaks** to **30** and select **Savitzky-Golay** from the **Detection method** dropdown list.

The Low amplitude cutoff is the percentage of the maximum peak height below which peaks will not be selected. This value depends on the intensity distribution of the background noise. For this example, there is no need to edit this, or any of the other parameters on the *Peaks* tab.

Click the **Search** button and close the Reflex Powder Indexing dialog.

Markers identifying the peaks that have been located are displayed in light blue in the Chart Viewer.



The chart document with peak markers.

If the automatic peak search gives unsatisfactory results, you can remove markers easily. If, for example, there are one or two markers identifying very small peaks, these can be removed individually. Alternatively, if many very small peaks are marked, the peak search can be rerun with a different Low amplitude cutoff.

3. To use the Marker tool on the Chart Viewer toolbar

New markers can be added using the Marker tool on the Chart Viewer toolbar.

Click the **Marker** button  on the **Chart Viewer** toolbar. Left click to place the marker.

You can force the marker to jump to the nearest data point by holding down the CTRL key while placing the marker.


Left-click on a data point for another marker, then hold down the **CTRL** key and drag the marker.

You can move an existing marker by left-clicking and dragging. Hold down the CTRL key while you drag to jump to the nearest data point. If you subsequently decide the original position was correct, you can press ESC to cancel the operation.

Left-click on one of the markers, keep the mouse button held down and move the cursor. Press the **ESC** key.

The X and Y coordinates of the marker can be examined and edited in the Properties Explorer.

Select **View | Explorers | Properties Explorer** from the menu bar to display the Properties Explorer.

Choose the **Selection** tool  and click on a marker in the Chart Viewer to select it. In the Properties Explorer, set the **Filter** to **Chart Markers**.

The Properties Explorer lists the attributes of the marker, including *IsUsed*, *X*, and *Y*.

Double-click on the **Value** for **Y** in the Properties Explorer to open the Edit Y dialog. If the marker is not the same height as the peak it is marking change the value of Y, click the **OK** button.

Tip: Alternatively you can view the X and Y coordinates of markers and other points using the crosshair. To show the crosshair, right-click on the chart and choose **Show Crosshair** from the context menu. The coordinates of data points and markers that are close to the mouse pointer are displayed in a tooltip.

You can delete one or more markers by selecting them and pressing DELETE.

Hold down the **SHIFT** key and left-click on several markers. Move the cursor away from the selected markers and press the **DELETE** key.

The selected markers are identified a blue circle with yellow fill at their tip. Pressing the DELETE key removes all of the currently selected markers. You can select all of the markers in a chart using CTRL + A.

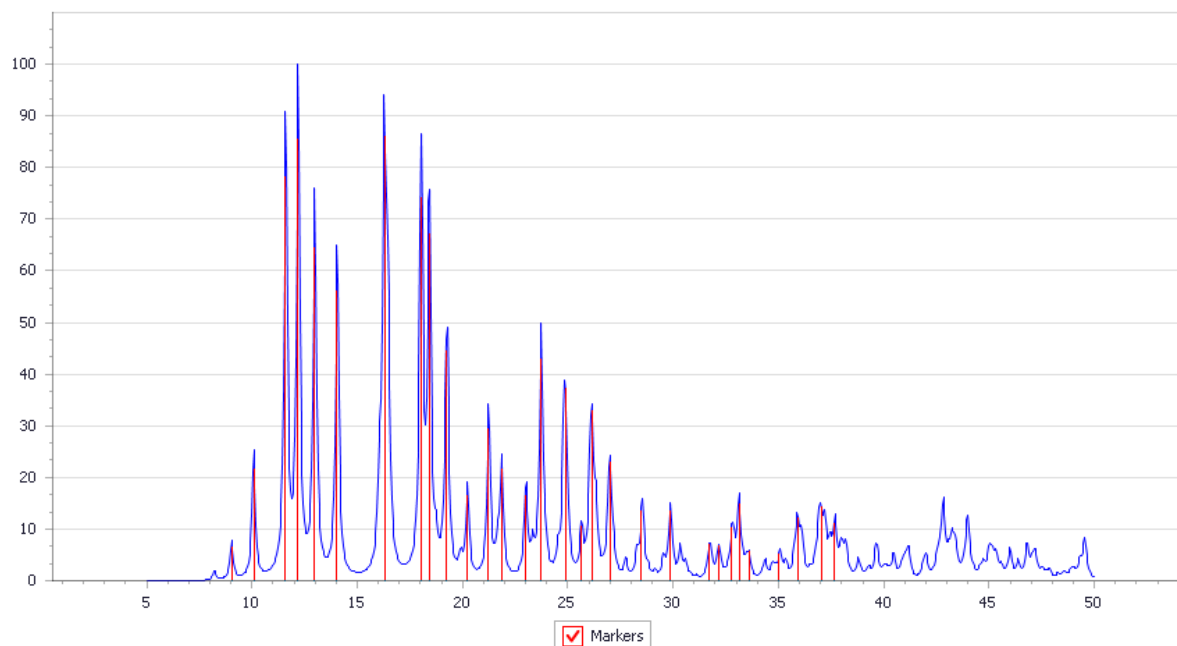
Press the **CTRL + A** key, then press the **DELETE** key.

4. To recalculate the peak list

Since you have added and removed peaks, you should perform the peak search again. This time you will change the *Low amplitude cutoff* to 3%.

Open the **Reflex Powder Indexing** dialog. On the **Peaks** tab, change the **Low amplitude cutoff** to **3** %. Click the **Search** button.

The new search results are displayed.



This time, the smaller peaks have not been marked as they are less than 3% of the height of the highest peak. This has improved the peak search but, before you index the pattern, there are still some peaks that need to be added and removed. You can remove the peaks by selecting them and pressing DELETE. You can add peaks using the *Marker* tool.

You are now ready to index the powder pattern.

5. To index the powder pattern

The selected peaks will be used to index your powder pattern. Four methods for indexing powder patterns are available with Materials Studio. TREOR90 ([Werner et al., 1985](#)) is a non-exhaustive trial-and-error method. DICVOL91 ([Boultif and Louër, 1991](#)) is a quasi-exhaustive algorithm that gives the user additional control over the peak position error, cell parameter limits and density constraints. ITO ([Visser, 1969](#)) searches for unit cells by first identifying groups of diffraction peaks that belong to the same plane of the reciprocal lattice. These planes are then combined to find the reciprocal lattice. X-Cell ([Neumann, 2003](#)) is a novel indexing algorithm, developed at BIOVIA, that makes use of systematic absences to facilitate the search for possible indexing solutions.

You will use the TREOR90 indexing program in this example. Before performing the indexing calculation you should specify which crystal systems you want to examine.

On the **Setup** tab of the Reflex Powder Indexing dialog, check all of the **Crystal systems to test** checkboxes. Click the **Index** button.

When the job is finished a dialog reports the status as completed.

Click the **OK** button on the Job Completed dialog.

A study table document containing the results of the calculation is displayed, as shown below.

A	B	C	D	E	F	G	H	I	J	K	L	
#	F O M	Peaks Found	System	a	b	c	alpha	beta	gamma	Volume	Program	
1	1	11.00000000	30 of 30	Monoclinic	11.36406100	10.80309500	10.33639300	90.00000000	108.74907000	90.00000000	1.201630e+003	TREOR90

Study table document showing results of indexing calculation.

TREOR90 only reports one solution. By contrast, the other indexing methods frequently find more than one possible unit cell and the various solutions are listed in separate lines of the study table document. These are rated according to their Figure of Merit (FOM). Each line contains information about the crystal system, the cell lengths, a, b, c, the cell angles, α , β , γ , and the cell volume.

Compare your results with the following: $a = 11.3620(7) \text{ \AA}$, $b = 10.8162(7) \text{ \AA}$, $c = 10.3344(7) \text{ \AA}$, $\beta = 108.730(6)^\circ$, $V = 1202.8(3) \text{ \AA}^3$, P21, monoclinic - see Wahle et al. ([1997](#)).

The final step in the indexing procedure is to create an empty unit cell using the new lattice parameters.

Click on the first row marker, **1**, in the study table document and click the **Create Cell** button on the Reflex Powder Indexing dialog, close the dialog.

A new 3D Atomistic document containing the empty unit cell is displayed in the Visualizer, called dihydrate1.xsd.

You might like to repeat the indexing procedure with different parameter settings. For example, try changing the Low amplitude cutoff to 1.0 or alter the number of peaks included in the analysis to more than 30.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.


Indexing the powder pattern of an inorganic compound

1. To import the data

First create a new folder to work in.

Right-click on the **Indexing** project and select **New | Folder** from the shortcut menu. Rename the folder **fin31**.

Now import the files containing the powder diffraction data into the fin31 folder.

Select the **fin31** folder. Click the **Import** button  to open the Import Document dialog. Ensure that **Chart Files** is selected from the **Files of type** dropdown list. Open **fin31.3cam**.

2. To remove the background noise

You can use the Pattern Processing tool to remove background noise from an experimental powder pattern.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. Select the **Pattern Preparation** tab and click the **Calculate** button.


The background noise is highlighted in red on the chart document.

Click the **Subtract** button on the **Pattern Preparation** tab.

A new chart document entitled **fin31 (Background Removed) .xcd** is added to the project and the background noise is removed from the powder pattern.

3. To use a Study Table document to add markers

In the first example you added markers directly to the chart document. However, you can instead type peak positions into a single column in a study table document, then copy and paste them into the chart document.

Click on the options arrow associated with the **New** button  on the toolbar and select **Study Table Document** from the dropdown list.

An empty study table document opens in the Visualizer. Now type in the positions of the peaks.

Type the following values in column A: **16.82, 21.84, 22.89, 25.81, 28.08, 29.04, 31.86, 32.20, 33.04, 34.08, 35.58, 39.26, 39.98, 42.16, 43.84, 46.82, 48.22, 49.52**.

These are the values of 2-theta where the peak markers will be placed. Now copy and paste column A into the chart document.

Click and hold on cell **A1**, and move the cursor down to **A18**. All the cells in column A are selected. Select **Edit | Copy** from the menu bar.

Make **fin31 (Background removed).xcd** the active document, right-click and select **Paste Markers** from the shortcut menu.

Markers are added to the chart document. The height of the markers defaults to 50% of the height of the highest peak

4. To index the powder pattern

Before running the indexing calculation, you should make sure that the correct experimental data are selected, as two data sets are available.

Select the **Experimental Data** tab on the Reflex Powder Indexing dialog and double-click on **fin31 (Background removed).xcd**.

Double-clicking ensures that the correct data set is used for indexing and makes the chart document active. Alternatively, you can simply single-click to select the powder pattern. You can now run the Indexing calculation.

On the **Setup** tab check all of the **Crystal systems to test** check boxes. Click the **Index** button.

After a few seconds, the study table document containing a solution is displayed. You can compare this result with the actual crystal structure.

When the job is finished a dialog reports the status as completed.

Click the **OK** button on the Job Completed dialog.

5. To compare the indexing result with the crystal structure

The crystal structure of fin31 is available in Materials Studio XSD format.

Use the Import Document dialog to import **Examples\Reflex\Structures\fin31.xsd**.

A 3D Viewer containing the crystal structure of fin31 is displayed in the Visualizer. You can use the Properties Explorer to compare the values of the cell parameters you calculated earlier with those of the known crystal structure. To access the unit cell parameters from the 3D Atomistic document, change the *Filter* to [Lattice 3D](#).

Select **Lattice 3D** from the **Filter** dropdown list. Scroll down the Properties Explorer to view the cell parameters LengthA, LengthB, and so on.

The unit cell parameters LengthA, LengthB, LengthC, AngleAlpha, AngleBeta and AngleGamma relate to the parameters a, b, c, α , β , and γ in the study table document. The values should be similar.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank Dr. S. Byrn of Purdue University for supplying some of the material for this tutorial.

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Indexing of 4-nitrophenylhexylurethane using X-Cell

Purpose: Illustrates how to use X-Cell to index challenging powder patterns.

Modules: Materials Visualizer, Reflex

Time: 

Prerequisites: [Indexing powder patterns](#)

Background

X-Cell ([Neumann, 2003](#)) is a novel indexing algorithm that has been developed at BIOVIA. It uses an extinction-specific dichotomy procedure to perform an exhaustive search of parameter space, to establish a complete list of all possible indexing solutions. Unlike DICVOL91 ([Boultif and Louër, 1991](#)), X-Cell allows for a certain number of impurity peaks among the experimentally observed reflections. The zero point shift of the diffraction pattern is determined as part of the search procedure. Systematic absences are explicitly taken into account and parameter space is searched in such a way that the number of observed diffraction peaks in the angular range being considered is gradually increased. This approach guarantees that the correct solution is found quickly if a high quality powder diffraction pattern is available. Regardless of whether or not a promising unit cell has already been found, the algorithm continues to search larger and larger portions of parameter space until the search is complete or until it is interrupted by the user. Demanding problems can be solved by running the algorithm for an extended period of time on a fast server. X-Cell has a significantly higher success rate than DICVOL91 ([Boultif and Louër, 1991](#)), TREOR90 ([Werner et al., 1985](#)) and ITO15 ([Visser, 1969](#)) combined.

Introduction

This tutorial shows you how to setup and run an X-Cell job using Materials Studio. It also describes how to analyze the results of the X-Cell run. You will index the powder diffraction pattern of 4-nitrophenylhexylurethane (NPHU). This powder pattern is strongly affected by preferred orientation and attempts to index it with ITO15 ([Visser, 1969](#)), TREOR90 ([Werner et al., 1985](#)) or DICVOL91 ([Boultif and Louër, 1991](#)) have, so far, failed.

This tutorial covers:

- [Getting started](#)
- [To pick diffraction peaks](#)
- [To set up the X-Cell job](#)
- [To run an X-Cell job](#)
- [To analyze the results](#)
- [Pawley refinement](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by creating a new project.

Open the **New Project** dialog and enter **NPHU** as the project name, click the **OK** button.

The new project is created with *NPHU* listed in the Project Explorer. Now import the experimental data you will be studying.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder, choose **Chart Files** from the **Files of type** dropdown list and double-click on **NPHU.xcd**.

2. To pick diffraction peaks

Next use the Reflex module in Materials Studio to pick the diffraction peaks for indexing automatically. The selection of diffraction peaks is a crucial part of the indexing procedure.

At low 2-theta values, peak intensities are high and peak overlap is small. Therefore, the probability of detecting peaks is fairly high and allowed reflections are likely to be selected for indexing. However, at high 2-theta values, peak intensities are low and peak overlap is strong so the detection probability is lower.

The performance of X-Cell depends strongly on the detection ratio - the number of reflections selected for indexing divided by the number of allowed reflections, within a given angular range - with the best performance being obtained if the detection ratio is high.

To obtain a high detection ratio, you should choose a maximum 2-theta value and try to assign peak markers to all of the features below this value that can be identified as diffraction peaks. Although the peak list should be as complete as possible, you should also try to avoid selecting spurious features. In principle, X-Cell can treat a certain number of reflections that do not correspond to the main crystalline phase as impurity peaks. In practice, however, the efficiency of X-Cell strongly decreases with the number of impurity peaks that are considered. Therefore, you should be careful not to select low intensity peaks that may be statistical noise. Furthermore, you may decide not to select weak peaks in the shoulder of stronger peaks as their position is frequently not very well defined. You should never select a couple of seemingly well defined peaks at high angle in addition to the low angle peaks as this will reduce the detection ratio significantly.

As a rule of thumb, you should always try to select at least 20 - 25 reflections. However, if the diffraction peaks are poorly resolved, you can attempt to run X-Cell with fewer peaks. In this tutorial, you will select only 15. If the unit cell to be determined is fairly flat or if the impurity content of the sample is high, it may be necessary to select significantly more than 25 reflections.

To facilitate the automatic peak picking, you should first subtract the background from the powder pattern.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. On the **Pattern Preparation** tab, in the **Background** section, increase the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.


A new chart document, *NPHU (Background Removed) .xcd*, is created, in which the background has been subtracted from the powder pattern. Now smooth the powder pattern. The best choice of the Gaussian width for smoothing depends on the noise level and the peak width and has to be found by trial and error. Begin by estimating the average peak width (Full Width Half Maximum).

Zoom in on the peak at **8.2 °** and determine the peak width.



An order of magnitude estimate will suffice. The peak width should be about 0.2 °.

Select the **Pattern Processing** tab. In the **Smoothing** section, set the **Gaussian width** to **0.1** and click the **Smooth** button. **Close** the Reflex Pattern Processing dialog.

A new chart document, NPHU (Background Removed) (Smoothed).xcd, is created, containing the smoothed powder diffraction pattern. Now select diffraction peaks using the automatic peak picking tool. Because you have already removed the background and smoothed the data you can turn off the automatic background elimination.

Click on the **Reflex** arrow  on the **Modules** toolbar and choose **Powder Indexing** from the dropdown list to open the Reflex Powder Indexing dialog.

On the **Peaks** tab set the **Max. number of peaks** to **15**, the **Low amplitude cutoff** to **2.5** and the **Start 2-Theta** to **5**. Uncheck the **Eliminate background during search** checkbox and click the **Search** button.

Use the **Zoom**  and **Translate**  tools to examine the powder diffraction pattern closely.

You should always examine the results of the automatic peak picking carefully. In this particular case, all of the peak markers are well positioned and no manual changes are required. The two intense peaks at about 38.5 and 44.5° can be attributed to scattering from the aluminum sample holder.

3. To set up the X-Cell job

Now you must specify the settings for the X-Cell search.

Begin by selecting the X-Cell algorithm.

On the **Setup** tab of the Reflex Powder Indexing dialog, choose **X-Cell** from the **Program** dropdown list.

Now specify the dimensionality of the X-Cell search. X-Cell can search for 1D (rows), 2D (zones) and 3D unit cells. In this case, you should use a 3D search.

Click the **More...** button on the **Setup** tab to open the X-Cell Options dialog. Ensure that **3D** is selected from the **Dimensionality of search** dropdown list on the **General** tab.

X-Cell is able to handle a certain number of impurity peaks among the experimentally observed peaks, through an impurity level setting.

In this case, you should use an impurity level of 1.

Set the **Impurity level** to **1** on the **General** tab of the X-Cell Options dialog.

If an impurity level greater than 0 is chosen, you can select an impurity mode which controls how the search will proceed.

Include lower levels has significant advantages and is selected by default. It ensures that solutions with a high number of calculated peaks and a low number of impurity peaks can be found, even if a high impurity level is specified.

Select **Include lower levels** from the **Impurity mode** dropdown list.

The number of calculated peaks considered is gradually increased until a maximum value is reached. This maximum value is defined by specifying the detection level.

The detection level can have any value between 0.0 and 1.0. Values are expressed as a percentage.

The default value for the detection level is 25%, which means that the number of calculated peaks can be four times higher than the number of observed peaks. In some cases, it may be necessary to set the detection level to lower values. However, in this case a detection level of 33% is more appropriate.

Change the **Detection level** to **33%**.

X-Cell also allows you to specify the expected zero point correction and the zero point search range.

Change the **Zero point search range** from 0.01 to **0.1** °. Leave the **Zero point correction** at the default value of **0.0** °.

Finally, you should specify the peak width you determined in the previous section.

Change the **Average peak width** from 0.15 to **0.2**. Click the **OK** button to close the X-Cell Options dialog.

If a 3D search is performed, you can specify which crystal systems should be searched. By default, the search is carried out in only the Cubic, Hexagonal and Tetragonal crystal systems. You should expand the search to include all crystal systems apart from Triclinic.

Ensure that all of the boxes apart from **Triclinic** are checked, in the **Crystal systems to test** section on the **Setup** tab of the Reflex Powder Indexing dialog.

4. To run an X-Cell job

X-Cell in Powder Indexing uses the client-server architecture implemented in Materials Studio. So, if your PC is connected to other computers on a network, it is possible to set up gateways to these computers and run the calculation remotely, thus avoiding using the resources of your own PC. However, your own PC is probably set up as a server and the gateway "My Computer" will be used by default.

Select the **Job Control** tab on the Reflex Powder Indexing dialog. Choose a suitable server from the **Gateway location** dropdown list. Click the **More...** button to open the Job Control Options dialog. Ensure that **Update study table** and **Update textual results** are checked and close the dialog.

Click the **Index** button on the Reflex Powder Indexing dialog to launch the X-Cell job on the selected gateway.

The Job Explorer appears, which informs you about the progress of the calculation. After some time, two new windows appear; a text document, `Status.txt`, and a study table document, `NPHU (Background Removed) (Smoothed).std`. These documents are updated regularly, as the job progresses.

The study table document consists of two sheets. The first sheet, labeled Best, contains all the solutions obtained by indexing which meet the selection criteria. A complete list of solutions is presented in the second sheet, labeled All.

The text document informs you about:

- The impurity level at which the search is currently being performed and the range of calculated peaks that is currently being considered.
- The crystal system in which the search is currently being performed. For a given impurity level and peak number range, the crystal systems are searched in the following order: hexagonal/trigonal, cubic, tetragonal, orthorhombic, monoclinic, triclinic.
- The number of possible indexing solutions found so far above (best) and below (total) a certain threshold. Solutions above the threshold are likely candidates for the correct unit cell.
- For each impurity level, you are informed about the maximum number of calculated peaks considered so far, the value of two additional control parameters called status and factor and the number of search steps.

You should wait until the X-Cell job finishes before proceeding. This may take some time, depending on the specification of the server machine on which you run the job.

5. To analyze the results

All of the solutions found by X-Cell are listed in the study table document, **NPHU (Background Removed) (Smoothed).std**. They are sorted by Relative Figure of Merit (Rel. FOM). The best solutions appear at the top of this list.

Make **NPHU (Background Removed) (Smoothed).std** the active document and select the **All** tab. Inspect the top ranked solutions.

The top ranked solution is in extinction class P21 and has a cell volume of about 692 \AA^3 , the next unique solution is a C2 cell, with a volume of around 1382 \AA^3 .

In order to identify which is the correct unit cell it is necessary to carry out Pawley refinement for the two best solutions. To do this, you must first create 3D Atomistic documents containing the different unit cells.

Select the row in the study table document, **NPHU (Background Removed) (Smoothed).std**, that contains the top ranked, P21 cell. Click the **Create Cell** button on the Reflex Powder Indexing dialog.

A new 3D Atomistic document, **NPHU (Background Removed) (Smoothed)1.xsd**, is created which contains the empty P21 unit cell.

Right-click on **NPHU (Background Removed) (Smoothed)1.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Rename the document **P21 Cell**. The **.xsd** extension is added automatically.

Now repeat the same procedure for the highest ranked C2 solution with the cell volume of approximately 1382 \AA^3 .

Select the row in the study table document, **NPHU (Background Removed) (Smoothed).std**, that contains the highest ranked solution with C2 extinction class. Click the **Create Cell** button and close the Reflex Powder Indexing dialog.

Right-click on the new file, **NPHU (Background Removed) (Smoothed)5.xsd**, in the Project Explorer and select **Rename** from the shortcut menu. Rename the document **C2 Cell**. The **.xsd** extension is added automatically.

6. Pawley refinement

Note: By default, Pawley refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run synchronously** from the **Job Control** tab.

Pawley refinement of the trial unit cells against the experimental data will indicate which is the correct cell. This is performed using the Powder Refinement tool in Reflex.

Open the **Reflex Powder Refinement** dialog.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

Changing the *Number of cycles* automatically changes the *Convergence quality* setting from *Medium* to *Customized*.

On the **Setup** tab, set the **2-Theta** range **Min** to **5 °** and **Max** to **30 °**.

On the **Exp. Data** tab, select **pattern 1** of the document **NPHU.xcd**.

On the **Pattern** tab, check the checkboxes for the refinement of **U**, **V**, **W** and **NA**. For the **Zero point**, enter the value from the X-Cell study table document, but do not refine this parameter. In the **Asymmetry** section choose **Finger-Cox-Jephcoat** from the **Correction** dropdown list. Change the **2-Theta limit** to **20**, and check the checkboxes for the refinement of the parameters **H/L** and **S/L**.

On the **Display** tab, check the **Display simulation/experiment difference** plot checkbox.

Ensure that **P21 Cell.xsd** is the active document and click the **Refine** button.

Note: If you run this refinement job on a remote computer the refined unit cell will be in the P21 Cell Reflex Pawley\P21 Cell.xsd file.

Now add the cell parameters and the zero point shift to the refinement.

On the **Setup** tab, click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **10** and click the **OK** button.

On the **Pattern** tab, check the checkbox for the refinement of **Zero point** shift.

Ensure that **P21 Cell.xsd** is the active document. On the **Lattice** tab, check the checkboxes for the refinement of all cell parameters. Click the **Refine** button.

After 10 cycles of refinement, the R_{wp} value should be about 15%.

Now repeat the Pawley refinement for the next best unique solution.

Click the **Reset** button on the Reflex Powder Refinement dialog.

Choose the **Setup** tab and click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

On the **Setup** tab, set the **2-Theta** range **Min** to **5 °** and **Max** to **30 °**.

On the **Exp. Data** tab, select **pattern 1** of the document **NPHU.xcd**.

On the **Pattern** tab, check the checkboxes for the refinement of **U**, **V**, **W** and **NA**. For the **Zero point**, enter the value from the X-Cell study table document, but do not refine this parameter. In the **Asymmetry** section choose **Finger-Cox-Jephcoat** from the **Correction** dropdown list. Change the **2-Theta limit** to **20**, and check the checkboxes for the refinement of the parameters **H/L** and **S/L**. Check the **Background coefficients** checkbox.

On the **Display** tab, check the checkbox for the **Display simulation/experiment difference** plot and choose **New** from the **Chart view** dropdown list.

Ensure that **C2 Cell.xsd** is the active document and click the **Refine** button.

Note: If you run this refinement job on a remote computer the refined unit cell will be in the C2 Cell Reflex Pawley\C2 Cell.xsd file.

Once again, perform 10 additional cycles of refinement, including the cell parameters and the zero point shift.

On the **Setup** tab, click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **10** and click the **OK** button.

On the **Pattern** tab, check the checkbox for the refinement of **Zero point** shift.

Ensure that **C2 Cell.xsd** is the active document. On the **Lattice** tab, check the checkboxes for the refinement of all cell parameters. Click the **Refine** button and close the dialog.

After 10 cycles, the R_{wp} for the C2 cell should be around 18%.

The lower residual factor obtained for the P21 cell suggests that it is correct. A single crystal diffraction study of NPHU ([Yakimanski et al., 1997](#)) confirms this. The P21 cell obtained by X-Cell is indeed the correct solution to the indexing problem.

As an exercise, you may like to try to index this diffraction pattern using ITO, TREOR or DICVOL.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank Dr. Ute Kolb for providing the experimental powder diffraction pattern of NPHU.

References

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- Boultif, A. and Louër, D., "Indexing of powder diffraction patterns for low-symmetry lattices by the successive dichotomy method", *J. Appl. Cryst.*, **24**, 987-993, (1991).
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Indexing a flat unit cell with X-Cell

Purpose: Illustrates how to use X-Cell to index challenging powder patterns for flat unit cells.

Modules: Materials Visualizer, Reflex, X-Cell

Time: 🕒 🕒

Prerequisites: [Indexing of 4-nitrophenylhexylurethane using X-Cell](#)

Background

Flat unit cells in real space have two short axes and one long axis in reciprocal space. Therefore, the first few diffraction peaks at low 2-theta values belong to a single zone in reciprocal space and define only the two short reciprocal axes and the angle between them. Flat unit cells are difficult to index for two main reasons:

- The number of low angle reflections belonging to a single zone may be quite high. As a result, it is possible that all of the reflections selected for indexing may belong to the same zone. This means that unit cell is not uniquely determined.
- Even if you are aware that a large number of low angle peaks belong to the same zone, it may be difficult to select enough peaks that define the remaining unit cell parameters because of peak overlap and the decrease in the scattering intensity at higher 2-theta values.

To facilitate the indexing of flat unit cells, X-Cell makes it possible to divide the task into two steps. Using only a small number of reflections at low 2-theta values, you first search for zones. If a zone is found that fits the experimental data, accurate 2D cell parameters and the zero point shift of the diffraction pattern can be determined by Pawley refinement. Comparing the reflections belonging to the zone with the experimental powder diffraction pattern, it is possible to identify the reflections that characterize the remaining cell parameters. In the second step, the peak positions, the lattice constants of the zone and the zero-point shift are used as the input to the 3D unit cell determination.

A similar approach can be used to index long unit cells.

Introduction

This tutorial will show you how to index the powder diffraction pattern of form II of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide (DFIYA). The powder diffraction pattern of DFIYA is particularly difficult to index, as it is strongly affected by preferred orientation. The intensities of the reflections belonging to the dominant zone are enhanced, while the intensities of reflections that define the remaining parameters are reduced.

This tutorial covers:

- [Getting started](#)
- [To pick diffraction peaks for a zone search](#)
- [To set up the X-Cell job for a zone search](#)
- [To run X-Cell for a zone search and analyze the results](#)
- [Pawley refinement of the dominant zone](#)
- [To pick diffraction peaks for a unit cell search](#)
- [To set up the X-Cell job for a unit cell search](#)
- [To run X-Cell and analyze the results of a unit cell search](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DFIYA** as the project name, click the **OK** button.

The new project is created with *DFIYA* listed in the Project Explorer. Now import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click on **DFIYA_II.xcd**.

2. To pick diffraction peaks for a zone search


Next pick the diffraction peaks to be used for the determination of the dominant zone. If the scattering at low 2-theta values is dominated by a single zone, about 10 reflections should be sufficient to find it.

To facilitate automatic peak picking, you should first subtract the background from the powder diffraction data.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. On the **Pattern Preparation** tab, in the **Background** section, increase the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document, *DFIYA_II (Background Removed).xcd*, is created, in which the background has been subtracted from the powder pattern. Now smooth the powder pattern.


Begin by estimating the average peak width.

Use the **Zoom** tool  to zoom in on the peak at **6.2 °** and determine the width of the peak at half of its maximum height (FWHM).

The peak width should be about 0.15 °.

Select the **Pattern Processing** tab. In the **Smoothing** section, set the **Gaussian width** to **0.05** and click the **Smooth** button. **Close** the Reflex Pattern Processing dialog.

A new chart document, *DFIYA_II (Background Removed) (Smoothed).xcd*, is created, containing the smoothed powder diffraction pattern. Now select diffraction peaks using the automatic peak picking tool.

Click the **Reflex** button  on the **Modules** toolbar and choose **Powder Indexing** from the dropdown list to open the Reflex Powder Indexing dialog.

Select the **Peaks** tab. Set the **Max. number of peaks** to **10**, the **Low amplitude cutoff** to **3.0** and the **Start 2-theta** to **5**. Click the **Search** button.

Use the **Zoom**  and **Translate**  tools on the **Chart Viewer** toolbar to examine the powder diffraction pattern closely.

You should always examine the results of the automatic peak picking carefully. In this particular case, all of the peak markers are well positioned and no manual changes are required.

3. To set up the X-Cell job for a zone search

Now specify the settings for the X-Cell search.

Select the **Setup** tab on the Reflex Powder Indexing dialog. Uncheck the λ_2 checkbox to ignore the contribution of the second wavelength. Choose **X-Cell** from the **Program** dropdown list.

Next specify the dimensionality of the X-Cell search.

Click the **More...** button on the **Setup** tab to open the X-Cell Options dialog. Select **2D** from the **Dimensionality of search** dropdown list on the **General** tab.

In case one of the selected reflections is an impurity peak (for example one belonging to another zone), you should set the impurity tolerance level to 1, and choose to search the impurity levels 0 and 1 in parallel. An *Impurity level* of 1 including lower levels is sufficient for this tutorial.

At low 2-theta values, the probability of observing symmetry allowed reflections is fairly high. You can therefore set the detection level to 50%. This means that X-Cell will consider all zones for which the number of calculated peaks in the selected 2-theta range is less than twice the number of experimental peaks.

Change the **Detection level** to **50%**.

X-Cell also allows you to specify the expected zero point correction and the zero point search range.

Change the **Zero point search range** from 0.01 to **0.1** °. Leave the **Zero point correction** at the default value of **0.0** °.

Finally, specify the peak width you determined in the previous section.

Ensure that the **Average peak width** is set to **0.15**. Click the **OK** button.

4. To run X-Cell for a zone search and analyze the results

Select the **Job Control** tab on the Reflex Powder Indexing dialog. Choose a suitable server from the **Gateway location** dropdown list.

Click the **Index** button on the Reflex Powder Indexing dialog, to launch the X-Cell job on the selected gateway.

You should wait until the X-Cell job finishes before proceeding. All of the solutions found by X-Cell are listed in the study table document, **DFIYA_II (Background Removed) (Smoothed).std**.

For rows and zones, a relative figure of merit cannot be calculated. So, in all output files, the solutions are ranked according to the figure of merit, and only the solution with the best figure of merit is given if the same zone is found in more than one 2D space group. The cell parameters *a*, *b* and γ specify the 2D unit cell in real space that is equivalent to the dominant zone in reciprocal space.

One of the two solutions in the study table document has a significantly higher figure of merit. In the next section you will verify that this solution corresponds to the dominant zone, using Pawley refinement. For both the solutions, the study table document indicates that there is one impurity peak. This may not mean that there really is a low angle peak that cannot be attributed to the dominant zone. In fact, the impurity peak may correspond to one of the calculated peaks, but if the deviation between the calculated and the observed peak position is fairly large, treating the observed peak as an impurity peak may significantly increase the figure of merit.

5. Pawley refinement of the dominant zone

The refinement carried out in this section is a multi-stage process. First, you limit the refinement to the angular range covered by the peaks used for indexing, to obtain an appropriate first guess of all parameters involved.

Then, you repeat the refinement for the full angular range, adjusting only the background parameters and the peak intensities. By visual comparison of the calculated and the experimental patterns, you can then determine the 2-theta value up to which all of the diffraction peaks belong to the dominant zone.

Next, you carry out another Pawley refinement of all parameters over the angular range identified in the previous step. The zero point shift and the 2D cell parameters obtained at this stage will be used as input parameters for 3D indexing in a later section.

Finally, you carry out a second Pawley refinement over the full angular range, with all parameters held fixed except for the background parameters and the peak intensities. The difference plot of the calculated and the experimental patterns obtained in this step is used for peak picking in the next section.

First you must build a model of the 2D unit cell, on which to perform the Pawley refinement.

Select the row in the study table document, **DFIYA_II (Background Removed) (Smoothed).std**, which contains the top ranked **p1** unit cell. Click the **Create Cell** button and close the Reflex Powder Indexing dialog.

A new 3D Atomistic document, **DFIYA_II (Background Removed) (Smoothed)1.xsd**, is created which contains the empty P1 unit cell.

Right-click on **DFIYA_II (Background Removed) (Smoothed)1.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Rename the document **cell_2D**. The **.xsd** extension is added automatically.

Now carry out the first Pawley refinement.

On the **Modules** toolbar, click the **Reflex** button  and select **Powder Refinement** to open the Reflex Powder Refinement dialog.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

The *Convergence quality* on the *Setup* tab will change to [Customized](#).

On the **Setup** tab, set the **2-Theta** range to **5-18 °**.

On the **Exp. Data** tab, select the original experimental pattern, **DFIYA_II.xcd pattern 1**, which has not had the background subtracted or been smoothed.

On the **Pattern** tab, check the checkboxes for the refinement of **U, V, W** and **NA**. For the **Zero point**, enter the value given in the **Zero** column of the study table document, **DFIYA_II (Background Removed) (Smoothed).std** for the top ranked 2D cell and check the checkbox for its refinement.

On the **Display** tab, check the checkbox for **Display simulation/experiment difference** in the **General** section.

Make **cell_2D.xsd** the active document. On the **Lattice** tab, check the checkboxes for the refinement of the cell parameters **a, b** and **gamma**.

Click the **Refine** button.

Examine the comparison of the calculated and the experimental powder diffraction patterns. All peaks within the chosen range can be attributed to the dominant zone. Now you will find out where the reflections that do not belong to the dominant zone begin to appear.

Ensure that **cell_2D.xsd** is still active. On the **Setup** tab, change the **2-Theta range** to **5-50°**.

On the **Pattern** tab, uncheck the checkboxes for the refinement of **U, V, W, NA**, and the **Zero point**.

On the **Lattice** tab, uncheck the checkboxes for the refinement of the cell parameters **a, b**, and **gamma**.

Click the **Refine** button.

Examine the comparison of the calculated and the experimental powder diffraction patterns. All peaks up to 19.5 ° belong to the dominant zone. The first feature that cannot be attributed to the dominant zone can be found at about 19.75 °.

Next repeat the Pawley refinement of all parameters over a slightly wider angular range.

Make **cell_2D.xsd** the active document. On the **Setup** tab, change the **2-Theta range** to **5-19.5 °**.

On the **Pattern** tab, check the checkboxes for the refinement of **U, V, W, NA** and the **Zero point**.

On the **Lattice** tab, check the checkboxes for the refinement of the cell parameters **a, b** and **gamma**.

Click the **Refine** button.

Finally, note down the zero point shift and the cell parameters generated by the latest Pawley refinement, for later use and generate a comparison of the calculated and the experimental patterns over the full angular range.

Make **cell_2D.xsd** the active document. On the **Setup** tab, change the **2-Theta range** to **5-50 °**.

On the **Pattern** tab, uncheck the checkboxes for the refinement of **U, V, W, NA** and the **Zero point**. Note down the value of **Zero point** for later use.

On the **Lattice** tab, uncheck the refinement of the cell parameters **a, b** and **gamma**. Note down the values of these parameters for later use.

Click the **Refine** button and close the dialog.

Examine the comparison of the calculated and the experimental powder diffraction patterns.

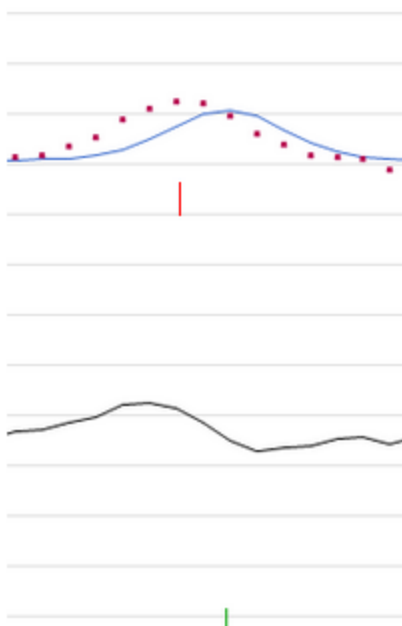
6. To pick diffraction peaks for a unit cell search


In this section, you pick the diffraction peaks used for indexing. The peak list has to contain reflections belonging to the dominant zone and reflections that define the remaining cell parameters. Within the angular range chosen for peak picking, you should try to identify as many reflections as possible.


The reflections defining the remaining cell parameters are all fairly weak and you should not rely on the automatic peak picking tool to find these. Instead, you should pick the peaks manually.

Since the dominant zone has already been refined, you can use the tick marks from the refinement to accurately position the peak markers for reflections that belong to it.

The reflections that define the remaining cell parameters should be picked very carefully. Many of these reflections are in the vicinity of reflections from the dominant zone (see below). In the Pawley refinement carried out in the last section, the intensity of reflections belonging to the dominant zone is overestimated in such cases. For peak positioning, you should use the experimental data rather than the difference plot.



Ensure that **cell_2D.xcd** is the active document. Use the **Zoom** tool  to zoom in on the patterns for peak selection.

Use the **Chart Viewer Marker**  to select all the diffraction peaks in the range from **5 °** to **29.5 °**. Use the tick marks from the previous refinements to help guide you to accurately position the peak markers for reflections that belong to the dominant zone. In this range, you should also be able to identify **10 reflections** that do not belong to the dominant zone.

These reflections can be found at the following 2-theta positions: 19.767112, 20.196377, 23.219712, 24.253705, 25.311651, 27.011796, 27.442203, 28.040301, 28.607701, and 29.264913.

If you are uncertain about your selection, you should inspect the sample file, **DFIYA_II_3D_peak_selection.xcd**, which is provided for comparison.

Now transfer the peak list from **cell_2D.xcd** to the original experimental pattern, before setting up the X-Cell unit cell search.

Make **cell_2D.xcd** your active document. Press **CTRL + A** to select all the peaks. Right-click on the chart and choose **Copy Markers** from the shortcut menu to copy them to the clipboard.

In Project Explorer, double-click on **DFIYA_II.xcd** to open it. Right-click on the document, and choose **Paste Markers** from the shortcut menu.

7. To set up the X-Cell job for a unit cell search

Now you must specify the settings for the 3D X-Cell search, in the same way as you did for the 2D search.

Select **File | Save Project** from the menu bar and close all of the windows except **DFIYA_II.xcd**.

Open the **Reflex Powder Indexing** dialog. On the **Setup** tab choose **X-Cell** from the **Program** dropdown list.

Now specify the dimensionality of the X-Cell search. This time you should use a 3D search.

Click the **More...** button to open the X-Cell Options dialog. Select **3D** from the **Dimensionality of search** dropdown list on the **General** tab.

In case one of the selected reflections is an impurity peak, you should set the impurity tolerance level to 1, and choose to search the impurity levels 0 and 1 in parallel.

This time, you should use a detection level of 33%.

Change the **Detection level** to **33%**.

The zero point shift is known from the 2D Pawley refinement.

Change the **Zero point correction** to the value obtained from the Pawley refinement of the 2D zone. Change the **Zero point search range** to **0.0 °**.

You should also keep the cell parameters of the dominant zone constant.

Select the **Cell Parameters** tab of the X-Cell Options dialog. Choose **a, b, gamma** from the **Known parameters** dropdown list.

Enter the cell parameters obtained from the previous Pawley refinement. Leave the **Error** at the default value of **0.0**. Click the **OK** button.

Ensure that all of the boxes are checked in the **Crystal systems to test** section of the **Setup** tab.

8. To run X-Cell and analyze the results of a unit cell search

Select the **Job Control** tab on the Reflex Powder Indexing dialog. Choose a suitable server from the **Gateway location** dropdown list.

Click the **Index** button to launch the X-Cell job on the selected gateway.

The indexing calculation is now running. Constant updates about the progress of the calculation are provided. You should wait until the X-Cell job finishes before proceeding.

In the Project Explorer, double-click on the study table document **DFIYA_II.std** in the folder of **DFIYA_II Reflex X-Cell**.

This study table document should contain several possible indexing solutions. As an exercise, you can try to identify the correct unit cell by Pawley refinement. The crystal structure of DFIYA_II has been determined by single crystal X-ray diffraction and the correct unit cell has a cell volume of about 963 \AA^3 with $a \sim 15.1 \text{ \AA}$, $b \sim 13.9 \text{ \AA}$, $c \sim 5.0 \text{ \AA}$, $\alpha \sim 86.9^\circ$, $\beta \sim 97.7^\circ$ and $\gamma \sim 111.0^\circ$.

The list of solutions will depend on which peaks were selected. If you chose the peak list provided in the file **DFIYA_II_3D_peak_selection.xcd** the top solution will be the correct one. If you used a different input you should be able to identify the correct unit cell by Pawley refinement.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank P.G. Varlashkin, M. Sacchetti, and J. Zhu from GlaxoSmithKline for supplying the experimental data.

Rietveld refinement of inorganics

Purpose: Introduces the Powder Refinement tool and applies it to refine a trial structure against its powder diffraction pattern.

Modules: Materials Visualizer, Reflex

Time: 

Prerequisites: [Working with powder diffraction patterns](#)

Introduction

This tutorial shows how the Powder Refinement tool can be used to refine a trial crystal structure. There are two different types of refinement implemented in Materials Studio. You will use Rietveld refinement, which iteratively improves an approximate (trial) structure to maximize the agreement between simulated and experimental diffraction patterns.

In this tutorial, you will use the experimental X-ray diffraction data provided to refine a suggested trial structure for the mineral akermanite.

This tutorial covers:

- [Getting started](#)
- [To calculate the powder diffraction pattern for akermanite](#)
- [To set the Rietveld refinement](#)
- [To refine the structure](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.


1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **akermanite** as the project name, click the **OK** button.

The new project is created with *akermanite* listed in the Project Explorer. Now you will import the input file you will be studying.

Now import the akermanite structure.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Structures** folder and double-click on **ak100.xsd**.

Before you calculate the diffraction pattern, you should also load the experimental powder pattern.

Open the **Import Document** dialog and choose **Chart Files** from the **Files of type**. Navigate to the **Examples\Reflex\Experimental Data** folder, locate and load the file **ak100.3cam**.

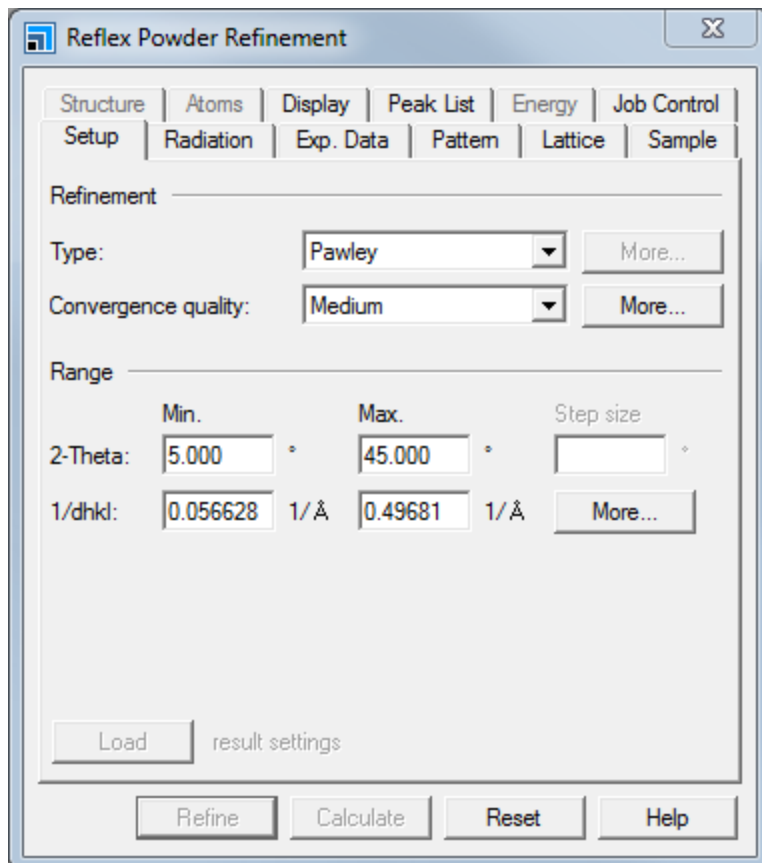
2. To calculate the powder diffraction pattern for akermanite

The next step is to calculate the powder diffraction pattern and display it on the same graph as the experimental data.

Note: It is also possible to begin refinement at this stage, but for the purposes of the tutorial, you will make a comparison between the simulated and experimental data, to determine the starting value of R_{wp} .

Click the **Reflex** arrow  on the **Modules** toolbar and select **Powder Refinement**.

This opens the Reflex Powder Refinement dialog is displayed.



Reflex Powder Refinement dialog, Setup tab

Now change some of the default variables.

Change the **Min. 2-Theta** value from 5.00 to **10.00** and the **Max. 2-Theta** value from 45.00 to **90.00**.

Change the refinement **Type** from Pawley to **Rietveld**.

Next you are going to change the graphical display settings.

Select the **Display** tab.

As the chart will already contain a lot of information, you should remove the observed markers that normally appear with the calculated pattern.

Uncheck the **Show observed reflection markers** checkbox.

Now calculate the powder pattern.

Select the **Exp. Data** tab and choose **ak100.xcd** to indicate that this data should be used for the calculation.

Make sure that **ak100.xsd** is the active document and click the **Calculate** button.

A chart document is created displaying the simulated and experimental powder patterns for akermanite. You should see that the *Structure* and *Atoms* tabs become active. This is because, unlike the Pawley method, the Rietveld method allows you to refine the structure and atom parameters.

Note: The step you have just performed is not a refinement calculation but merely the first step in the procedure. It is comparable to performing a single point energy calculation, as opposed to an energy minimization.

You can compare the patterns in more detail by zooming in using the selection rectangle and translating the pattern.

Hold down the **R** key and left-click on the chart. Drag the mouse to draw a bounding box around the area you wish to magnify. Release the mouse button.

Examine the fit in detail. Although the calculated pattern clearly matches the experimental one, there is an offset between the two. The Rietveld R_{wp} and R-factors are displayed at the top of the chart.

An R-factor can be considered to be a figure of merit for the quality of the structure.

$$R = 100 \frac{\sum_{i=1}^n |I_{obs}^i - I_{calc}^i|}{\sum_{i=1}^n |I_{obs}^i|}$$

Where, I_{obs}^i is the observed (experimental) intensity; I_{calc}^i is the calculated intensity with all the refined parameters; and n is the number of data points in the range.

The R_{wp} -factor is much the same except that a weighting, w_i , is applied to give more importance to the fit at higher angles.

$$R_{wp} = 100 \frac{\sum_{i=1}^n w_i (I_{obs}^i - I_{calc}^i)^2}{\sum_{i=1}^n w_i (I_{obs}^i)^2}$$

3. To set up the Rietveld refinement

Now you are going to set up the Rietveld calculation ready for refinement. The first step is to change the 2-theta range to 10 - 50.

Note: Certain parts of the Reflex module are linked, so for example, if you change the 2-theta range in the Powder Diffraction dialog, it changes in the Powder Refinement dialog. The radiation type used is also set globally.

On the **Reflex Powder Refinement** dialog select the **Setup** tab, change the **Max. 2-Theta** from 90 to **50**.

Now check that the radiation type is set correctly.

Select the **Radiation** tab.

Confirm that the default values of λ_1 and λ_2 for a copper source, of 1.540562 and 1.54439 respectively, are being used.

4. To refine the structure

Next you must set up the Rietveld refinement by fitting a background function and modifying the unit cell dimensions. The scale factor is adjusted automatically by Reflex.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **2** and click the **OK** button.

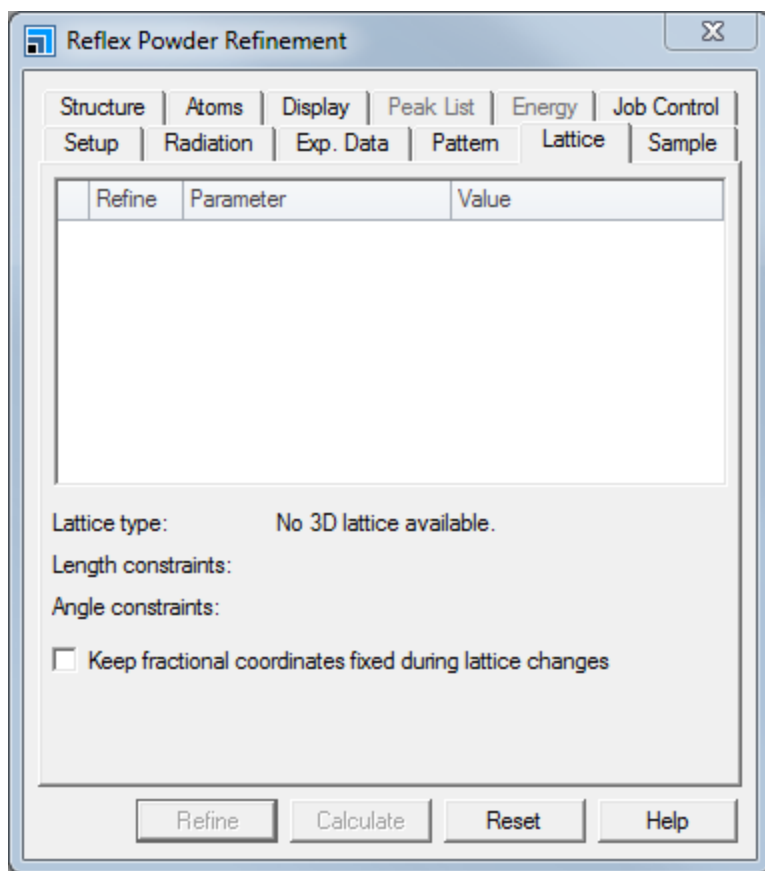
Now set the background settings.

In Rietveld refinement, the X-ray or Neutron background is refined as a polynomial of whatever order you choose. The default is a polynomial with 20 coefficients and that is sufficient for most calculations. Scroll down the grid on the *Pattern* tab and you will see that the refine checkbox is automatically checked on for the background coefficients.

Note: In this case, you are not going to refine the zero point. Although an error in zero point does lead to a systematic peak shift, such as you see in this example, the peak shift may also be due to inaccurate cell dimensions. If you ever do choose to refine the zero point, then the refinement should always be carried out after cell dimension refinement.

You will however refine the lattice parameters.

Choose the **Lattice** tab and make **ak100.xsd** the active document.



Reflex Powder Refinement dialog, Lattice tab

Note: If no information is displayed in this tab, you should ensure that the structure you are refining is active.

Now choose which cell parameters you wish to refine.

Check the **a** and **c** checkboxes in the **Refine** column.

Note: When you select the *a* parameter, the *b* parameter is automatically selected and you cannot select the α , β , and γ angles. This is because of the tetragonal symmetry of the structure.

Before you continue, you should ensure that the fractional coordinates are kept fixed during the calculation.

Check the **Keep fractional coordinates fixed during lattice changes** checkbox.

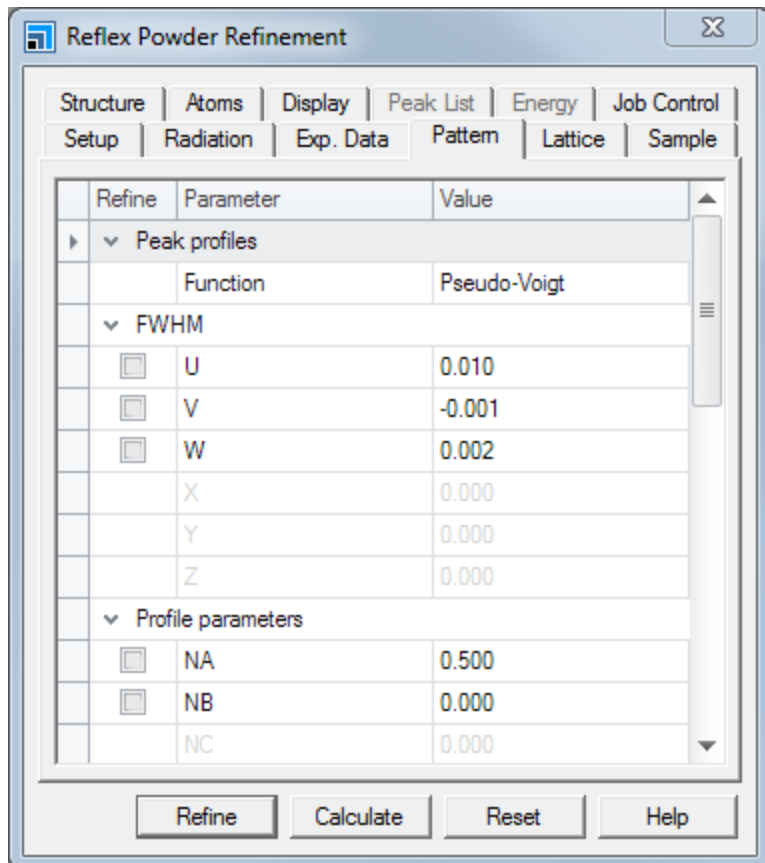
Now you can set up the refinement of the peak profiles. Rietveld refinement offers a choice of nine profile types. The default is Pseudo-Voigt. A Pseudo-Voigt (*pV*) peak is a mixture of the Gaussian (*G*) and Lorentzian (*L*) peak forms:

$$pV = \eta L + (1 - \eta)G$$

$$\eta = A + B(2\theta)$$

Where A and B are refinable "mixing" parameters.

Select the **Pattern** tab.



Reflex Powder Refinement dialog, Pattern tab

Check the **U**, **V**, and **W** options in the **FWHM** section. Change the value of **W** to **0.2** and the values of both **U** and **V** to **0.00**. In the **Profile parameters** section check the **NA** and **NB** mixing parameters.

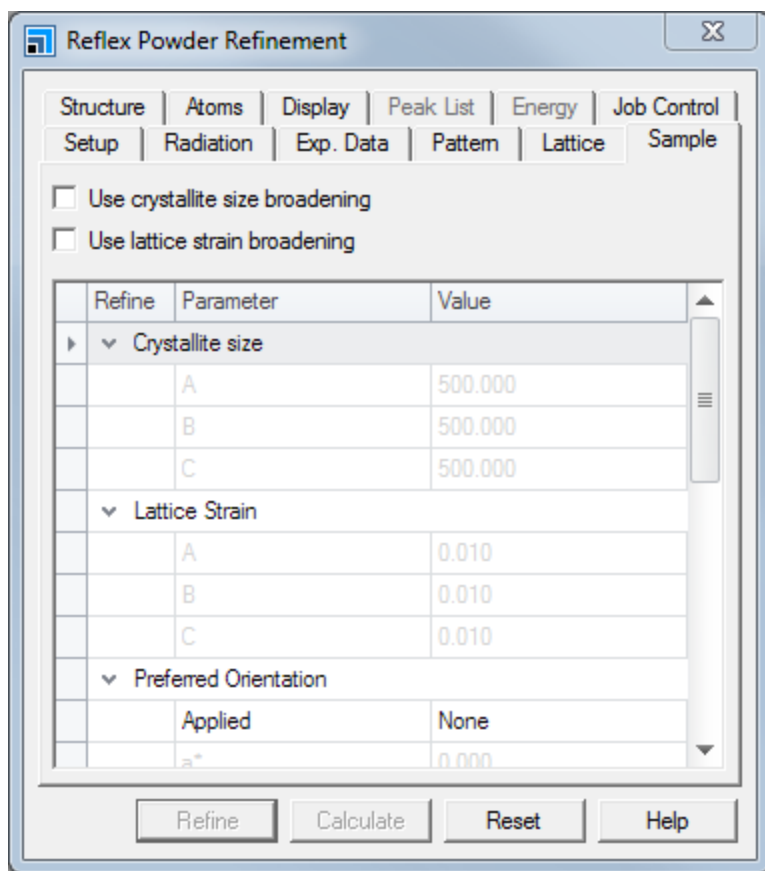
The *FWHM* parameters define how the profiles vary with diffraction angle, and the mixing parameters define the relative Lorentzian/Gaussian character of the profiles. If the initial lattice parameters are a long way from the true values, you get no overlap between the experimental and the observed values. This means that the refinement is likely to fail. Changing the values of *U* and *V* to 0.00, you increase the width of the peaks being refined and so you have a better chance of performing the refinement correctly.

Now you are ready to perform the refinement.

Click the **Refine** button on the Reflex Powder Refinement dialog.

The R_{wp} value should refine to around 10% and R_p should refine to around 7%. These are very low and indicate that the structure is almost certainly the correct one.

The final step is to refine the preferred orientation parameter. This is located on the *Sample* tab.



Reflex Powder Refinement dialog, Sample tab

In the **Preferred orientation** section choose **March-Dollase** from the **Applied** dropdown list. Check the **R0** checkbox.

Refining the orientation parameter will account for some of the texture in the sample, which, when present, can grossly alter the relative intensities of peaks. The direction of the texture may be chosen using the *Direction* boxes but the default of (0 0 1) is fine in this case.

Ensure that **ak100.xsd** is the active document. Click the **Refine** button.

This time there is a slight improvement in the fit quality. The R_{wp} value should decrease to around 8%.

Note: By default, Rietveld refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run synchronously** on the **Job Control** tab.

The low R-factor indicates that this is probably the correct crystal structure of akermanite. You can examine the chart document to see how well the simulated pattern fits to the experimental one.

Use the **Zoom** and **Translation** tools to inspect the chart.

Now that you have performed a refinement of the structure, try some different refinement strategies. You should repeat the calculation but try refining after each change you make. Why does this give a higher R-factor than the one observed if you refine all in one go?

This is because if you refine one variable at a time, you can get trapped in a local minimum. When performing these calculations, you should generally refine all the variables in one go. If this does not converge as you thought it would, you can repeat the steps individually but generally this will not give you a better result.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Rietveld refinement with energetic considerations

Purpose: Illustrates how the incorporation of energy information into an all-atom Rietveld refinement process allows for structure solutions being both chemically viable and in close agreement with the experimental diffraction pattern.

Modules: Materials Visualizer, Reflex, COMPASS

Time: 🕒 🕒

Prerequisites: [Rietveld refinement of inorganics](#)

Background

Occasionally, the available powder diffraction data do not contain enough information for a successful Rietveld refinement. For example, in systems with a large number of degrees of freedom such as all-atom refinements and/or refinements using low quality powder data. In these instances, Rietveld refinements will typically lead to chemically unviable structures because the information content of the powder pattern is too low to accurately determine all the degrees of freedom.

To overcome this problem, Reflex allows you to incorporate an accurate description of potential energy in conjunction with the R_{wp} in the Rietveld refinement process, optimizing a combined figure of merit. The aim is to find solutions that optimally meet two different and possibly conflicting objectives:

- The simulated pattern has to match the experimental diffraction data.
- The potential energy of the structure has to be close to the minimum.

A priori elucidation of the energy weight factor determining the relative importance of the energy contribution might not be intuitive; in such cases a Pareto optimization (*a posteriori* preference calculation) can be used to obtain an appropriate value.

Introduction

In this tutorial, the crystal structure of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide will be refined using Rietveld refinement and Rietveld refinement with energies. March-Dollase preferred orientation correction will be included in the structure refinement. The correction factors were determined by crystal structure solution based on powder diffraction data, as described in the Reflex Plus tutorial [Structure solution in the presence of preferred orientation](#).

This tutorial covers:

- [Getting started](#)
- [Refinement with Pawley fitting](#)
- [Rietveld refinement](#)
- [Rietveld refinement with energies and Pareto optimization](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Start Materials Studio and create a new project called **Rietveld with energies**.

Now load the powder diffraction pattern of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list and navigate to the **Examples\Reflex\Experimental Data** folder, double-click on **(E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.xcd**. In the Project Explorer, right-click on the imported document and select **Rename** from the shortcut menu. Change the filename to **data**. The file extension **.xcd** is automatically appended.

Next load the crystal structure of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide.


Open the **Import Document** dialog, select **3D Atomistic Files** from the **Files of type** dropdown list. Navigate to the **Reflex** folder, which is one level up from the **Experimental Data** directory. Double-click on the **Structures** folder and select the file **(E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.xsd**. Click the **Open** button.

In the Project Explorer, right-click on the imported document and select **Rename** from the shortcut menu. Change the filename to **structure**. The file extension **.xsd** is automatically appended.

2. Refinement with Pawley fitting

The purpose of Pawley refinement is to provide cell parameters, background parameters, profile parameters and the zero-point shift of the diffraction pattern for the structure solution step. The peak intensities are not related to the unit cell contents at this stage.

In Reflex, the fitting algorithm is stable enough to refine all parameters simultaneously.

Click the **Reflex** button  on the **Modules** toolbar and select **Powder Refinement** from the dropdown list to display the Reflex Powder Refinement dialog.

On the **Pattern** tab enable refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and of the **Zero point Line shift** using the check boxes. The refinement of **20** background coefficients is enabled by default.

Make sure that the 3D Atomistic document **structure.xsd** is active and check the appropriate checkboxes to enable refinement of all cell parameters on the **Lattice** tab.

On the **Display** tab check the **Display simulation/experiment difference** checkbox.

Since the CPU time required for structure solution is approximately proportional to the number of diffraction peaks, you should limit the 2θ range used for structure solution and Pawley refinement to a subsection of the complete powder diffraction pattern.

On the **Setup** tab select **Pawley** as the refinement **Type**. Click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

Changing the *Number of cycles* automatically changes the *Convergence quality* setting from *Medium* to *Customized*.

On the **Setup** tab, change the **Max. 2-Theta** value from 45 to **40** °.

On the **Exp. Data** tab, select the **data.xcd** data set.

The powder pattern was recorded using a copper anode and a graphite (0 0 2) monochromator. The (0 0 2) reflection of graphite corresponds to a d-spacing of 3.4 Å.

On the **Radiation** tab all the default settings are appropriate except for the monochromator settings. In the **X-ray** section, select a **Single** monochromator and set **dhkl** to **3.4 Å**.

Click the **Refine** button on the Reflex Powder Refinement dialog.

While the Pawley refinement is being carried out, the cycle number and the current R_{wp} value are shown at the bottom of the Materials Visualizer window. After five cycles, the R_{wp} value should be about 6.7%. You should repeat the Pawley refinement until no further improvement in the R_{wp} value is obtained.

Ensure that **structure.xsd** is active and click the **Refine** button and close the Reflex Powder Refinement dialog.

You should obtain a minimum value for R_{wp} of about 6.3%.

Note: By default, Pawley or Rietveld refinement jobs are run synchronously on the Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote server. To do this uncheck the *Run synchronously* checkbox on the *Job Control* tab of the Reflex Powder Refinement dialog.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

3. Rietveld refinement

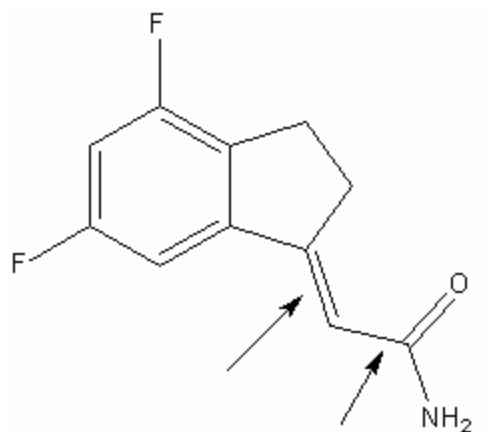
Next perform Rietveld refinement of some parameters. You should start by making a copy of the structure solution.

In the Project Explorer, double-click on **structure.xsd** and select **Edit | Copy** from the menu bar.

Right-click on the project name and choose **New | Folder** from the shortcut menu. Change the name of the new folder to **refinement**.

Right-click on **refinement** in the Project Explorer and select **New | 3D Atomistic Document** from the shortcut menu. Change the filename of the new document to **refined structure.xsd**. Select **Edit | Paste** from the menu bar. Click anywhere in the 3D Viewer for **refined structure.xsd** to deselect everything.

For the Rietveld refinement, two flexible torsions (as shown below) will be added to the parameters refined so far.



Molecular structure of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide

Click the **Measure/Change** arrow  on the **Sketch** toolbar and select **Torsion** from the dropdown list.

Choose one molecule in **refined structure.xsd** and click on the double bond that links the acetamide fragment to the carbon ring system. A new torsion monitor will appear. Repeat the same procedure for the other torsion.

Choose the **Selection** tool .

Now you will define the whole molecule as a motion group. This means that the position and orientation of all atoms in the molecule are described by a single set of translational and rotational parameters, in addition to the torsional degree of freedom you have just defined.

In the 3D Viewer for **refined structure.xsd**, click on one of the atoms to select it. Right-click on the structure and choose **Select Fragment** from the shortcut menu to select the entire molecule.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Setup** tab change the **Type** from Pawley to **Rietveld**.

On the **Structure** tab click the **Create motion group(s) from selection as Single group** button and check all of the structural parameters checkboxes for refinement. Click anywhere in **refined structure.xsd** to deselect everything.

For Rietveld refinement, the global isotropic temperature factor is also added to the refinable parameter list.

On the **Sample** tab, in the **Temperature factors** section set the **Applied** temperature factor to **Global Isotropic**. Check the checkbox to refine the **Global isotropic** temperature factor.

Next enter the preferred orientation correction factors. For Rietveld refinement, you need a good estimate of the preferred orientation vector. You can use Powder Solve to determine the crystal

structure and the preferred orientation parameters simultaneously as described in the Reflex Plus tutorial [Structure solution in the presence of preferred orientation](#).

Alternatively, you can make a reasonable estimate for the correction factors based on the length of the lattice vectors. In this tutorial, a good starting point seems to be $a^* = 1.0$, $b^* = 3.0$, $c^* = 1.0$, with the default value $R0 = 1.0$.

On the **Sample** tab of the Reflex Powder Refinement dialog, in the **Preferred orientation** section set the **Applied Preferred orientation** method to **March-Dollase**.

Set **a^*** , **b^*** , **c^*** , and **$R0$** to **1.0**, **3.0**, **1.0**, and **1.0**, respectively. Check the checkboxes to refine all preferred orientation parameters.

For Rietveld refinement, you should use the full range of the powder diffraction pattern. In addition, you want the comparison between the calculated and the experimental patterns to be displayed in a new chart document.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

On the **Setup** tab, change the **Max. 2-Theta** value to **50 °**.



On the **Display** tab, in the **General** section, check the **Display simulation/experiment difference** checkbox. In the **View management** section, change **Chart view** from Replace to **New**.

Click the **Refine** button.

The R_{wp} value for the Rietveld refinement is about 12.4%. Next, you should examine the crystal structure.

In the Project Explorer, double-click on **refinement\refined structure.xsd**.



Right-click in the 3D Viewer and choose **Display Style** from the shortcut menu to open the Display Style dialog. Select the **Lattice** tab and set the **Max** values for **A**, **B**, and **C** to **2.00**. Close the dialog.

Click the **Calculate Hydrogen Bonds** button  on the **Atoms and Bonds** toolbar, then click the **Calculate Close Contacts** button .

To make the crystal structure clearer, you can switch off the display of motion groups.

Press the **ALT** key and double-click on a motion group. All motion groups are selected. Select **View | Explorers | Properties Explorer** from the menu bar to display the Properties Explorer. Double-click on **IsVisible** to open the Edit IsVisible dialog. Select **No / False** and click the **OK** button. Click anywhere in **refinement\refined structure.xsd** to deselect everything.

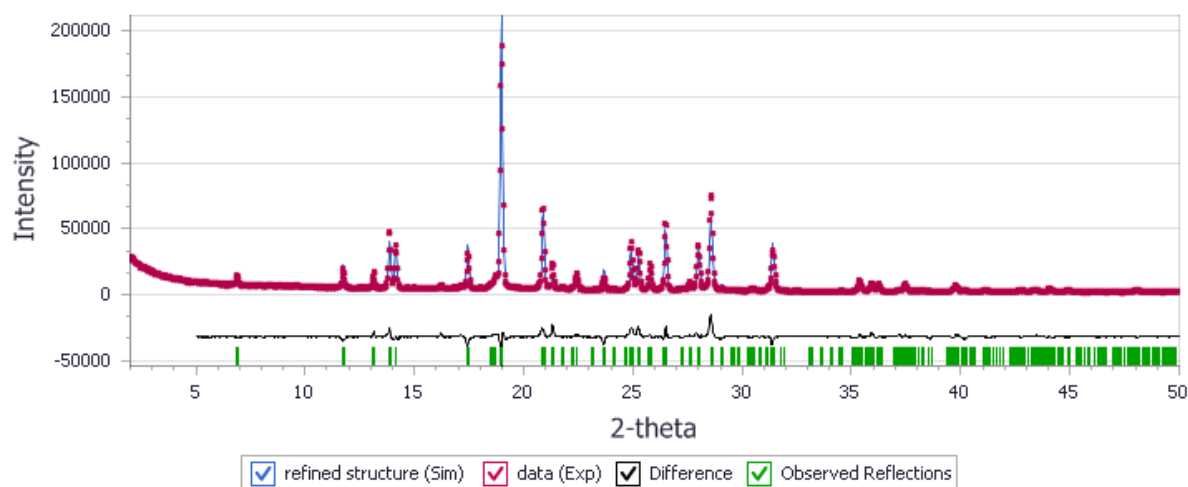
Examine the crystal structure - there are some minor close contacts. Next, you should examine the comparison of the simulated and the experimental powder diffraction patterns.

Click on the **Hydrogen Bonds** arrow  and select **Delete Hydrogen Bonds** from the dropdown list. Click on the **Close Contacts** arrow  and select **Delete Close Contacts**.

In the Project Explorer, double-click on the chart document **refined structure.xcd** and examine it.

The overall intensity distribution of the experimental powder diffraction pattern is well reproduced, although some regions show intensity differences as indicated in the difference plot in the chart document below.

Powder Refinement: $R_{wp} = 12.40\%$ $R_{wp}(w/o\ bck) = 21.63\%$
 $R_p = 9.49\%$



Comparison between the simulated powder pattern obtained by Rietveld refinement and the experimental powder pattern

Optionally, you can generate an HTML document that summarizes the results of the Rietveld refinement.

Ensure that **refined structure.xsd** is the active document. Select the **Display** tab of the Reflex Powder Refinement dialog. In the **View management** section, check the **Generate HTML report** checkbox. Click the **Calculate** button, close the Reflex Powder Refinement dialog and examine the HTML report.

The HTML document contains all the refined parameters.

Select **File | Save Project** from the menu bar. Close all of the open documents, apart from **refined structure.xsd**.

4. Rietveld refinement with energies and Pareto optimization

Now you will improve the structure solution by including energy information in the Rietveld refinement by optimizing a combined figure of merit.

First the energy weight factor determining the relative importance of the energy contribution has to be selected. The optimum value of this parameter depends not only on the quality of the experimental data and the accuracy of the forcefield energy expression, but also on your chosen objective: is it more

important that the solution matches the experimental pattern or should the lattice energy be close to its minimum? In this case, Pareto optimization can be used to calculate automatically a set of possible optimum refinement solutions using a sequence of Rietveld refinement with energies calculations with differing energy weights.

Select **File | Save As...** from the menu bar to open the Save As dialog. Enter the filename **pareto** and click the **OK** button.

Next you define each atom as an individual motion group for an all-atom Pareto optimization calculation. This means that each atom is described by three translational parameters. Start by deleting the motion groups and torsions defined previously.

Open the **Display Style** dialog and select the **Lattice** tab. Choose **In-Cell** from the **Style** dropdown list and close the dialog.

Select all the motion groups and press the **DELETE** key.

Repeat the same procedure to delete the torsions.

Select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu to select one complete molecule.

Open the Reflex Powder Refinement dialog. On the **Structure** tab choose **Individual groups** for the motion group selection and click the **Create** button. Ensure that all of the refinement checkboxes are checked and that the **Use hydrogens** checkbox is checked.

Click anywhere in the 3D Viewer to deselect everything.

Now use Pareto optimization to calculate a set of possible optimum refinement solutions automatically.

On the **Setup** tab, set the **Refinement Type** to **Pareto optimization**. Click the **More...** button to open the Pareto Optimization Options dialog.

The number of points specify the total number of points to be calculated on a Pareto curve. The energy window describes the tolerance window above the global minimum within which realistic structure solutions can be expected. In this tutorial, you should use the default settings.

Close the Pareto Optimization Options dialog.

On the **Energy** tab of the Reflex Powder Refinement dialog, change the **Forcefield** to **COMPASS** and ensure that **Forcefield assigned** is selected from the **Charges** dropdown list.

On the **Job Control** tab, select an appropriate **Gateway location**. Click the **Refine** button and **close** the Reflex Powder Refinement dialog.

Close the **pareto.xsd** 3D Viewer and click the **Yes** button when asked if you want to save the changes.

Note: Before you start a Pareto optimization, it is important that you choose an appropriate energy expression/forcefield and verify that it calculates the geometry and potential energy surface of the molecular fragments with sufficient accuracy.

Note: Pareto calculations are run as remote jobs.

Once the calculation starts, a new folder called `pareto Reflex Pareto` is created in the Project Explorer. The parameter settings for this job are automatically saved in a file called `pareto - Powder Diffraction`.

The Job Explorer informs you about the progress of the calculation. After some time, two new windows appear, a text document, `Status.txt`, and a chart document `pareto E vs Rwp.xcd`. These documents are updated regularly as the job progresses.

The text document informs you about:

- The number of optimization cycles performed so far
- The energy weight factor (mixing factor)
- R_{comb} (combined figure of merit), R_{wp} , and R_e (energetic figure of merit)
- The total potential energy for the current structure and the energy difference between that and the global minimum

The chart document contains the set of optimum solutions found so far and the corresponding energetic and R_{wp} values. Wait until the job finishes before proceeding.

Note: The first step of a Pareto optimization is a minimization of the potential energy of the crystal with fixed lattice parameters. This energy minimum provides the reference for the energy contribution to the combined figure of merit.

Next you should analyze the Pareto optimization results.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

In the **Project Explorer**, double-click on `pareto.txt` in the **pareto Reflex Pareto** folder.


The text file contains the values of all the settings used as input for the calculation and a short summary of the calculation results.

Close `pareto.txt`.

In the **Project Explorer**, double-click on `pareto.xtd` followed by `pareto E vs Rwp.xcd` in the **pareto Reflex Pareto** folder.


Select **Window | Tile Vertically** from the menu bar.

In the energy versus R_{wp} chart, the optimum solutions form a curve called the Pareto front. The continuum of all potential solutions exists only in the region above the Pareto front, whereas no solutions are possible below. In nearly all cases, the absolute optimum solution having minimum energy and minimum R_{wp} is part of an inaccessible region. `pareto.xtd`, which contains all the optimum solutions is linked dynamically with the chart file.

Choose the **Selection** tool  and click on any point in `pareto E vs Rwp.xcd`.

You can see how the points on the chart relate to the trajectory frames. Alternatively, you can use the animation controls to select a trajectory frame and relate it to the corresponding point on the graph.

If the **Animation** toolbar is not visible, select **View | Toolbars | Animation** from the menu bar.

Make **pareto.xtd** the active document. Click on the **Animation Mode** arrow  and choose **Options** from the dropdown list to open the Animation Options dialog. Enter **1** in the **Current frame** textbox and press the **TAB** key. Alternatively, use the spin controls to specify the frame number.

Next examine the optimized parameters for frame 1 and the weight of the energy contribution to the R_{comb} .

Open the **Reflex Powder Refinement** dialog.

On the **Setup** tab, click the **Load result settings** button. Click the **More...** button for **Refinement Type** in the **Refinement** section to open the Rietveld with Energies Options dialog. Examine the **Weight** and click the **OK** button.

Repeat the same procedure for other frames in **pareto.xtd**, reloading the results settings each time.

The *Weight* reported on the *Rietveld with Energies Options* dialog is different for each frame.

Close the **Animation Options** and **Reflex Powder Refinement** dialogs.

Select **Window | Close All** from the menu bar. Click the **No to All** button when asked if you want to save the changes.

The Pareto optimization suggests the best solution which is closest to the absolute optimum (minimum R_{wp} , minimum E). In the energy versus R_{wp} chart **pareto E vs Rwp.xcd**, this solution should have the shortest distance from the origin. It is saved automatically in the project at the completion of the Pareto optimization. You should examine the crystal structure.

In the **Project Explorer**, double-click on **pareto.xsd** in the **pareto Reflex Pareto** folder.

Click the **Calculate Hydrogen Bonds** button  then the **Calculate Close Contacts** button .

To make the crystal structure clearer, you can switch off the display of motion groups. Press the **ALT** key and double-click on a motion group. In the Properties Explorer, double-click on **IsVisible**. In the **Edit IsVisible** dialog, select **No / False** and click the **OK** button.

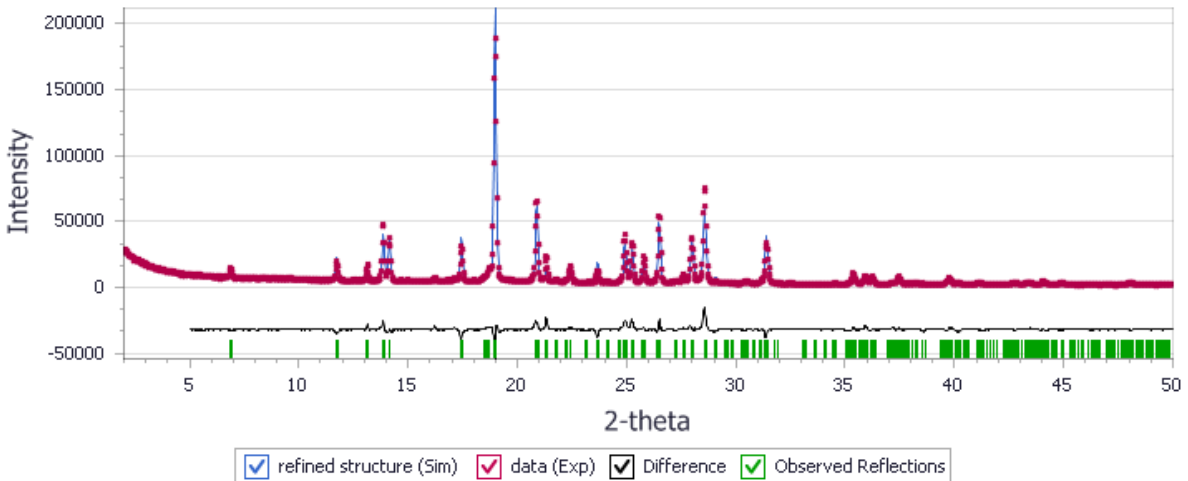
Close **pareto.xsd** and click the **No** button when asked if you want to save the changes.

Next examine the comparison of the simulated and the experimental powder diffraction pattern.

In the **Project Explorer**, double-click on the Chart Document **pareto Reflex Pareto\pareto.xcd** and examine it.

The R_{wp} should be reduced to 11.2% compared to 12.40% obtained from regular Rietveld refinement. The overall intensity distribution of the experimental powder diffraction pattern is well reproduced. The inclusion of energy information into the Rietveld refinement process optimizing a R_{comb} allows for an improved structure solution.

Powder Refinement: $R_{wp} = 12.40\%$ $R_{wp}(w/o\ bck) = 21.63\%$
 $R_p = 9.49\%$





Comparison between the simulated powder pattern obtained by Rietveld refinement and experimental powder pattern

Note: Pareto optimization only provides the set of optimum solutions. Although it suggests a 'best solution', it by no means indicates the solution that is actually the best solution. The decision on which of the optimum solutions to select cannot be automated and has to be taken by the user according to specific criteria: is it more important in this particular case to have a good fit with the experimental pattern or is it critical that the energy is close to its minimum?

You should compare the crystal structure obtained from Rietveld refinement with energies with that obtained from Rietveld refinement by overlaying the two structures.

Close **pareto.xcd**. Right-click on the project root and select **New | Folder** from the shortcut menu. Rename the new folder **preferred_orientation**.

In the **Project Explorer**, double-click on **pareto.xsd** in the **refinement\pareto Reflex Pareto** folder. Press the **ALT** key and double-click on a motion group, then press the **DELETE** key.

Copy the contents of the document by clicking the **Copy** button . In the **Project Explorer**, right-click on the folder **preferred_orientation** and choose **New | 3D Atomistic Collection Document** from the shortcut menu. Click the **Paste** button .

In the **Project Explorer**, right-click on **3D Atomistic Collection.xod** and select **Rename** from the shortcut menu. Change the name of the document to **overlay.xod**.

Right-click on the **overlay.xod** structure and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Atom** tab, set **Coloring to Custom** and choose red from the Color chooser. Click the **OK** button.

On the **Lattice** tab, set the **Color** to red.


Close **pareto.xsd** and click the **No** button when asked if you want to save the changes.

In the **Project Explorer**, double-click on **refined structure.xsd** in the **refinement** folder. Press the **ALT** key and double-click on a torsion, press the **DELETE** key.

Copy the contents of the document by selecting **Edit | Copy** from the menu bar. In the Project Explorer, double-click on **overlay.xod** and select **Edit | Paste** from the menu bar.


On the **Atom** tab of the Display Style dialog, set **Coloring to Custom** and choose white from the Color chooser. Click the **OK** button and close the dialog.

Close **refined structure.xsd** and click the **No** button when asked if you want to save the changes.

Expand the **overlay.xod** window by clicking on the **Maximize** button . Click once in the window to deselect everything.

The two structures (**pareto.xsd** in red and **refined structure.xsd** in white) are quite similar, with the differences mainly in the hydrogen positions. You should examine the hydrogen bonding scheme and close contacts.

Double-click on one of the atoms in red to select all of the **pareto.xsd** molecular fragment. Click the

Calculate Hydrogen Bonds button .

Click anywhere in the 3D Viewer to deselect everything. Repeat the same procedure for **refined structure.xsd**.

The two structures have very similar hydrogen bonding schemes. Next, you should examine the close contacts.

Press the **ALT** key and double-click on a hydrogen bond, then press the **DELETE** key.

Double-click on one of the atoms in red to select all of the **pareto.xsd** molecular fragment. Click the

Calculate Close Contacts button .

Click anywhere in the 3D Viewer to deselect everything. Repeat the same procedure for **refined structure.xsd**.

There should be fewer close contacts for the structure solution obtained by Rietveld with energies. The inclusion of energy contribution in this case provides more accurate atomic positions, for example the hydrogen atoms.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank P. G. Varlashkin, M. Sacchetti, and J. Zhu from GlaxoSmithKline for supplying the experimental data.

Determining the degree of crystallinity of lactose monohydrate samples

Purpose: Illustrates how to estimate the degree of crystallinity from powder X-Ray data

Modules: Materials Visualizer, Reflex Powder Crystallinity

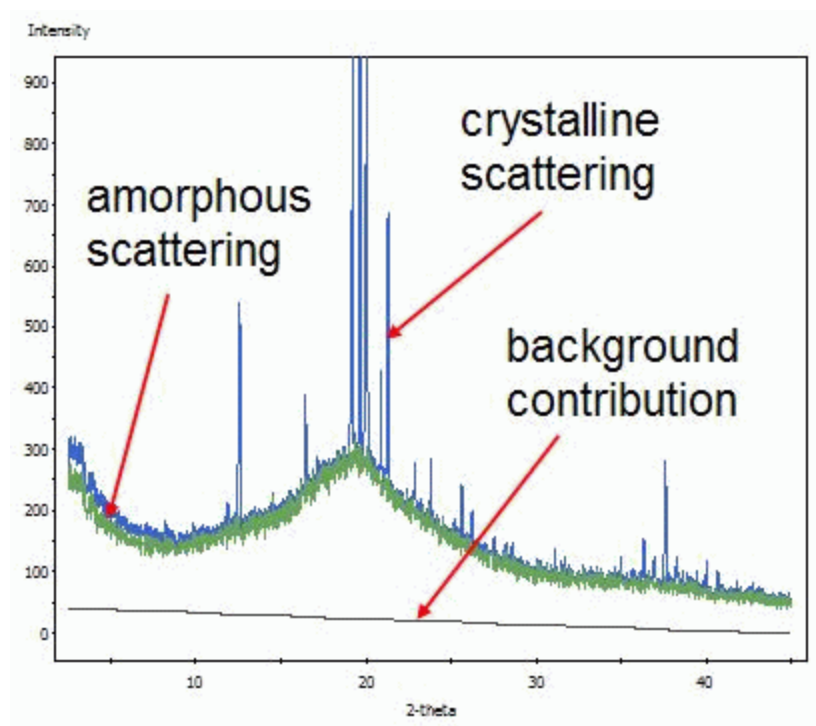
Time: 🕒 🕒

Prerequisites: [Indexing powder patterns](#), Using scripting to calculate the interaction energy between two layers

Background

In many cases crystallization does not result in a 100% pure single crystalline phase. Instead it can yield a mixture of crystalline phases, a mixture of a single crystalline phase and an amorphous phase, or mixtures of different crystalline and amorphous phases. Powder X-ray diffraction data can be used to probe for these conditions, for example identifying and quantifying different crystalline phases from powder diffraction data, as described in the tutorial [Quantitative phase analysis of organic mixture samples](#).

In order to determine the degree of crystallinity based on X-ray data, the pattern needs to be deconvoluted into three scattering contributions: crystalline, amorphous, and background. The area difference between the crystalline and amorphous contributions determines the degree of crystallinity whereas the background contribution represents the background noise caused by, for example, the scattering from the sample holder.



Scattering contributions relevant for estimating the amorphous content

This tutorial discusses two methods for estimating the degree of crystallinity: background subtraction and phase analysis. Background subtraction can estimate the amorphous content from only the X-ray pattern. By contrast, the more accurate phase analysis method requires a diffraction pattern of the purely crystalline and amorphous phases as input.

Introduction

Lactose is an excipient used in pharmaceutical formulations as a binder and filler. In this tutorial you will analyze a series of X-ray powder diffraction patterns where lactose monohydrate, a common crystalline form of lactose, has been mixed with amorphous lactose at controlled weight ratios.

This tutorial covers:

- [Getting started](#)
- [To estimate the degree of crystallinity using the background subtraction method](#)
- [To estimate the degree of crystallinity using the phase analysis method](#)
- [To compare both methods using the scripting API](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **lactose** as the project name, click the **OK** button.

The new project is created with *lactose* listed in the Project Explorer. Now import the input files you will be studying.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder and find all relevant files by typing **lactose*** into the **File name** textbox, press the **ENTER** key.

Several files are displayed. You should see eleven files of the type `lactose_XX%.xrdml` where "XX" indicates the degree of crystallinity, ranging from 10% to 100% ([Moizan et al., 2004](#)). You should also see `lactose_amorphous.xrdml` and `lactose_empty.xrdml`.

On the **Import Document** dialog, hold the **SHIFT** key and click on the first file then the last file in the list to select all files. Click the **Open** button.

All files are imported into Materials Studio. Now save the project and close all open windows.

Choose **File | Save Project** from the menu bar followed by **Window | Close All**.

2. Estimating the degree of crystallinity using the background subtraction method

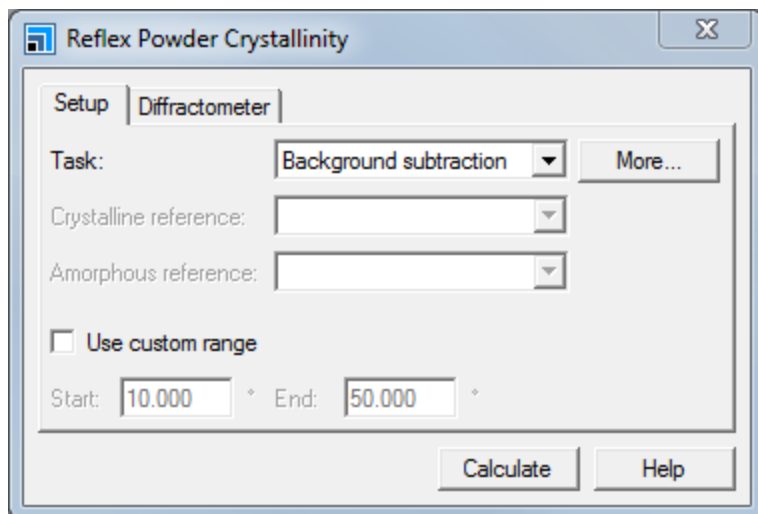
In this section you will use the background subtraction method to estimate the degree of crystallinity of some of the files you have just imported. Initially, you will use the Powder Crystallinity tool without providing any supplementary information.

Open the diffraction pattern for the sample with a degree of crystallinity of 20%.

In the Project Explorer double-click on **lactose_20%.xcd**.

Open the Reflex Powder Crystallinity tools.

Select **Modules | Reflex | Powder Crystallinity** from the menu bar.



Reflex Powder Crystallinity dialog

The *Task* dropdown list lets you choose between the background subtraction and phase analysis methods. The *Crystalline reference* and *Amorphous reference* options allow you to select the respective reference patterns. These are enabled only if the *Task* is set to *Phase analysis*. *Use custom range* allows you to restrict the range over which the analysis is performed.

On the Reflex Powder Crystallinity dialog set the **Task** to **Background subtraction** and click the **Calculate** button.



A new document entitled `lactose_20% Decomposition.xcd` is generated. The degree of crystallinity is estimated at 52.4%. *Coverage* indicates the fraction of intensity that was fitted. In this case all of the intensity was accounted for by the algorithm, so the coverage is 100%.

The degree of crystallinity has been significantly overestimated. To improve this result, you will now load a background reference pattern.

In the Project Explorer double-click on `lactose_20%.xcd` to make it the active document. On the Reflex Powder Crystallinity dialog, click the **More...** button for **Task** to open the Background Subtraction Options dialog. Click the **Use background reference** radio button and select `lactose_empty.xcd` from the dropdown list and close the dialog. On the Reflex Powder Crystallinity dialog click the **Calculate** button.

A new document named `lactose_20% Decomposition (2).xcd` is generated. The degree of crystallinity is estimated to 32.8%, in better agreement with the experimental value of 20%.

Now inspect both decompositions using the zoom and translate tools.

Select the **Zoom** tool  on the **Chart Viewer** toolbar. Click in the **Chart Document** and move the mouse to the left and right and up and down while holding down the left mouse button. Select the **Translation** tool  and move the mouse around the **Chart Document**.

Notice that there is a clear difference in the decomposition for high 2-Theta values. In `lactose_20% Decomposition (2).xcd` the background has lower intensities. The remaining intensity primarily

affects the amorphous scattering intensity which explains the lower degree of crystallinity. For `lactose_20% Decomposition.xcd`, where no experimental background was provided, the background intensity was estimated to be significantly higher, leading to a significantly lower estimate of the amorphous scattering and higher estimate of the degree of crystallinity.

If you want try using the *Use custom range* feature on the *Setup* tab to verify that changing the low 2-Theta values has little effect on the estimates of the degree of crystallinity.

Select **Window | Close All** from the menu bar and click the **No to All** button when asked whether you want to save any documents as a part of this project. Choose **File | Save Project** from the menu bar.

3. Estimating the degree of crystallinity using the phase analysis method

In this section you will use crystalline and amorphous reference patterns to obtain a high quality prediction of the degree of crystallinity.

Double-click on `lactose_80%.xcd` in the Project Explorer. On the **Reflex Powder Crystallinity** dialog change the **Task** to **Phase analysis**. Select `lactose_100%.xcd` from the **Crystalline reference** dropdown list. Select `lactose_amorphous.xcd` from the **Amorphous reference** dropdown list. Click the **Calculate** button.

The degree of crystallinity is reported to be 80.9%, which is in excellent agreement with experiment. *Coverage* is reported at 93.0% which means that 7.0% of the scattering intensity could not be fitted. Again, inspect the pattern by using the *Zoom* and *Translate* tools.

Select **Window | Close All** from the menu bar, click the **No to All** button when asked whether you want to save any documents as a part of this project. Choose **File | Save Project** from the menu bar.

4. To compare both methods using the scripting API

To compare the performance of both methods you could run calculations for each of the ten data files by hand. However, a much faster and more convenient way is to use the scripting capabilities of this module. For a general introduction on how to use the Materials Studio scripting API please see the tutorial *Using scripting to calculate the interaction energy between two layers*.

First open a new Perl document.

Select **File | New** from the menu bar to open the New Document dialog, double-click on **Perl Script**.

A new Script Viewer opens. Next, create a Perl script by copying the script below into the empty Perl document.

Copy and **paste** the following Perl script into the new Script document.

```
# "@docs" is the list of diffraction files to analyze
my @docs = ("lactose_95%.xcd", "lactose_90%.xcd", "lactose_80%.xcd",
            "lactose_70%.xcd", "lactose_60%.xcd", "lactose_50%.xcd",
            "lactose_40%.xcd", "lactose_30%.xcd", "lactose_20%.xcd", "lactose_
10%.xcd");

# Alias some shortcuts for the modules
my $reflex = Modules->Reflex;
my $crystallinity = $reflex->PowderCrystallinity;
```

```

# assign the amorphous, crystalline, and background reference
$crystallinity -> SetAmorphousReference ( $Documents{"lactose_
amorphous.xcd"} );
$crystallinity -> SetCrystallineReference( $Documents{"lactose_100%.xcd"} );
$crystallinity -> SetBackgroundReference ( $Documents{"lactose_empty.xcd"}
);

# These are the settings for the phase analysis
my @SettingsPA = (
    CrystallinityMethod => "Phase analysis",
    WriteLevel      => "Silent"
);

# These are the settings for the phase background subtraction
my @SettingsBG_empty = (
    CrystallinityMethod => "Background subtraction",
    WriteLevel      => "Silent",
    UseAutoBackground => "No"
);

# These are the settings for the phase background subtraction
my @SettingsBG = (
    CrystallinityMethod => "Background subtraction",
    WriteLevel      => "Silent",
    UseAutoBackground => "Yes"
);

# Create a study table to hold the results
my $StudyTable = Documents->New("Crystallinity Report.std");

#Setup some Header information in the StudyTable
$StudyTable->ColumnHeading(0) = "Diffraction file";
$StudyTable->ColumnHeading(1) = "Crystallinity (Background Subtraction)";
$StudyTable->ColumnHeading(2) = "Crystallinity (Background Subtraction,
empty sample holder)";
$StudyTable->ColumnHeading(3) = "Crystallinity (Phase Analysis)";

# "index" is the row index in the results study table
my $index = 0;

# This executes the Powder Crystallinity calculation for all files
foreach my $file (@docs) {

    # Load in the chart document

```

```

my $chartDoc = $Documents{$file};

# Run the Background subtraction method
$reflex->ChangeSettings(\@SettingsBG);
my $resultsBG = $crystallinity->Run($chartDoc);

# Run the Background subtraction method
$reflex->ChangeSettings(\@SettingsBG_empty);
my $resultsBG_empty = $crystallinity->Run($chartDoc);

# Run the Phase analysis method
$reflex->ChangeSettings(\@SettingsPA);
my $resultsPA = $crystallinity->Run($chartDoc);

# Store the results into the study table
$StudyTable->Cell($index, 0) = $file;
$StudyTable->Cell($index, 1) = $resultsBG->Crystallinity;
$StudyTable->Cell($index, 2) = $resultsBG_empty->Crystallinity;
$StudyTable->Cell($index, 3) = $resultsPA->Crystallinity;


# Close the chart document
$chartDoc->Close;

# increment "index" to store the next row of results
++$index;
}

```

Now run the script.

Make sure **Perl Script.pl** is in focus by double-clicking on it in the Project Explorer. Change the name of the Perl script to **Crystallinity Report.pl**.

Click on the **Run on Server** tool  on the **Scripting** toolbar.

Once the calculation finishes the results are collected in a folder called *Crystallinity Report Script*. The important information is collected in a study table called *Crystallinity Report.std*.

In the **Project** explorer double-click on **Crystallinity Report.std**, which should contain the following data:

Diffraction file	Crystallinity (Background Subtraction)	Crystallinity (Background Subtraction, empty sample holder)	Crystallinity (Phase Analysis)
lactose_95%.xcd	74.2	83.3	95.6
lactose_90%.xcd	80.9	79.3	85.0

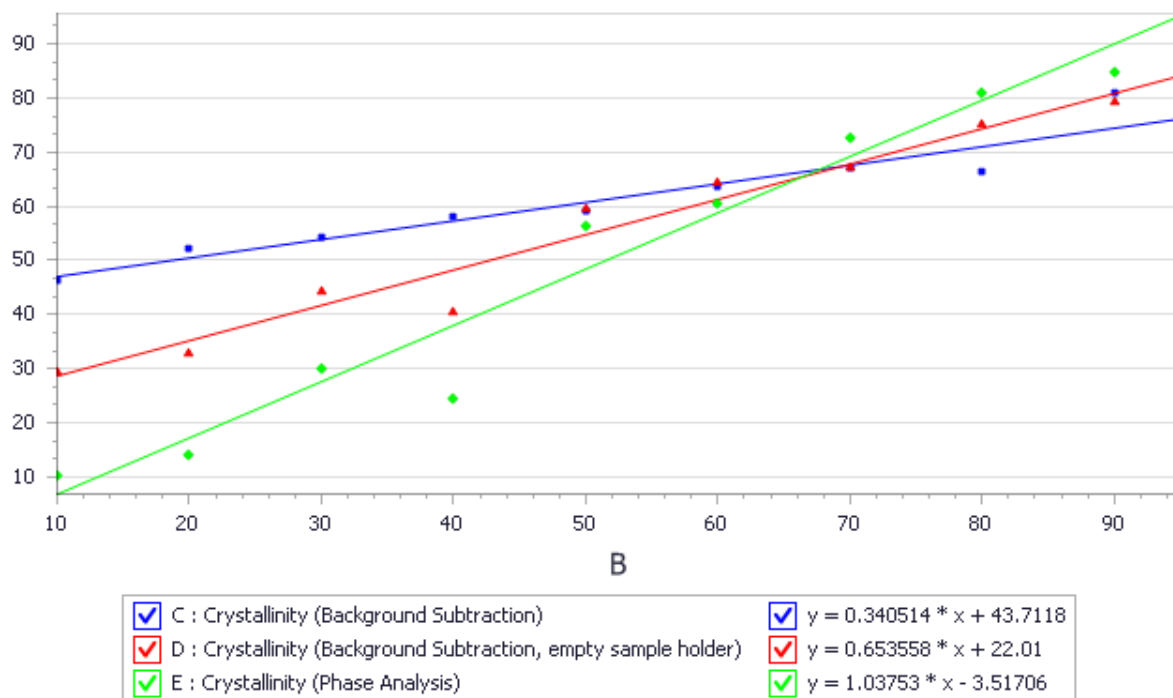
Diffraction file	Crystallinity (Background Subtraction)	Crystallinity (Background Subtraction, empty sample holder)	Crystallinity (Phase Analysis)
lactose_80%.xcd	66.5	75.0	80.9
lactose_70%.xcd	67.2	67.3	72.8
lactose_60%.xcd	63.8	64.4	60.6
lactose_50%.xcd	59.1	59.7	56.3
lactose_40%.xcd	58.0	40.6	24.4
lactose_30%.xcd	54.3	44.4	30.2
lactose_20%.xcd	52.4	32.8	14.3
lactose_10%.xcd	46.3	29.4	10.2

Next you will analyze this data using the plotting capabilities of Materials Studio.

Select column **B**, right-click and select **Insert | Left** from the shortcut menu. Type in the experimental values for the degrees of crystallinity (**95** next to **lactose_95%.xcd**).

Hold the **SHIFT** key and click **B** then **E** to select the columns to plot. Select **Tools | Plot Graph** from the menu bar to open the Plot Graph dialog. Set **Graph type** to **Scatter (2-D)** and **X-axis** to **B**. Check **Show best fit line** checkbox and click the **Plot** button.

The scatter plot should look like this:



Scatter plot for the various predictions of the degree of crystallinity

Note that all methods correctly reproduce the trend in the change of the degree of crystallinity. Furthermore, overall the phase analysis method is in excellent agreement with experiment.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank V. Moizan, T. Larsson, L. Briggner, and J. Giovannini from Astra Zeneca for supplying the experimental data.

References

Virginie Moizan^{1,2}, Tomas Larsson¹, Lars-Erik Briggner¹, Julien Giovannini¹, 2004, "in silico procedures for phase identification and quantitative phase analysis using state-of-the-art in X-Ray Powder Diffraction", MSc Thesis report, ¹AstraZeneca, ²Rennes University.

Reflex QPA tutorials

The following tutorial illustrates how to utilize the capabilities of Powder Quantitative Phase Analysis.

- [Quantitative phase analysis of organic mixture samples](#)

Quantitative phase analysis of organic mixture samples

Purpose: Illustrates how to determine the relative amounts of different phases in a mixture from a powder diffraction pattern of the mixture.

Modules: Materials Visualizer, Reflex, Reflex QPA

Time:  

Prerequisites: [Rietveld refinement with energetic considerations](#)

Background

Quantitative phase analysis (QPA) refers to the determination of the relative amounts of different phases in multi-phase samples. It is widely used to analyze the phase composition of a material in a rapid and simple manner. Its applications include forensic analysis, mineral assays, fiber analysis, characterization of pharmaceuticals, corrosion products, intermetallics, and contaminants.

Introduction

In Reflex QPA, the pure component phases that comprise a mixture may be represented by:

- crystal structures (Rietveld method) - pattern, sample, lattice, and structural parameters can be refined for each phase.
- experimental powder diffraction patterns (standardless method or internal standard method) - parameters associated with line shift corrections can be refined for each phase.
- a mixture of crystal structures and experimental powder diffraction patterns.

This tutorial aims to explain the different steps involved in the analysis of an acetohexamide mixture. Acetohexamide is used to treat type II (non insulin-dependent) diabetes, particularly in people whose diabetes cannot be controlled by diet alone.

This tutorial covers:

- [Getting started](#)
- [To prepare the pure phase crystal structures](#)
- [To set up, run, and analyze the results of QPA with the Rietveld method](#)
- [To prepare the powder diffraction patterns with an internal standard](#)
- [To set up, run, and analyze the results for internal standard QPA](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.


1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **QPA** as the project name, click the **OK** button.

The new project is created with *QPA* listed in the Project Explorer. Now you will import the input file you will be studying.

You will load the powder diffraction pattern of a three-component-phase mixture, comprising 40% of the stable polymorphic form of acetohexamide (Form A), 40% of the metastable polymorphic form of acetohexamide (Form B), and 20% corundum (internal standard).

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder, change the **Files of type** to **Chart Files**, and double-click on **Acetohexamide_Mixture.xcd**.

Close **Acetohexamide_Mixture.xcd** and click the **Yes** button when asked if you want to save the document as part of the project.

Tip: After loading the experimental powder diffraction pattern, you may wish to process it further using the Pattern Processing tool. You could, for example, remove $K\alpha_2$ peaks due to the secondary emission lines of the X-ray anode, or smooth the pattern and remove any noise. These $K\alpha_2$ stripping and smoothing steps are optional and are not prerequisites for a successful Powder QPA calculation.

You will now import the crystal structures of Form A, Form B, and corundum.


Open the **Import Document** dialog. Select **3D Atomistic Files** from the **Files of type** dropdown list. Navigate to the folder **Examples\Reflex\Structures**. Hold down the **CTRL** key and select the files **Acetohexamide_FormA.xsd** and **Acetohexamide_FormB.xsd**. Click the **Open** button.

Open the **Import Document** dialog. Navigate to and select the file **Structures\metal-oxides\Al2O3.msi**, then click the **Open** button.

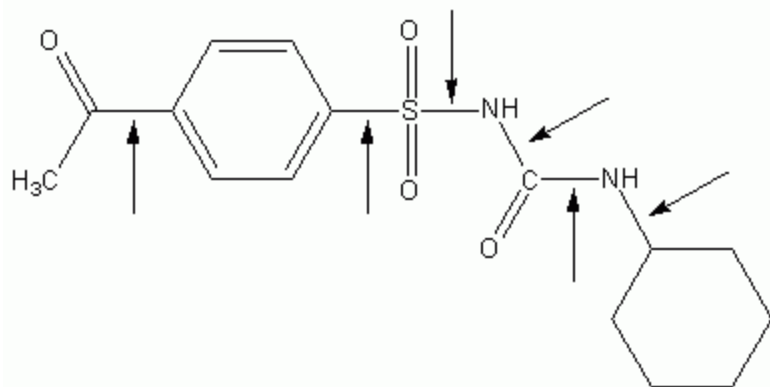
2. To prepare the pure phase crystal structures

This section shows you how to prepare the input files for a Powder QPA calculation using the Rietveld method, where the pure component phases are represented by their crystal structures. The diffraction pattern of the mixture is decomposed into a superposition of powder diffraction patterns simulated from these structures.

You will define the structural degrees of freedom for each of the crystal structures starting by specifying the intramolecular torsions of the molecular fragment in the unit cell.

Make **Acetohexamide_FormA.xsd** the active document. Click the **Measure/Change** arrow  on the **Sketch** toolbar and select **Torsion** from the dropdown list.


Choose one molecule in **Acetohexamide_FormA.xsd**. Six flexible single bonds are identified in the figure below. Click on them in turn, starting from one end of the chain and working your way through the others.



Molecular structure of acetohexamide

Note: You can define the measurements on any symmetry image of a molecular fragment in the periodic structure. You do not need to define all measurement degrees of freedom on the same molecular fragment. However, you need to ensure that you do not define the same measurement twice on two different symmetry images since in such a case you artificially increase the number of degrees of freedom and it will take a longer time to locate the optimal structure.

In the next step, you will define the whole molecule as a motion group. This means that the position and orientation of all atoms in the molecule are described by a single set of translational and rotational parameters in addition to the torsional degree of freedom you have just defined.

Choose the **Selection** tool  from the **3D Viewer** toolbar.

In the 3D Viewer for **Acetohexamide_FormA.xsd**, click on one of the atoms to select it. Right-click on the structure and choose **Select Fragment** from the shortcut menu to select the entire molecule.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Setup** tab, change the refinement **Type** from Pawley to **Rietveld**.

On the **Structure** tab choose **Single group** for the motion group selection and click the **Create** button.

All the checkboxes for the structural degrees of freedom (torsions and motion groups) are switched on automatically for refinement.

Note: It is recommended that you turn off the refinement of the structural degrees of freedom by default. Once the major phases have been identified from an initial QPA run, the results may be improved by enabling the refinement of the structural degrees of freedom just for the major phases.

On the **Structure** tab, switch off the **Refine** checkboxes for all the structural degrees of freedom.

Close **Acetohexamide_FormA.xsd** and click the **Yes** button when asked if you want to save the document as part of the project.

Repeat the same procedure to define the torsional degrees of freedom and motion groups for **Acetohexamide_FormB.xsd**. Ensure that none of the structural parameters checkboxes are switched on for refinement. Close **Acetohexamide_FormB.xsd** and save the document as part of the project.

Next you will define the structural degrees of freedom for corundum.

Make **Al2O3.xsd** your active document and press **CTRL + A** to select the entire structure.

On the **Structure** tab of the Reflex Powder Refinement dialog, choose **Individual groups** for the motion group selection and click the **Create** button. Ensure that none of the structural parameters checkboxes are checked for refinement.

Close **Al2O3.xsd** and click the **Yes** button when asked if you want to save the changes.

There are a range of non-structural parameters that can be refined for a crystal structure as part of a Powder QPA calculation, including profile, background, and sample parameters. The default settings for all these parameters are imported from the current settings in Reflex and applied to each pure component phase. Therefore, you need to define the general settings for these refinement parameters.

On the **Setup** tab of the Reflex Powder Refinement dialog, change the **Max. 2-Theta** value from 45° to **70.001°**.

The data for this tutorial were measured with copper λ_1 radiation only, so you should deselect λ_2 radiation for the refinement.

On the **Radiation** tab, uncheck the λ_2 checkbox in the **X-ray** section.


On the **Pattern** tab, enable refinement of the profile parameters **U, V, W, NA, and NB** and of the **Zero point Line shift**. The refinement of 20 **Background coefficients** is enabled by default.

In the Project Explorer, double-click on **Acetohexamide_Mixture.xcd** to make it your active document.

On the **Exp. Data** tab, select the chart document **Acetohexamide_Mixture.xcd** as the experimental powder diffraction data. Close the Reflex Powder Refinement dialog.

3. To set up and run a Powder QPA with the Rietveld method

In this section, you will perform a Powder QPA calculation using the Rietveld method. Two separate Powder QPA tasks are available in Materials Studio, full refinement and refine weights. In this tutorial, you will run a full refinement calculation.

Click the **Reflex** arrow  on the **Modules** toolbar and select **Powder QPA** from the dropdown list to open the Reflex Powder QPA dialog.

On the **Setup** tab, set the **Type** to **Full refinement**.

Note: The calculation of weight fraction is only available for X-ray diffraction data. If you use electron or neutron diffraction sources, you will be able to calculate the scattering intensity fraction of each phase in the mixture but not the weight fractions.

On the **Setup** tab the **Convergence quality** should be set to **Medium**. Check the **Create individual chart document for each phase** checkbox.

This option determines whether the chart documents containing the calculated powder diffraction patterns will be inserted into the Powder QPA study table when a calculation is complete.

Tip: Since the chart documents are produced for all the component phases, the size of the study table containing the results of a Powder QPA job can become very large.

Next you will define the potential pure component phases in the mixture.

On the **Phases** tab, click the **Add new phases** button to open the Add QPA Phases dialog. Hold down the **CTRL** key and select **Acetohexamide_FormA.xsd**, **Acetohexamide_FormB.xsd**, and **Al2O3.xsd**. Click the **Open** button.

A study table called Powder QPA.std is automatically created in the Project Explorer. In addition to the structures, the corresponding cell formulas for the pure component phases are extracted and entered into the study table. A phase ID is assigned to each phase with the name being taken from the crystal structure file.

You may wish to examine or edit the refinement parameters settings for individual phases.

Click on the **Al2O3** row in the study table document **Powder QPA.std** to select it. Click the **Edit parameters** button for **Al2O3 parameters** on the Reflex Powder QPA dialog.

This opens the Phase Al2O3 dialog.

When a phase is loaded into the input study table, default settings for the refinement parameters are also imported. In the case of crystal structures, the lattice parameters, structural degrees of freedom, and atomic temperature factors are taken from the .xsd document. All the other non-structural refinement parameters, for example pattern parameters and sample parameters, are imported from Reflex.

On the **Pattern** tab of the Phase Al₂O₃ dialog, make sure that the appropriate checkboxes are checked to enable the refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and of the **Zero point Line shift**. The refinement of **2θ Background coefficients** should also be enabled.

On the **Lattice** tab, check on the refinement of the cell parameters **a**, **b** and, **c**, and check the **Keep fractional coordinates fixed during lattice changes** checkbox.

On the **Structure** tab, make sure that the checkboxes for all the structural degrees of freedom are switched off. Click the **OK** button.

Click anywhere in the study table document to deselect the **Al₂O₃** row.

For molecular crystals, it is advisable to keep the Cartesian coordinates fixed in order to avoid distortion of bond angles and distances in the asymmetric unit as a result of lattice parameter refinement. However, this is not possible for Al₂O₃ because the Al and O atoms are sitting in special positions, and therefore you need to preserve their fractional coordinates. This is very common for many inorganics. If you wish, you can continue to review the refinement settings for component phases Acetohexamide_FormA and Acetohexamide_FormB.

In the study table document **Powder QPA.std**, click the **Acetohexamide_FormA** row to select it. Click the **Edit** button for **Acetohexamide_FormA parameters** to open the Phase Acetohexamide_FormA dialog.

On the **Pattern** tab, check on refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and of the **Zero point Line shift**.

On the **Lattice** tab, check on the refinement of the cell parameters **a**, **b**, and **c**, and ensure that the checkbox of **Keep fractional coordinates fixed during lattice changes** is unchecked.

On the **Structure** tab, make sure that the checkboxes for all the structural degrees of freedom are switched off. Click the **OK** button.

Repeat the same procedure for Acetohexamide_FormB. Click anywhere in the study table document **Powder QPA.std** to deselect everything.

Tip: You can propagate the refinement settings from one structure document to any or all of the others in the input study table using the Export parameters to Powder Refinement and Import parameters from Powder Refinement functionalities on the *Phases* tab of the Reflex Powder QPA dialog. These tools allow Powder Refinement to be used as an intelligent clipboard - refinement settings for one structure can be sent to the Powder Refinement dialog, modified if required, and then imported into any or all of the other structures in the study table. Refinement parameters can be exported to or imported from Powder Refinement for crystal structures in the study table.

You should now check that the correct experimental powder pattern for the mixture is selected for the calculation.

Select the **Experimental Data** tab on the Reflex Powder QPA dialog. Make sure that **Acetohexamide_Mixture.xcd** is selected.

The background contribution of the mixture diffraction pattern can be fitted as part of the Powder QPA run. In this tutorial you will use the default setting of a *Polynomial order* equal to **20** to refine the background.

On the **Job Control** tab on the Reflex Powder QPA dialog, select **My Computer** as the **Gateway location**. Uncheck the **Automatic** checkbox and enter **no struct DOF** as the **Job description**.

Ensure that **Powder QPA.std** is the active document. Click the **Refine** button and close the Reflex Powder QPA dialog.

Close **Powder QPA.std** and click the **Yes** button when asked if you want to save the document as part of the project.

The Job Explorer informs you about the progress of the calculation. Once the calculation starts, a new folder called **no struct DOF Reflex QPA Job** is created in the Project Explorer. The parameter settings for this job are automatically saved in a file called **no struct DOF - Powder Diffraction**. The input experimental powder diffraction document and study table document are also listed in the folder.

After some time, a new text document, **Status.txt** appears, which gives a summary of the calculation as it currently stands. In addition, a chart document **no struct DOF.xcd** is created in the **no struct DOF Reflex QPA Job** folder to show the contribution of the individual pure phases to the input mixture powder pattern. These documents are updated regularly as the job progresses.

You should wait until the job finishes before proceeding. Depending on the specification of your computer, this may take several minutes.

Once the calculation is finished, the main output is inserted into the input study table document and displayed as the active document. The calculated dataset includes the weight fraction of each potential component phase in the experimental mixture and chart documents showing the contribution of each potential phase to the experimental mixture pattern. The weight fractions for FormA, FormB, and corundum are approximately 44%, 36%, and 20%, respectively.

Now examine the text output file.

In the Project Explorer, double-click on the text document **no struct DOF Reflex QPA Job\nno struct DOF.txt**.

The document contains all the calculation settings and a summary of the main results of the Powder QPA calculation. The R_{wp} value is quite large at about 36.3%. The integrated residual intensity is approximately 13.2%, which indicates that a significant amount of the intensity in the mixture powder diffraction pattern is not accounted for. Next, you should look at the chart file.

In the Project Explorer, double-click on the chart document **no struct DOF Reflex QPA Job\nno struct DOF.xcd**.

The intensity distributions of the simulated and experimental powder patterns are significantly different, confirming that the refinement has not been completed successfully. One reason for this is that the refinement has not been performed including the structural degrees of freedom parameter. Since there

is no prior knowledge of the potential phases, the Powder QPA job results indicate that the three input component phases are the major phases.

Next you will perform a second Powder QPA job, this time including the structural degrees of freedom parameter.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Open the **Reflex Powder QPA** dialog and select the **Phases** tab. In the Project Explorer, double-click on **no struct DOF Reflex QPA Job\no struct DOF.std** to make it your active document.

Select the **Al2O3** row in the **no struct DOF.std** Study Table Viewer. On the Reflex Powder QPA dialog click the **Edit** button for **Al2O3 parameters** to open the Phase Al2O3 dialog.

On the **Structure** tab, check the checkboxes for motion groups and all the torsions. Click the **OK** button.

Repeat the same procedure for **Acetohexamide_FormA** and **Acetohexamide_FormB**.

The structural degrees of freedom for Al2O3, Acetohexamide_FormA, and Acetohexamide_FormB are **2**, **12**, and **12**, respectively. All of the other settings, from the previous run, should remain unchanged. You are now ready to start the job.

Click anywhere in the study table document **no struct DOF.std** to deselect everything.

Select the **Job Control** tab from the Reflex Powder QPA dialog and enter **struct DOF** as the **Job description**.

Click the **Refine** button and close the dialog. Close **no struct DOF.std** and click the **No** button when asked if you want to save the changes to the document.

The Job Explorer informs you about the progress of the calculation. Depending on the specification of your computer, the calculation may take a few minutes since the total number of degrees of freedom has been increased.

When the calculation is complete, examine the results, starting with the study table document. The calculated weight fractions for Acetohexamide_FormA, Acetohexamide_FormB, and corundum are approximately **43.0%**, **38.7%**, and **18.3%**, respectively.

Next you will examine the text output.

In the Project Explorer, double-click on the text document **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF.txt**.

The R_{wp} value is about **21.5%**, this is a significant improvement on the R_{wp} value of **36.3%** which was obtained above without employing the structural degrees of freedom parameter in the refinement.

The integrated residual intensity has reduced to **4.5%**, which indicates that a majority of the intensity in the mixture has been attributed to the three component phases.

In the Project Explorer, double-click on the chart document, **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF.xcd**.

There is still a discrepancy between the intensity of the simulated and experimental powder diffraction patterns. There are several reasons which can account for this, one of them being preferred orientation. The lattice parameters of corundum are $a = b = 4.76 \text{ \AA}$, $c = 12.99 \text{ \AA}$. As the c-axis is about three times longer than the other two axes, the c^* -axis of the reciprocal unit cell is about three times shorter than the a^* -axis and the b^* -axis. Preferred orientation might be playing a role here. It is therefore appropriate to try a QPA calculation again, this time including a preferred orientation correction.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Open the **Reflex Powder QPA** dialog and select the **Phases** tab.

In the Project Explorer, double-click on **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF.std** to make it your active document. Select the **Al2O3** row of **struct DOF.std** and, on the Reflex Powder QPA dialog, click the **Edit** button for **Al2O3 parameters** to open the Phase Al2O3 dialog.

On the **Sample** tab, scroll down to **Preferred orientation**. Change the **Applied** correction from None to **March-Dollase** and check the checkboxes for **a***, **b***, **c*** and **R0**. Click the **OK** button.

Repeat the same procedure for **Acetohexamide_FormA** and **Acetohexamide_FormB**.

Tip: The Powder QPA results can vary slightly depending on the starting values of the preferred orientation a^* , b^* , and c^* . Experimental microscope data on crystal morphology can help provide some educated guesses on the potential preferred orientation. Alternatively, you can calculate the crystal morphology for a crystal structure using the Morphology module in Materials Studio.

In this tutorial, you will use the default values for the preferred orientation and coefficients. All of the other settings, from the previous run, should remain unchanged. You are now ready to start the calculation.

Click anywhere in the study table document **struct DOF.std** to deselect everything.

Select the **Job Control** tab from the Reflex Powder QPA dialog. Enter **struct DOF PO** as the **Job description**. Click the **Refine** button and close the dialog.

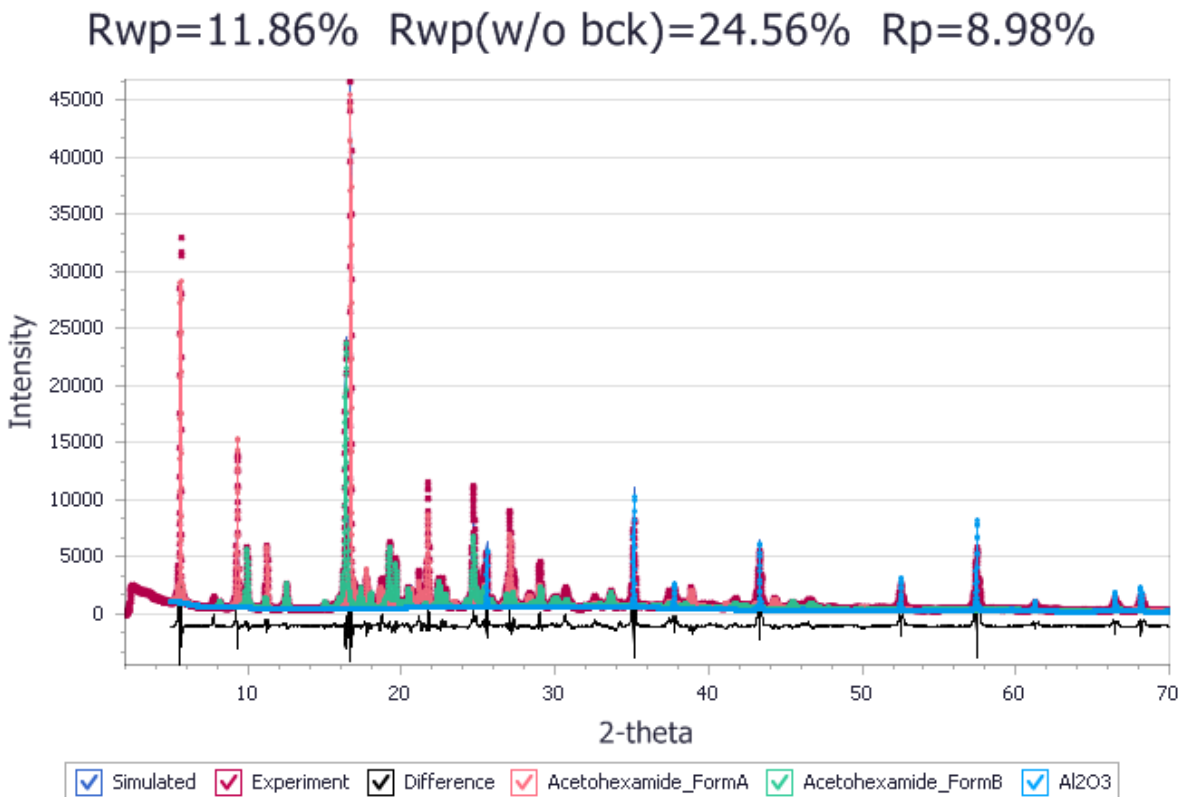
Close **struct DOF.std** and click the **No** button when asked if you want to save the changes to the document.

When the calculation is complete, examine the results, starting with the study table document. The results show that the weight fractions for Acetohexamide_FormA, Acetohexamide_FormB, and corundum are approximately 37.3%, 39.5%, and 23.2%, respectively. These values are in good agreement with the actual composition of 40%, 40%, and 20% for the respective phases.

Now examine the text output.

In the Project Explorer, double-click on the text document **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF PO Reflex QPA Job\struct DOF PO.txt**.

The R_{wp} value is about 11.8%, and the integrated residual intensity is about 1.4%. The overall intensity distribution of the experimental powder diffraction pattern is well reproduced, although some regions show intensity differences as indicated in the difference plot in the chart document below.



Comparison between the simulated powder pattern obtained by QPA and the experimental powder pattern of the mixture phase

You may wish to explore the effects of other refinement parameters, for example temperature factors, crystallite size broadening, or lattice strain broadening among others, on the final results of the weight fractions.

Note: The number of degrees of freedom can become quite large so that the information contained in the experimental powder diffraction pattern of the phase mixture may not be sufficient to uniquely determine all the refinable parameters. As a result, parameter or structure values may become unphysical, leading to incorrect results. To avoid this, it is recommended that you refine only those parameters that strongly affect the simulated diffraction pattern and include only those phases that make large contributions to the intensity of the powder diffraction pattern of the phase mixture.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To prepare the powder diffraction patterns with an internal standard

This section describes how to prepare the input files for an internal standard QPA calculation.

The internal standard method uses the experimental powder diffraction patterns of the potential pure component phases as input. A fixed weight fraction of a standard material (corundum in this tutorial) is added to all pure phases as well as the mixture phase before their powder diffraction patterns are recorded. In order to calculate the component weight fraction, the internal standard method requires that all the powder diffraction patterns are rescaled such that the scattering intensity contribution from

the standard is the same for all the patterns. This approach provides a means to correct for varying experimental conditions, sample adsorption, and matrix effects.

Note: The standardless method also uses the experimental powder diffraction patterns of the pure component phases as input. It differs from the internal standard method in that all the powder diffraction patterns must be recorded under identical experimental conditions. No scaling is required for the standardless method.

Start by importing the powder diffraction patterns for Acetohexamide Form A and Form B. Both patterns contain 20% corundum.

In the Project Explorer, click on the **QPA** project.

Open the Import Document dialog and select **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** directory, hold down the **CTRL** key and select **Acetohexamide_FormA.xcd**, **Acetohexamide_FormB.xcd**, and **corundum.xcd**. Click the **Open** button.

Next determine the scaling factor required for normalizing the powder diffraction patterns with respect to the internal standard. To do so, you will first calculate the integrated scattering intensity of the internal standard in any given powder diffraction pattern. The scale factor is calculated as the ratio of the target value for the diffraction contribution of the standard (an arbitrary but constant value for all the component phases and the mixture phase) and the calculated integrated scattering intensity of the standard.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

In the Project Explorer, double-click on **Acetohexamide_FormA.xcd** to make it the active document.

Open the **Reflex Powder QPA** dialog. On the **Phases** tab, click the **Add new phases** button to open the Add QPA Phases dialog. Select **corundum.xcd** and click the **Open** button.

A study table called Powder QPA (2).std is automatically created in the Project Explorer.

In the Project Explorer, right-click on **Powder QPA (2).std** and select **Rename** from the shortcut menu. Change the filename to **corundum_FormA**. The file extension **.std** is automatically appended.

Once you have loaded a pattern, you should prepare it in exactly the same way as you prepared the mixture pattern, so if you stripped out the $K\alpha_2$ peaks or smoothed the experimental mixture pattern, you should carry out the same procedure for the pure phase patterns.

When a powder diffraction pattern is inserted into a study table, you will need to manually enter the cell formula for each phase in the *Cell formula* column. Since you are only concerned about the integrated intensity of the corundum, instead of the weight fraction, at this point, you can proceed without entering the cell formula for corundum.

Note: When a phase is loaded into the input study table, default settings for the line shift refinement parameters are imported from the current settings in Reflex and applied to all phases that are added to the study table.

In the study table document, **corundum_FormA.std**, click on the row containing **corundum**.

On the **Phases** tab of the Reflex Powder QPA dialog, click the **Edit** button for **corundum parameters** to open the Phase corundum dialog. Make sure the checkbox for **Zero point** is checked on the Phase corundum dialog and click the **OK** button.

Click anywhere in the study table document **corundum_FormA.std** to deselect everything.

Select the **Experimental Data** tab on the Reflex Powder QPA dialog. Make sure that the chart document **Acetohexamide_FormA.xcd** is selected as the experimental powder diffraction data.

On the **Job Control** tab, enter **formA_scaled** as the **Job description**.

Click the **Refine** button and close the dialog.

Close **corundum_FormA.std** and click the **Yes** button when asked if you want to save the document as part of the project.

Note: Refinement parameters cannot be exported to Powder Refinement for powder patterns in the study table. However, you can import refinement settings from Powder Refinement for the powder patterns.

The calculation takes a few seconds. When it is complete, you should examine the results in the study table document.

The integrated intensity for corundum is **1.038259e+004**. Assuming the target value is 1000, the scale factor for the Acetohexamide_FormA powder diffraction pattern is calculated as below:

Scale factor (Acetohexamide_FormA) = $1000/1.038259e+004 = 0.096315081$

Tip: You can select the most appropriate part of the powder patterns for calculating the diffraction contribution from the standard by specifying the 2θ range and/or using excluded regions. For instance, to obtain intensity ratios for a single isolated peak, specify a simulation range comprising just this single peak.

Note: The individual calculated scale factors will strongly depend on the 2θ range used during the QPA analysis. However, the weight fractions calculated during internal standard QPA depend on the ratio of the scale factors only. It is essential that you normalize all patterns to the same value of the diffraction contribution of the standard and that you use the same 2θ range for quantitative phase analysis with an internal standard.

Repeat the same procedure to calculate the scale factors for **Acetohexamide_FormB.xcd** and **Acetohexamide_Mixture.xcd**, rename the study table documents **corundum_FormB** and **corundum_Mixture**.

Scale factor (Acetohexamide_FormB) = $1000/9.811742e+003 = 0.101918701$

Scale factor (Acetohexamide_Mixture) = $1000/1.141771e+004 = 0.087583237$

You are now ready to normalize the experimental powder diffraction patterns using the obtained scale factors.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

In the Project Explorer, double-click on **Acetohexamide_FormA.xcd** to make it your active document.

Open the **Reflex Pattern Processing** dialog. On the **Pattern Processing** tab, set the **Scaling factor** to **0.096315081** and click the **Scale** button.

A new chart document, **Acetohexamide_FormA (Scaled).xcd**, is created, in which the original powder diffraction pattern has been normalized using the scaling factor for **Acetohexamide_FormA**. You may calculate the contribution from background scattering and then subtract this background contribution. This is necessary if you wish to exclude the background calculation from the quantitative phase analysis. Since the background of a potential component phase pattern is not fitted in a Powder QPA calculation, you will subtract the background from the powder diffraction patterns for the pure component phases.

On the **Pattern Preparation** tab of the Reflex Pattern Processing dialog, in the **Background** section, increase the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document, **Acetohexamide_FormA (Scaled) (Background Removed).xcd**, is created, in which the background has been subtracted from the powder pattern.

In the Project Explorer, right-click on **Acetohexamide_FormA (Scaled) (Background Removed).xcd** and select **Rename** from the shortcut menu. Change the filename to **Acetohexamide_FormA (Prep).xcd**. Repeat the same procedure for **Acetohexamide_FormB.xcd**.

It is not recommended to subtract the background from the experimental mixture phase pattern. Instead, the full pattern should be used for evaluating the R_{wp} figure of merit during the QPA optimization. The background contribution of the mixture diffraction pattern should be fitted as part of a QPA run.

In the Project Explorer, double-click on **Acetohexamide_Mixture.xcd** to make it the active document.

On the **Pattern Processing** tab of the Reflex Pattern Processing dialog, set the **Scaling factor** to **0.087583237** and click the **Scale** button.

Close the Reflex Pattern Processing dialog.

5. To set up, run, and analyze the results for the internal standard QPA

In this section, you will perform a Powder QPA calculation using the internal standard method. First you will prepare an input study table document.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Open the **Reflex Powder QPA**. On the **Setup** tab, set the **Type** to **Full refinement** and check the **Patterns contain internal standard** checkbox.

On the **Phases** tab, click on the **Add new phases** button to open the Add QPA Phases dialog. Hold down the **CTRL** key, select **Acetohexamide_FormA (Prep).xcd** and **Acetohexamide_FormB (Prep).xcd**, and click the **Open** button.

A study table called **Powder QPA (2).std** is automatically created in the Project Explorer.

In the Project Explorer, right-click on **Powder QPA (2).std** and select **Rename** from the shortcut menu. Change the filename to **Patterns_internstd.std**.

Note: If you are using powder patterns from samples containing an internal standard, cell formula information is not required to calculate weight fractions.

Note: If you use standardless QPA and the cell formula is not known for any of the potential component phases, it is still possible to run a Powder QPA calculation to obtain the intensity fractions. However, weight fractions will not be calculated for any phases for which the cell formula is not given in the input study table.

Select the **Experimental Data** tab on the Reflex Powder QPA dialog. In the Project Explorer, double-click on **Acetohexamide_Mixture (Scaled).xcd** to make it the active document. Make sure that the chart document **Acetohexamide_Mixture (Scaled).xcd** is selected as the experimental powder diffraction data.

On the **Job Control** tab, enter **internal standard** as the **Job description**.

Make **Patterns_internstd.std** the active document.

Click the **Refine** button and close the dialog.

Close **Patterns_internstd.std** and click the **Yes** button when asked if you want to save the document as part of the project.

When the calculation is complete, examine the results, starting with the study table document. The results show that the weight fractions for Acetohexamide_FormA and Acetohexamide_FormB are approximately **39.5%** and **48.1%**, respectively.

Note: Absolute weight fractions may be obtained using the internal standard method, even in cases where not all the pure phases are known or included in the analysis.

For the internal standard QPA method, the reported weight fractions are not normalized to 100% over all phases for which the cell formula information was provided.

For the standardless QPA method, the reported weight fractions are normalized to 100% over all the phases for which the cell formula information was provided. Since these weight fractions cannot take account of any phases for which the cell formula was not supplied, they would not represent the actual absolute weight fraction in the mixture. However, the ratio of the weight fraction of two component phases will still be the same as would be observed in the whole mixture.

In this tutorial, the sum of the total weight fraction is 87.6%.

The underestimation might be due to:

- missing pure component phases
- errors associated with the scaling factors
- preferred orientation
- treatment of background
- micro absorption effects
- crystallinity of the internal standard

A missing component phase is not likely to be the reason in this case, since the integrated residual intensity is only 0.9% (see below). Phases with a higher linear absorption coefficient may display microabsorption effects, which invariably yield an underestimate of the phase weight.

The individual calculated scale factors will strongly depend on the 2θ range used during the QPA analysis. There is no rule of thumb on how to select the 2θ range. The single peak method is widely used in the industry. However, preferred orientation is the major source of variation for this method. In this tutorial, the full powder diffraction pattern corundum was used for the estimation of the scaling factors. Therefore preferred orientation is somewhat compensated.

Higher order polynomials are usually used to model background. However, the extent of the correction is hard to control. A larger number allows a more accurate background fit. However, if the number chosen is too large, the background function may try to model individual peak shapes, which is undesirable. Furthermore, the correlations between the background polynomial coefficients and other parameters are largely unknown, although the polynomial coefficients have been shown to affect displacement parameters.

Now examine the text output.

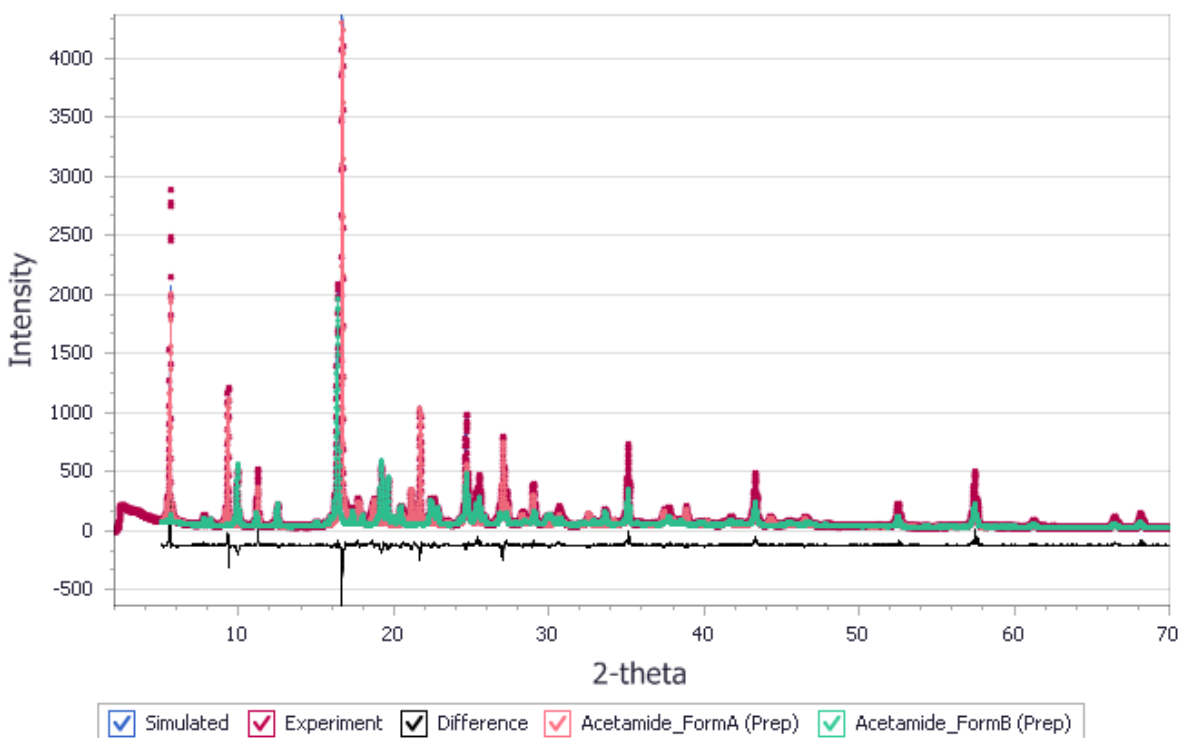
In the Project Explorer, double-click on the text document **internal standard Reflex QPA Job\internal standard.txt**.

The R_{wp} value is about 9.6%. The integrated residual intensity is 0.9%, which indicates that a majority of the intensity in the mixture has been accounted for within the two component phases.

In the Project Explorer, double-click on the chart document **internal standard Reflex QPA Job\internal standard.xcd** to examine its content.

The overall intensity distribution of the experimental powder diffraction pattern is well reproduced, although some regions show intensity differences as indicated in the difference plot in the chart document below.

Rwp= 9.62% Rwp(w/o bck)=14.04% Rp=7.12%



Comparison between the simulated powder pattern obtained by QPA and the experimental powder pattern of the mixture phase

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank G. Stephenson, G. Clanton, and B.A. Diserod from Eli Lilly for supplying the experimental data.

Reflex Plus tutorials

The following tutorials illustrate how to utilize Powder Solve's capabilities.

- [Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus](#)
- [Structure solution in the presence of preferred orientation and energetic considerations in structure refinement](#)
- [Structure solution of the inorganic compound FIN31](#)
- [Structure solution of 4-nitrophenylhexylurethane using a close-contacts penalty](#)

Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus

Purpose: Introduces the Powder Solve tool and illustrates how it is used to solve crystal structures from experimental powder diffraction data.

Modules: Materials Visualizer, Reflex Plus, Forcite

Time: 🕒 🕒

Prerequisites: [Indexing powder patterns](#)

Background

Reflex Plus in Materials Studio is a module for determining a crystal structure from powder diffraction data. Structure determination using Reflex Plus is a four-step process. The steps are indexing, Pawley fitting, structure solution, and Rietveld refinement.

In the first step, the crystal class and approximate lattice parameters are derived from the peak positions in the powder diffraction pattern, using either TREOR90 ([Werner et al., 1985](#)), DICVOL91 ([Boultif and Louër, 1991](#)), ITO15 ([Visser, 1969](#)), or X-Cell ([Neumann, 2003](#)).

Next, accurate lattice constants and various parameters related to the experimental setup and the texture of the sample are determined by Pawley fitting. The refined parameters include the zero point shift of the diffractogram, background parameters and profile parameters. All peak intensities are treated as independent parameters at this stage and are not related to the unit cell contents. The peak intensities obtained by Pawley refinement can be used to automatically determine the most likely space groups in the given crystal system ([Markvardsen et al., 2000](#)).

In the third step, the atomic arrangement in the asymmetric unit is determined with Powder Solve ([Engel et al., 1999](#)). Powder diffraction patterns are calculated for a large number of trial structures and compared to the experimental powder pattern. The trial structures are generated using a Monte Carlo/simulated annealing algorithm or a Monte Carlo/parallel tempering algorithm.

Both approaches are designed to locate the global minimum of the weighted R-factor, R_{wp} , which is a measure of the similarity between the experimental powder data and the simulated powder patterns. Lattice symmetry is explicitly taken into account. The atoms in the asymmetric unit are gathered together into motion groups. Each motion group is described by three translational and three rotational degrees of freedom, as well as a certain number of torsional, angular, and distance parameters.

Typically, each molecular fragment in the asymmetric unit corresponds to a motion group. Apart from the specified torsional, angular, and distance degrees of freedom, the conformation of each motion group has to be determined prior to structure solution using potential energy calculations or structural

information from related crystal structures. In the Monte Carlo search, only the specified translational, rotational, torsional, angular, and distance degrees of freedom of the motion groups are considered. Structure solution has to be attempted separately for all relevant space groups.

Finally, the result of the structure solution step is further improved by Rietveld refinement.

Introduction

This tutorial shows how the Powder Solve tool can be used to solve a crystal structure from powder diffraction data, in Materials Studio. You will learn how to index a powder pattern, perform a Pawley refinement, select a space group, supply a molecular model, solve the crystal structure and perform a final Rietveld refinement.

In this tutorial you will use the experimental powder diffraction data provided to solve the crystal structure of 3-chloro-trans-cinnamic acid (CTCA). You will run the structure solution stage three times to see the effect of using different degrees of freedom.

This tutorial covers:

- [Getting started](#)
- [To index the diffraction pattern](#)
- [To carry out Pawley refinement and select the space group](#)
- [To sketch and optimize the molecule](#)
- [To solve the crystal structure using torsional degrees of freedom](#)
- [To solve the crystal structure using torsional and angular degrees of freedom](#)
- [To solve the crystal structure using torsional, angular, and distance degrees of freedom](#)
- [Rietveld refinement](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **structure_solution** as the project name, click the **OK** button.

The new project is created with *structure_solution* listed in the Project Explorer. Now you will import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click on **3-Chloro-trans-cinnamic_acid.3cam**.



In the Project Explorer, right-click on **3-Chloro-trans-cinnamic_acid.xcd** and select **Rename** from the shortcut menu. Change the filename to **CTCA**. The file extension **.xcd** is automatically appended.

2. To index the diffraction pattern


Next, identify the peaks that will be used to index the pattern. To facilitate the automatic peak search, you must first subtract the background and smooth the powder diffraction pattern. This can be done as part of the peak picking process.

Choose **Modules | Reflex | Powder Indexing** from the menu bar to open the Reflex Powder Indexing dialog. On the **Peaks** tab, change the **Low amplitude cutoff** to **1**. Check the **Eliminate background during search** and **Smooth** checkboxes, and set the **Width** to **0.05**. Click the **Search** button.

For indexing it is very important to select all diffraction peaks in the low angle region of the diffraction pattern and to avoid picking features that do not correspond to diffraction peaks. Therefore, you should always inspect the results of the automatic peak search, visually.

Use the **Zoom**  and **Translation**  tools to examine the powder diffraction pattern in the range 4° to 20°.

See the Chart mouse and keyboard actions topic for more information about how to manipulate charts.

If changes are necessary, you can add and move peaks using the *Chart Viewer Marker Mode* . However, in this case, no changes are required.

Now you are ready to index the powder diffraction pattern.

Select the **Setup** tab on the Reflex Powder Indexing dialog. Select **TREOR90** from the **Program** dropdown list and **check** all the **Crystal systems to test** checkboxes.

The diffraction pattern was measured using copper radiation so you do not have to change the default wavelength in this case.

Click the **Index** button.

After TREOR90 has finished, a Study Table document opens, containing the results of the indexing procedure. Examine the results. The quality of the proposed unit cell is measured by the figure of merit (FOM).

In the case of CTCA, the correct unit cell belongs to the monoclinic crystal system and has a volume of about 856 Å³, with $a \sim 14.0$ Å, $b \sim 5.0$ Å, $c \sim 12.4$ Å and $\beta \sim 94^\circ$.

Using the result from TREOR90, it is possible to generate a 3D model of the empty unit cell.

Make the new Study Table the active document. On the **Reflex Powder Indexing** dialog, click the **Create Cell** button.

A new 3D Atomistic document called CTCA1.xsd is created, containing an empty unit cell matching the solution from the powder indexing run.

In the Project Explorer, rename **CTCA1.xsd** to **CTCA**.

Move the file to the top level of the project by dragging it onto the **structure_solution** item at the top of the project tree.

3. To carry out Pawley refinement and select the space group

In a Pawley refinement, all peak intensities are treated as variable parameters and adjusted together with background parameters, profile parameters, cell parameters and the zero point shift of the diffraction pattern to obtain the best possible agreement between a simulated and the experimental diffraction pattern.

Using Pawley refinement, the correctness of the unit cell can be verified easily, since an incorrect unit cell will, in general, result in significant differences between the simulated and the experimental powder patterns. The space group associated with the unit cell should have no systematic absences at this point and by default, the lattice symmetry of a monoclinic unit cell is set to P2.

The fitting algorithm is stable enough to refine all parameters simultaneously.

Select the **Space Groups** tab on the **Reflex Powder Indexing** dialog and click the **Refine...** button to open the Reflex Powder Refinement dialog.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Change the **Number of cycles** from 2 to **5** and click the **OK** button.

Changing the *Number of cycles* automatically changes the *Convergence quality* setting from *Medium* to *Customized*.

The experimental data were measured with copper λ_1 radiation only.

On the **Radiation** tab uncheck the λ_2 checkbox.

On the **Pattern** tab select the **Pseudo-Voigt** function from the **Peak profiles** dropdown list. Switch on the refinement of the profile parameters **U**, **V**, **W**, **NA** and **NB** and the **Zero point Line shift**.

Change the **Asymmetry Correction** from None to **Berar-Baldinozzi** and enable the refinement of the parameters **P1**, **P2**, **P3** and **P4**. The refinement of 20 background coefficients is switched on by default.

Make sure that the 3D Atomistic document containing the empty unit cell is active and on the **Lattice** tab, switch on the refinement of all the cell parameters.

Select the **Display** tab and check **Display simulation/experiment difference**.

On the **Exp. Data** tab, select **Pattern 1** from the chart document CTCA.xcd.

Click the **Refine** button.

Note: By default, Pawley or Rietveld refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run synchronously** from the **Job Control** tab.

While the Pawley refinement is carried out, the cycle number and the current R_{wp} value are shown at the bottom of the Materials Visualizer window. After five cycles, the R_{wp} value should be about 7.0%. At the end of the calculation, a new chart document is displayed.

Compare the simulated and the experimental powder patterns.

The agreement between the calculated and the experimental powder pattern should be good, confirming that the unit cell is correct.

The final R_{wp} value is displayed at the top of the chart document. R_{wp} (w/o bck) is the weighted Rietveld parameter calculated after the background has been subtracted.

Now identify the space group to which the crystal structure is likely to belong. Reflex provides functionality to estimate the likelihood of all space groups in a given crystal system, based on the intensities obtained by Pawley refinement.

Ensure that **CTCA.xsd** is the active document and click the **Search** button on the **Space Groups** tab of the Reflex Powder Indexing dialog.

A study table document is generated, in which all monoclinic space groups are ranked according to their figure of merit. The space group with the highest figure of merit is P 21/c, the monoclinic space group most frequently observed in nature. You should now generate a 3D Atomistic document containing the unit cell with the correct space group settings.


Select the first row of the study table document **CTCA.std**. Click the **Create Cell** button on the Reflex Powder Indexing dialog.

A new 3D Atomistic document, **CTCA1.xsd**, is created. Using this document, you should now repeat the Pawley refinement in the chosen space group.

Click the **Refine** button on the Reflex Powder Refinement dialog.

Once again, the simulated and the experimental powder diffraction pattern should be in excellent agreement. You should obtain a R_{wp} value of about 7%.

With each new Pawley refinement, the parameters describing the diffraction profile are modified. Sometimes, it is helpful to save the current set of parameters for later use.

Click the **Reflex** arrow  on the **Modules** toolbar and select **Save Settings...** from the dropdown list to open the **Save Reflex Settings** dialog. Enter **CTCA** and click the **OK** button.

A settings document called **CTCA - Powder Diffraction** is created and placed in the current project. By double-clicking on this file in the Project Explorer, the corresponding parameters can be loaded.

Before you go on to the next section of this tutorial, you should save the results obtained so far.

Close the Reflex Powder Indexing and Reflex Powder Refinement dialogs. Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To sketch and optimize the molecule

You now have to create a model of the molecule that you want to use in the structure solution step.

In the **Project Explorer**, right-click on **structure_solution** and choose **New | 3D Atomistic Document** from the shortcut menu. Change the filename of the new model document to **molecule**. The **.xsd** file extension is automatically appended.

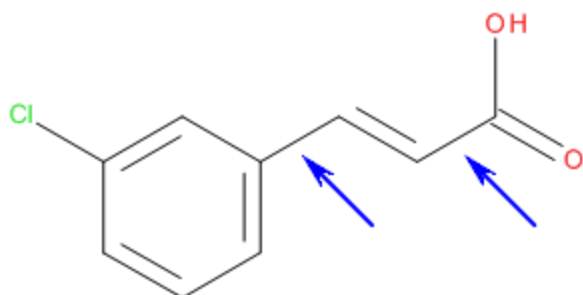
Use the **Sketch** tools to sketch a molecule of CTCA, adjust the hydrogens, and clean the geometry.

See 3D Sketcher for more information about sketching.

To make things easier later on, you should move the molecule so that its center of geometry will automatically fall inside the unit cell when it is placed in the crystal.


Select **View | Explorers | Properties Explorer** from the menu bar to display the Properties Explorer. Select **Molecule** from the **Filter** dropdown list. Inspect the coordinates shown for the **CenterOfGeometry**. Double-click on any atom in the molecule to select all the atoms. Press the **ALT + SHIFT** keys and use the right mouse button to move the molecule so that each of the CenterOfGeometry coordinates is in the range 0.0 to 2.0.

The figure below shows the molecular structure of CTCA with two specific flexible torsion angles marked.



Molecular structure of CTCA showing flexible torsion angles

Structure solution by Monte Carlo methods or simulated annealing requires that the molecular geometry, apart from the flexible torsion angles, is determined prior to the structure solution step. You should now therefore optimize the molecular geometry using the COMPASS forcefield in Forcite.

Click the **Forcite** arrow  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the Forcite Calculation dialog.


On the **Setup** tab select **Geometry Optimization** from the **Task** dropdown list and on the **Energy** tab set the **Forcefield** to **COMPASS**.

Click the **Run** button.

The results of the calculation are placed in the new folder, molecule Forcite GeomOpt.

Close the Forcite Calculation dialog and the text document **molecule Forcite GeomOpt\molecule.txt**.

The 3D Atomistic document, molecule Forcite GeomOpt\molecule.xsd should now be active. This model contains the optimized molecular geometry. The O-H bond of the hydroxyl group should be roughly parallel to the closest C-C bond. Depending on the starting point for the geometry optimization, this may not be the case. The orientation of the hydrogen atom is not important for the structure solution step because X-ray scattering from hydrogen atoms is weak. However, since a non-parallel configuration is rather unlikely, you should make sure that the O-H bond adopts a parallel conformation.


Click the **Measure/Change** arrow  and select **Torsion** from the dropdown list. Click on the C-O bond next to the O-H bond to create a torsion monitor.

In the **Properties Explorer**, select **Torsion** from the **Filter** dropdown list. Double-click on the value for **Angle** to open the Edit Angle dialog. Enter **180°** or **0°**, depending on which value is appropriate, and click the **OK** button.

Click the **Selection** button . Select the **torsion monitor** in the model window and press the **DELETE** key.

Close the **Properties Explorer**.

You should prepare the molecule by marking the two flexible torsions as shown on the diagram [above](#).

Click the **Measure/Change** arrow . Click on each of the two flexible C-C bonds, as indicated in the diagram above to create two new torsion monitors.

Click the **Selection** button .

5. To solve the crystal structure using torsional degrees of freedom

You first have to introduce the CTCA molecule into the empty unit cell and select the degrees of freedom that are to be varied during the structure solution search.

Click in the 3D Viewer for **molecule Forcite GeomOpt/molecule.xsd** and press the **CTRL + C** keys.

In the **Project Explorer**, double-click on **CTCA1.xsd** to open the 3D Viewer containing the empty unit cell. Press the **CTRL + V** keys to paste the molecule into the unit cell.

Application of the space group symmetry generates four copies of the molecule in the unit cell. The molecule has already been prepared to contain the torsion definitions but you still have to define each molecule as a motion group. A motion group is a set of atoms described by the same translational and rotational degrees of freedom in the structure solution search.

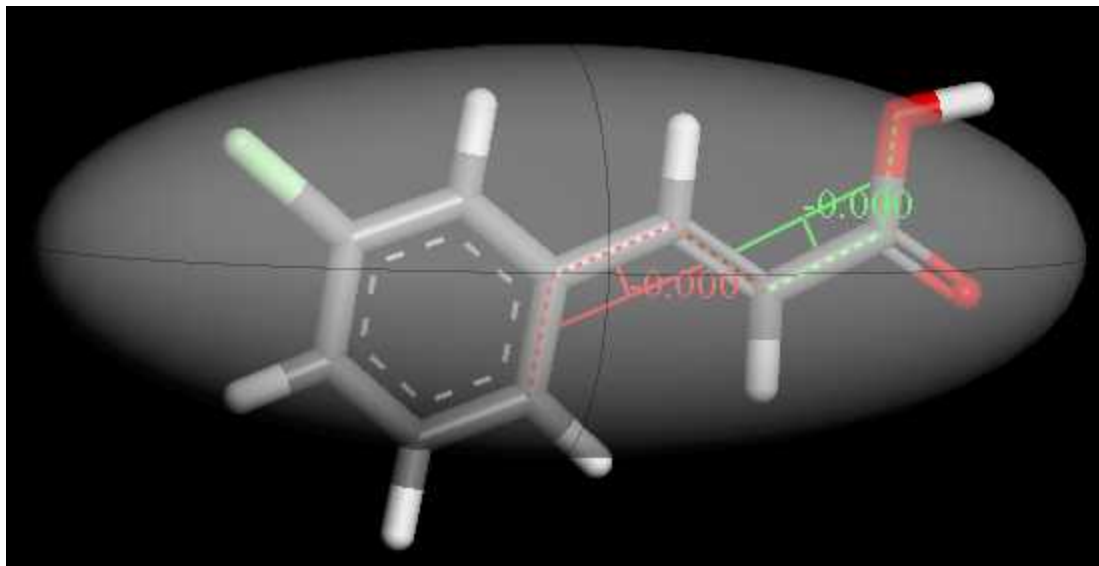
Select **Modules | Reflex | Powder Solve** from the menu bar to open the Reflex Powder Solve dialog.

In the 3D Viewer for **CTCA1.xsd**, select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu, to select one complete molecule.

In the **Reflex Powder Solve** dialog, select the **Structure Params** tab and click the **Create motion group(s)** button, ensuring that the **selection** is set to **Single group**.

Click anywhere in the 3D Viewer to deselect everything.

After you have defined the motion groups, the molecule should look like the one shown below, although the torsion angles may be slightly different.



CTCA molecule defined as a motion group with two torsional degrees of freedom.

All degrees of freedom are summarized in the *Structure Params* tab.

Ensure that all of the refinement checkboxes on the **Structure Params** tab are checked.

The amount of CPU time per Monte Carlo step is approximately proportional to the number of atoms, and X-ray scattering from hydrogen atoms is fairly weak compared to other elements. By ignoring scattering from hydrogen atoms, the speed of the calculation can be increased significantly. On the other hand, neglecting the weak contribution of scattering from hydrogen atoms to the total scattering intensity introduces a small additional error that can make structure solution more difficult. There is no clear rule whether scattering from hydrogen atoms should be taken into account or not. In this tutorial, scattering from hydrogen atoms will be neglected in the structure solution step, but will be included in the final refinement step.

Uncheck the **Use hydrogens** checkbox.

The experimental powder diffraction pattern was selected in the Pawley refinement step. However, sometimes you may wish to verify that you are using the right data set.

On the **Experimental Data** tab make sure that **Pattern 1** of the chart document CTCA.xcd is selected as the experimental powder diffraction data.

The Monte Carlo/simulated annealing procedure in Powder Solve is governed by several parameters, including the start temperature, the final temperature, the step width and the number of Monte Carlo steps. By default, all of these parameters are estimated automatically from the number of degrees of freedom and the roughness of the R_{wp} hypersurface. Because of the stochastic nature of the Monte Carlo/simulated annealing approach, there is no guarantee that the structure solution will be found in a single Monte Carlo simulated annealing cycle. The Monte Carlo/simulated annealing procedure should therefore be repeated several times.

On the **Setup** tab select **Simulated Annealing** from the **Method** dropdown list in the **Solve** section and set the **Number of cycles** to **10**.

Usually the number of steps is calculated automatically depending on the number of degrees of freedom, but in this tutorial, to achieve speedy results, a fixed number of steps will be used.

Make sure that the 3D Viewer for **CTCA1.xsd** is active. Examine the number of steps proposed by the automatic calculation.

Uncheck the **Automatic** checkbox and set the **Number of steps** to **100000**.

Click the **More...** button for the **Method** on the **Setup** tab to open the Powder Solve Options dialog.

The highest temperature, the lowest temperature, and the step width will be determined automatically. The values of these parameters are not yet indicated, since they will be calculated at the beginning of the Monte Carlo/simulated annealing run.

Close the **Powder Solve Options** dialog.

Powder Solve makes use of the client-server architecture implemented in Materials Studio. If your PC is connected to other computers on a network, it is possible to set up gateways to these computers and run the calculation remotely, thus avoiding using the resources of your own PC. Your own PC is probably set up as a server, and the gateway "My Computer" will be used by default.

By default, the current structure is written to a trajectory file each time that a new, best R_{wp} value is obtained in the current cycle. At the end of the calculation, the best solutions found in each cycle can be extracted from the trajectory file.

You are now ready to start Powder Solve.

Ensure that the 3D Viewer for **CTCA1.xsd** is active. Click the **Solve** button.

The Job Explorer informs you about the progress of the calculation. After some time, two chart windows will be displayed. While the calculation is running, you may wish to rearrange the open documents and close some of them.

Select **File | Save Project** from the menu bar.

Close all documents, other than those starting with **CTCA1 Reflex PSolve...**

Examine the output in the two chart windows.

After the calculation has finished, the best crystal structure found is shown in the 3D Atomistic document **CTCA1 Reflex PSolve\CTCA1 Solution.xsd**.

The best crystal structure obtained at the end of several Monte Carlo simulated annealing cycles is not necessarily the right structure solution. The true crystal structure may have been missed because an insufficient number of cycles were performed or because the search was not carried out in the right space group. It is also possible for the structure solution to fail because the bond lengths and bond angles in the molecular model were not determined accurately enough prior to the structure solution step. To decide whether or not the crystal structure has been solved, the best proposed crystal structure has to be examined carefully.

To start with, you should compare the calculated and the experimental powder patterns.

In the **Project Explorer**, double-click on the chart document **CTCA1 Reflex PSolve\CTCA1 Solution.xcd**. Compare the calculated and experimental diffraction patterns visually.

The overall intensity distribution of the simulated and the experimental powder patterns should look very similar, even though there are significant differences for some of the diffraction peaks. The R_{wp}

value should fall around 19%, approximately 2.5 times larger than the value obtained by Pawley refinement. The exact R_{wp} value of the best crystal structure depends to a certain extent on the molecular conformation for which the forcefield optimization was carried out.

Since all peak intensities are independent parameters in the Pawley refinement, the R_{wp} value resulting from it is a lower limit for the R_{wp} value obtained for the structure solution. So, although a difference of 2.5 times between these values after structure solution is quite large, it is not uncommon. Visual inspection of the calculated and the observed diffraction pattern indicates that the crystal structure has been solved.


Another criterion which should be used to assess the success of a structure solution is the number of cycles in which the best solution has been found. If the best solution has been obtained several times and the corresponding R_{wp} value is significantly lower than the best R_{wp} value observed in the other cycles, it can be assumed that the global minimum on the R_{wp} -hypersurface has been found. If, however, the best solution has been found only once and several other cycles result in different crystal structures with similar R_{wp} values, it is likely that the R_{wp} -hypersurface has not been sampled correctly. In these circumstances the calculation should be repeated with a higher number of Monte Carlo steps per cycle and/or a higher number of cycles.

In the **Project Explorer**, double-click on the text document **CTCA1 Reflex PSolve\CTCA1.txt** and examine its contents.

The solution with the lowest R_{wp} value has been found in several cycles. Differences of about 0.1% are negligible. Therefore you can assume that the global optimum has been found.

Finally, you should examine the crystal structure that corresponds to the best solution, concentrating on atomic overlap and the hydrogen bonding scheme.

In the **Project Explorer**, double-click on the 3D Atomistic document **CTCA1 Reflex PSolve\CTCA1 Solution.xsd**.

Click the **Calculate Hydrogen Bonds** arrow  and select **Hydrogen Bond Options** from the dropdown list to open the Hydrogen Bond Calculation dialog. Select **N, O, S + Halogens + C as Donor** as the H-bonding scheme and click the **Calculate** button. Close the dialog.

Examine the crystal structure.

To increase the lattice display range in order to get a better appreciation of the hydrogen bonding network, right-click in the 3D Viewer and choose **Display Style** from the shortcut menu to open the Display Style dialog.

Increase the lattice display range in the a, b and c directions on the **Lattice** tab.

Visual inspection should not reveal any significant atomic overlap. The CTCA molecules pack together forming hydrogen bonded dimers. The crystal structure looks very plausible and it is appropriate to conclude that the crystal structure has indeed been solved.


You may also wish to look at other structures generated during the structure search.

In the **Project Explorer**, double-click on the trajectory document **CTCA1 Reflex PSolve\CTCA1.xtd**.

Open the **Reflex Powder Solve** dialog and select the **Analysis** tab. Click the **Analyze** button and close the dialog.

A chart has been generated showing the R_{wp} values of the crystal structures in the trajectory file. Each new cycle starts with a high R_{wp} value that decreases monotonically throughout the cycle.

Ensure that the chart with the R_{wp} values and the trajectory document **CTCA1 Reflex PSolve\CTCA1.xtd** are both visible in the workspace.

Choose the **Selection**  tool from the Chart Viewer toolbar. Click on data points in the chart document to show the corresponding crystal structures in the trajectory document.

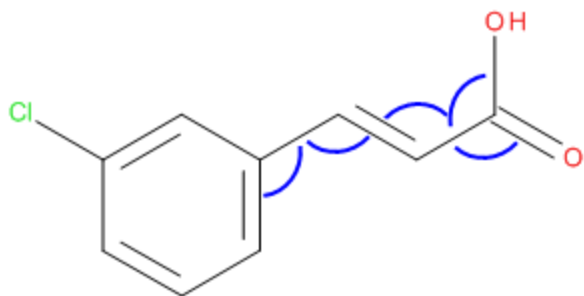
Before finishing this section, you should save the results obtained so far.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

6. To solve the crystal structure using torsional and angular degrees of freedom


In this section you will perform a second Powder Solve calculation, this time allowing flexibility in significant angles in the structure. In Powder Solve angular and distance degrees of freedom are treated slightly differently from torsional degrees of freedom. Torsional degrees of freedom are allowed to vary through the complete 360° range, so the initial value is not important. However, angular and distance degrees of freedom are each allowed to vary by only a small amount relative to their initial value, so it is important that the initial configuration has these values reasonably optimized. By default, angles are allowed to vary by up to 10° from their initial values and distances are allowed to vary by up to 10% of their initial values. These defaults are generally satisfactory although the solution should be checked to see if any distances or angles are at the extreme ends of their permitted ranges.

You now have to prepare the molecule with the desired angles marked as well as the torsions. These angles are those shown in the figure below.



Molecular structure of CTCA showing angles for variation

Open the document **molecule Forcite GeomOpt\molecule.xsd**.

Click the **Measure/Change** arrow  and select **Angle** from the dropdown list. Create an angle monitor for each of the five angles shown above, in addition to the torsions that are present from the previous stage.

Click the **Selection** button .

You will create a new crystal structure containing the modified molecule as the basis for the new Powder Solve calculation.

In the **Project Explorer**, double-click on **CTCA.std** to open the study table showing all the monoclinic space groups.

Select the first row of the study table document. Open the **Reflex Powder Indexing** dialog and click the **Create Cell** button.

A new 3D Atomistic document called **CTCA1 (2) .xsd** is created. This should be renamed and then you will paste in the prepared molecule.

Rename **CTCA1 (2).xsd** to **CTCA2**. The file extension **.xsd** is automatically appended.

Click in the 3D Viewer for **molecule Forcite GeomOpt/molecule.xsd** and press the **CTRL + C** keys.

In the 3D Viewer for **CTCA2.xsd** press the **CTRL + V** keys to paste the molecule into the unit cell.

You should repeat the procedures used in [section 5](#) to define the motion groups and to ensure that all of the refinement checkboxes on the **Structure Params** tab are checked.

You should see that there are 13 degrees of freedom defined and that all of them can be refined. You are now ready to run Powder Solve again.

Click the **Solve** button.

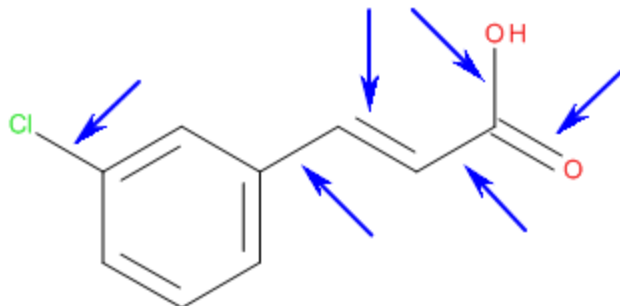
When the job has completed select **File | Save Project** from the menu bar.

When the job has finished you can compare the results with those obtained previously where the torsions were the only degrees of freedom within the motion groups. As expected, because there are more degrees of freedom a better fit to the experimental data is obtained. The R_{wp} value obtained from this run should be about 16.8%. However because no account was taken of possible close contacts or energetic considerations you should assess for yourself (such as by checking close contacts or hydrogen bonding patterns) whether the solution presented is viable.

7. To solve the crystal structure using torsional, angular, and distance degrees of freedom


As well as varying angles it is also possible to vary bond distances in a motion group, although if the original molecular structure is well optimized you will probably see little improvement.

You will prepare the molecule with the desired distances marked as well as the torsions and angles. The desired distances are those shown in the figure below.



Molecular structure of CTCA showing distances for variation

Open the document **molecule Forcite GeomOpt\molecule.xsd**.

Click the **Measure/Change** arrow  and select **Distance** from the dropdown list. Create a distance monitor for each of the six distances shown above, in addition to the torsions and angle monitors from the previous stages.

Click the **Selection** button .

Follow the remainder of the steps in [section 6](#). You should rename the new 3D Atomistic document to **CTCA3.xsd**.

You will see that there are now 19 refinable degrees of freedom. With this number of degrees of freedom you should ideally use more steps in the Powder Solve process, but the current value will suffice for this tutorial. However when the job completes you might notice that the best solution has been found in fewer cycles than when only torsions were being refined, showing less confidence that the solution found corresponds to the global minimum. In this case the best solution should be about 16.3%, a slight improvement on that with just torsions and angles being refined. As previously, you should assess for yourself whether this solution is viable.

Before finishing this section, you should close some windows.

Select **File | Save Project** from the menu bar and close all dialogs.

Close all windows apart from **CTCA3 Reflex PSolve\CTCA3 Solution.xsd** and **CTCA.xcd**.

8. Rietveld refinement

In Rietveld refinement, various parameters are optimized simultaneously to improve the agreement between the calculated and the experimental powder diffraction pattern. You should start by refining profile parameters, background parameters, the cell constants, the zero point shift of the diffraction pattern, the position and orientation of motion groups and torsion angles.

Prepare a new 3D Atomistic document for Rietveld refinement.

In the Project Explorer select **CTCA3 Reflex PSolve\CTCA3 Solution.xsd** and right-click, select **Copy** from the shortcut menu.

In the **Project Explorer**, right-click on **structure_solution** and choose **Paste** from shortcut menu. Rename the new copied document to **CTCA_Rietveld**.

Select **File | Save Project** from menu bar.

Now you will set up the Rietveld refinement.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, change the **Type** of refinement from Pawley to **Rietveld**.

Examine the various tabs on the **Reflex Powder Refinement** dialog. By default, all parameters varied earlier on in the Pawley refinement and the structure solution search should be selected for refinement.

On the **Structure** tab, check the **Use hydrogens** checkbox.

Ensure that the 3D Atomistic document **CTCA_Rietveld.xsd** is active. On the **Lattice** tab switch on the refinement of all the cell parameters and check the **Keep fractional coordinates fixed during lattice changes** checkbox.

Click the **Refine** button.

The Rietveld refinement should decrease the R_{wp} value by about 2% - 3%. The R_{wp} value can be further improved by increasing the number of refined parameters. However, the crystal structure determination of CTCA is effectively complete.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Boultif, A.; Louër, D. "Indexing of Powder Diffraction Patterns for Low-Symmetry Lattices by the Successive Dichotomy Method", *J. Appl. Cryst.*, **24**, 987-993 (1991)

Engel, G.E.; Wilke, S.; Harris, K.D.M.; Leusen, F.J.J. *J. Appl. Cryst.*, **32**, 1169 (1999).

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Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

Purpose: Illustrates how the March-Dollase correction implemented in Reflex Plus enables you to solve structures using data with strong preferred orientation, and how the incorporation of energy information into an all-atom Rietveld refinement process allows for structure solutions to be both chemically viable and in close agreement with the experimental diffraction pattern.

Modules: Materials Visualizer, Reflex Plus

Time: 

Prerequisites: [Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus](#)

Background

During the structure solution process, huge numbers of trial structures are generated and their simulated powder patterns are compared to experimental data. To calculate a powder diffraction pattern for a trial structure, the distribution function describing the orientation of crystallites in the powder has to be known. In general, it is assumed that the powder particles are randomly oriented and their distribution function is supposed to be isotropic. However, significant deviations from this assumption can occur, especially if the compound under investigation forms plate- or needle-like crystals. Needles and plates tend to align themselves with respect to the sample holder, resulting in a loss of isotropy.

If the orientation of powder particles is not completely random, the distribution function and the crystal structure have to be determined simultaneously. In Rietveld refinement, this approach is quite common and it has been observed that relatively simple preferred orientation corrections frequently describe deviations from isotropy fairly well. Two of these corrections, March-Dollase ([Dollase, 1986](#)) and Rietveld-Toraya ([Rietveld, 1969](#) and [Toraya and Marumo, 1981](#)) are implemented in the Reflex module. If preferred orientation is weak, crystal structures can be solved assuming an isotropic distribution, and the preferred orientation correction can be added in the subsequent Rietveld refinement. In the presence of strong preferred orientation, on the other hand, the preferred orientation correction has to be determined during the structure solution phase.

The ability to determine the preferred orientation correction during the structure solution phase is a unique feature of Reflex Plus. The preferred orientation corrections add 3 or 4 parameters to the total number of degrees of freedom during the structure solution phase. It has to be stressed that the use of a preferred orientation correction increases the complexity of the search problem significantly.

Therefore, such a correction should only be applied if there is a reason to expect preferred orientation, such as microscope images showing plate or needle-like crystals. If possible, it is generally preferable to reduce the effect of preferred orientation experimentally, for example by using a spinning capillary for the experimental measurement.

Both available corrections assume that the correction factor for integrated peak intensities only depends on the angle between the preferred orientation direction and the reciprocal lattice vector that corresponds to a given reflection. This assumption is valid for rod or disk shaped crystals which have axial symmetry in combination with cylindrical sample symmetry. While the second condition can always be enforced by spinning the sample, strong deviations of the average particle shape from axial symmetry can occur, leading to particle distributions that are not well described by the March-Dollase or

the Rietveld-Toraya correction. Despite the fact that the Rietveld-Toraya correction offers a higher number of adjustable parameters, the March-Dollase correction is considered to be more accurate. This is related to the fact that the functional form of the March-Dollase correction, unlike the functional form of the Rietveld-Toraya correction, is based on physically reasonable assumptions. For structure solution, the March-Dollase correction should be used.

Occasionally, the available powder diffraction data do not contain enough information for a successful Rietveld refinement, for example, systems with a large number of degrees of freedom as occurring in all-atom refinements, and/or for refinements using low quality powder data. In these instances, Rietveld refinements will typically lead to chemically unviable structures because the information content of the powder pattern is too low to accurately determine all degrees of freedom.

To overcome this problem, Reflex allows you to incorporate an accurate description of potential energy in conjunction with the R_{wp} in the Rietveld refinement process optimizing a combined figure of merit. The aim is to find solutions that optimally meet two different and possibly conflicting objectives:

- The simulated pattern has to match the experimental diffraction data
- The potential energy of the structure has to be close to the minimum

A priori elucidation of the energy weight factor determining the relative importance of the energy contribution might not be intuitive; in such cases a Pareto optimization (*a posteriori* preference calculation) can be used to obtain an appropriate value.

Introduction

In this tutorial, the crystal structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide will be solved using the March-Dollase correction. The preferred orientation present in the sample is rather strong, certain intensity ratios being modified by about a factor of 50.

This tutorial covers:

- [Getting started](#)
- [To build an empty unit cell and set the space group](#)
- [Pawley fitting](#)
- [To sketch and optimize a molecule](#)
- [To attempt structure solution without preferred orientation correction](#)
- [Structure solution with preferred orientation correction](#)
- [Rietveld refinement](#)
- [Rietveld refinement with energies and Pareto optimization](#)
- [To interpret preferred orientation parameters](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **preferred_orientation** as the project name, click the **OK** button.

The new project is created with *preferred_orientation* listed in the Project Explorer. Now import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder, change the **Files of type** to **Chart Files** and double-click on **(E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.xcd**.

In the **Project Explorer**, right-click on the imported document and select **Rename** from the shortcut menu. Change the filename to **data**. The file extension **.xcd** is automatically appended.

2. To build an empty unit cell and set the space group

The polymorph of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide studied here, crystallizes in space group $P2_1/c$ with $a = 14.26 \text{ \AA}$, $b = 5.11 \text{ \AA}$, $c = 15.06 \text{ \AA}$ and $\beta = 116.9^\circ$. The diffraction pattern was recorded using a copper anode and the $K_{\alpha 2}$ emission line was not filtered out.

First, you have to create a new 3D Atomistic document.

In the **Project Explorer**, right-click on **preferred_orientation** and select **New | 3D Atomistic Document** from the shortcut menu. Rename the new document **cell**.

Now build the unit cell.

Make sure that **cell.xsd** is active and choose **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog.

On the **Space Group** tab change the space group from P1 to **P21/c**.

On the **Lattice Parameters** tab set **a**, **b**, **c** and **β** to **14.26**, **5.11**, **15.06** and **116.9**, respectively.

Click the **Build** button.

3. Pawley fitting

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Pattern** tab check the checkboxes for the refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and the **Zero point Line shift**. The refinement of 20 background coefficients is switched on by default.

Make sure that the 3D Atomistic document **cell.xsd** is active. On the **Lattice** tab, check the checkboxes for the refinement of all cell parameters.

On the **Display** tab check the **Display simulation/experiment difference** checkbox.

Since the CPU time required for structure solution is approximately proportional to the number of diffraction peaks, you should limit the 2θ range used for structure solution and Pawley refinement to a subsection of the complete powder diffraction pattern.

On the **Setup** tab select **Pawley** from the refinement **Type** dropdown list. Click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

On the **Setup** tab, change the **Max. 2-Theta** value from 45 to **40** °.

On the **Exp. Data** tab, select the **data.xcd** data set.

The powder pattern was recorded using a copper anode and a graphite (002) monochromator. The (002) reflection of graphite corresponds to a d-spacing of 3.4 Å.

On the **Radiation** tab all default settings are appropriate except for the monochromator settings. In the **X-ray** section, select a **Single** monochromator and set **dhkl** to **3.4 Å**.

Click the **Refine** button.

After five cycles, the R_{wp} value should be about 6.7%. You should repeat the Pawley refinement until no further improvement in the R_{wp} value is obtained.

Ensure that **cell.xsd** is active and click the **Refine** button, close the Reflex Powder Refinement dialog.

You should obtain a minimum value for R_{wp} of about 6.3%.

Note: By default, Pawley refinement or Rietveld refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run Synchronously** from the **Job Control** tab.

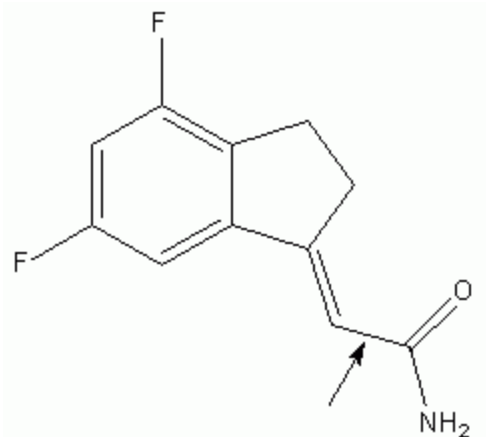
4. To sketch and optimize a molecule

You now have to create a model of the molecule that you want to use in the structure solution step.

Create a new 3D Atomistic document in the **preferred_orientation** project and rename the file **Molecule**.


Use the tools available on the **Sketch** toolbar to sketch one molecule. See 3D Sketcher for more information about how to sketch molecules. Remember to adjust the hydrogens and clean the structure.

The molecular structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide is shown below.



Molecular structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.

Now optimize the molecular geometry using the COMPASS forcefield in Forcite.

Click the **Forcite** arrow  and select **Calculation** from the dropdown list to open the Forcite Calculation dialog.

Change the **Task** from Energy to **Geometry Optimization** and the **Quality** to **Fine**.

On the **Energy** tab, change the **Forcefield** to **COMPASS** and ensure that **Forcefield assigned** is selected in the **Charges** dropdown list. Leave all the other settings unchanged.

Click the **Run** button and close the dialog.

The results of the calculation are placed in the folder, molecule Forcite GeomOpt.


Close the text document **Molecule Forcite GeomOpt\Molecule.txt**.

The 3D Atomistic document, Molecule Forcite GeomOpt\Molecule.xsd, should now be active. This model contains the optimized molecular geometry.

5. To attempt structure solution without preferred orientation correction

In this section, you will try to solve the crystal structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide without using a preferred orientation correction. To begin with, you have to prepare a starting model for structure solution. Start by defining the torsional degrees of freedom. In this example, there is only one.

Ensure that **Molecule Forcite GeomOpt/Molecule.xsd** is the active document.

Click the **Measure/Change** arrow  from the **Sketch** toolbar and select **Torsion** from the dropdown list.

Click on the bond indicated by an arrow in the molecular structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide, above. A torsion monitor will appear around the bond.

In the next step, you define the whole molecule as a motion group. This means that the position and orientation of all atoms in the molecule are described by a single set of translational and rotational parameters, in addition to the torsional degree of freedom you have just defined.

Select **Modules | Reflex | Powder Solve** from the menu bar to open the Reflex Powder Solve dialog.

In the 3D Viewer for **Molecule Forcite GeomOpt\Molecule.xsd**, double-click on one of the atoms to select the entire molecule.

On the Reflex Powder Solve dialog, select the **Structure Params** tab and click the **Create** button.

Press the **CTRL + D** keys to deselect everything.

Finally, copy the molecule into the unit cell.

Make sure that **Molecule Forcite GeomOpt\Molecule.xsd** is the active document. Choose **Edit | Copy** from the menu bar.

In the **Project Explorer**, double-click on **cell.xsd** to make it the active document. Select **Edit | Paste** from the menu bar.

In this tutorial, you use parallel tempering as the global search algorithm. By default, the approximate number of Monte Carlo steps required for structure solution is estimated from the total number of degrees of freedom. To increase the chances of finding the global minimum, you should carry out several cycles. If the same best solution is obtained in more than one cycle, this is a strong indication that the global minimum has been found.

On the **Setup** tab in the **Solve** section, select **Parallel tempering** as the **Method**. Increase the **Number of cycles** from 2 to 5. Examine the proposed **Number of steps**.

Select the **Job Control** tab and examine its contents. Choose the **Gateway location** you want to use.

Switch off the automatic assignment of the **Job description** and enter **no PO correction** as the **Job description**.

All other settings should be correct, since they were already used for the Pawley refinement.

Select **File | Save Project** from the menu bar. Close all of the open documents apart from **cell.xsd**.

Click the **Solve** button on the **Reflex Powder Solve** dialog.

The Job Explorer informs you about the progress of the calculation. When the calculation is complete, two chart documents are displayed. Depending on the specification of your computer, this may take several minutes.

When the calculation is complete, examine the results, starting with the text output.

In the **Project Explorer**, double-click on the text document **no PO correction Reflex PSolve\no PO correction.txt** and examine its contents.

The lowest R_{wp} value should be about 35.3% and has probably been obtained in several cycles, indicating that the global minimum has been found for the given choice of variables. Compared to the R_{wp} value of 6.3%, obtained during the Pawley refinement, the R_{wp} value of the best solution is very high and you should conclude that the structure has not been solved.

You should also compare the simulated and the experimental powder diffraction patterns.

In the **Project Explorer**, double-click on the chart document **no PO correction Reflex PSolve\no PO correction Solution.xcd** to make it active.

The intensity distributions of the simulated and the experimental powder patterns are somewhat different, confirming that the crystal structure has not been solved.

Finally, you should take a look at the crystal structure corresponding to the lowest R_{wp} value.

In the **Project Explorer**, double-click on the 3D Atomistic document **no PO correction Reflex PSolve\no PO correction Solution.xsd** and examine it.

Right-click on the structure and choose **Display Style** from the shortcut menu to open the Display Style dialog. Select the **Lattice** tab and set the **Max** values for **A**, **B** and **C** to **2.00**. Close the dialog.

Click the **Calculate Hydrogen Bonds** button  on the **Atoms and Bonds** toolbar.

To make the crystal structure clearer you should switch off the display of motion groups.

Press the **ALT** key and double-click on a motion group. All motion groups should now be selected.

Choose **View | Explorers | Properties Explorer** from the menu bar. In the **Project Explorer**, double-click on **IsVisible** to open the Edit IsVisible dialog. Click the **No / False** radio button and click the **OK** button.

The molecules do not overlap but there are some fairly close contacts and a reasonable hydrogen bonding pattern cannot be found. Once again confirming that the crystal structure has not been solved.

6. Structure solution with preferred orientation correction

There are several reasons why a structure solution may fail, one of them being that the search has not been carried out in the right space group. If there are no experimental indicators for preferred orientation, trying a different space group would probably be the next step. In this case, however, examination of the sample under a microscope would have revealed needle-like crystals and it is therefore appropriate to try structure solution in $P2_1/c$ again, this time including a preferred orientation correction.

Make sure that **cell.xsd** is the active document. Open the **Reflex Powder Solve** dialog.

On the **Job Control** tab change the **Job description** to **MD PO correction**.

On the **Sample Params** tab, scroll down to **Preferred Orientation**. Change the **Applied** correction from None to **March-Dollase** and check the checkboxes for **a***, **b***, **c*** and **R0**.

Select the **Setup** tab and examine the proposed **Number of steps**.

Including the March-Dollase correction has increased the number of parameters from 7 to 10. The refinement of a^* , b^* and c^* (the components of the preferred orientation direction) adds only 2 parameters, since the length of this vector is meaningless. Because of the increased number of degrees of freedom, Powder Solve now suggests making 300,000 steps instead of 80,000.

All of the other settings, from the previous run, should remain unchanged. You are now ready to start Powder Solve.

Select **File | Save Project** from the menu bar. Close all of the open documents apart from **cell.xsd**.

Click the **Solve** button on the Reflex Powder Solve dialog and close the dialog.

The Job Explorer informs you about the progress of the calculation. Depending on the specification of your computer, the calculation may take up to one hour.

When the calculation is complete you should analyze the Powder Solve output.

In the **Project Explorer**, double-click on the text document **MD PO correction Reflex PSolve\MD PO correction.txt** and examine its contents.

The lowest R_{wp} value should be about 15.6% and has probably been obtained in several cycles, indicating that the global minimum has been found for the given choice of variables. The best R_{wp} value obtained with the March-Dollase correction is significantly lower than the result obtained without a preferred orientation correction (35.3%) and it seems likely that the crystal structure has been solved.

Next, you should examine the comparison of the simulated and the experimental powder diffraction patterns.

In the **Project Explorer**, double-click on the Chart Document **MD PO correction Reflex PSolve\MD PO correction Solution.xcd** and examine it.

Even though there are still some differences, the overall intensity distribution of the experimental powder diffraction pattern is well reproduced.

Finally, you should examine the crystal structure.

In the **Project Explorer**, double-click on the 3D Atomistic document **MD PO correction Reflex PSolve\MD PO correction Solution.xsd**.

Right-click on the structure and choose **Display Style** from the shortcut menu. Select the **Lattice** tab and set the **Max** values for **A**, **B**, and **C** to **2.00**.

Click the **Calculate Hydrogen Bonds** button .

Switch off the display of motion groups.

There are no significant close contacts and a 1D hydrogen bonding scheme parallel to the b-axis is clearly recognizable. You can conclude that the crystal structure has been solved.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

7. Rietveld refinement

This section describes how to perform Rietveld refinement of a limited number of parameters. Start by making a copy of the structure solution.

In the **Project Explorer**, double-click on **MD PO correction Reflex PSolve\MD PO correction Solution.xsd** to make it active and select **Edit | Copy** from the menu bar.

Right-click on the project name and choose **New | Folder** from the shortcut menu. Change the name of the new folder to **refinement**.

Right-click on **refinement** and select **New | 3D Atomistic Document** from the shortcut menu. Change the filename of the new document to **refined structure**. Choose **Edit | Paste** from the menu bar and press **CTRL + D** to deselect everything.

At the end of the structure solution procedure, the preferred orientation parameters of the best solution are saved in a parameter file. These parameters must now be restored.


In the **Project Explorer**, double-click on **MD PO correction Reflex PSolve\MD PO correction - Powder Solve** to load the preferred orientation and other parameters used in the previous Powder Solve run.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab change the **Type** from Pawley to **Rietveld**.

Select the **Sample** tab and examine the preferred orientation parameters.

For the Rietveld refinement, a global isotropic temperature factor and an additional flexible torsion will be added to the parameters refined so far.

Open the **Display Style** dialog and reset the display range for **refined structure.xsd** so that only a single unit cell is visible.

Select the **Measure/Change** tool for torsions .

Choose one molecule in the 3D Viewer and click on the double bond that links the acetamide fragment to the carbon ring system. A new torsion monitor should appear.

Choose the **Selection** tool .

Select the **Structure** tab on the **Reflex Powder Refinement** dialog and ensure that all of the structural parameters are checked for refinement.

On the **Sample** tab scroll down to the **Temperature Factors** section and set the **Applied** temperature factor to **Global Isotropic**. Check to refine the **Global Isotropic** temperature factor.

For Rietveld Refinement, you should use the full range of the powder diffraction pattern. In addition, you want the comparison between the calculated and the experimental patterns to be displayed in a new chart document.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

On the **Setup** tab, change the **Max. 2-Theta** value to **50 °**.



On the **Display** tab, in the **General** section, check the **Display simulation/experiment difference** checkbox. In the **View management** section, change **Chart view** from **Replace** to **New**.

Click the **Refine** button.

The Rietveld refinement should reduce the R_{wp} value to about 14.2%. Next, you should examine the crystal structure.

In the **Project Explorer**, double-click on the 3D Atomistic document **refinement\refined structure.xsd**.

On the **Display Style** dialog, select the **Lattice** tab and set the **Max** values for **A**, **B** and **C** to **2.00**. Close the dialog.

Click the **Calculate Hydrogen Bonds** button  and then the **Calculate Close Contacts** button .

Switch off the display of motion groups.

There are some minor close contacts. Next, you should examine the comparison of the simulated and the experimental powder diffraction pattern.

In the **Project Explorer**, double-click on the Chart Document **refinement\refined structure.xcd** and examine it.

The overall intensity distribution of the experimental powder diffraction pattern is well reproduced, although some regions show intensity differences as indicated in the difference plot in the chart document below.

Powder Refinement: $R_{wp} = 12.40\%$ $R_{wp}(w/o\ bck) = 21.63\%$
 $R_p = 9.49\%$



Comparison between the simulated powder pattern obtained by Rietveld refinement and experimental powder pattern.

Optionally you can generate an HTML document that summarizes the results of the Rietveld refinement. The HTML document contains error bars for all the refined parameters.

Make **refinement\refined structure.xsd** the active document then select the **Display** tab of the Reflex Powder Refinement dialog. In the **View management** section, check the **Generate HTML report** checkbox. Click the **Calculate** button.

Examine the HTML report.

8. Rietveld refinement with energies and Pareto optimization

In this section, you will improve the structure solutions by including energy information into the Rietveld refinement process by optimizing a combined figure of merit.

Before a Rietveld refinement with energies calculation is performed, the energy weight factor determining the relative importance of the energy contribution has to be selected. Pareto optimization can be used to calculate a set of possible optimum refinement solutions automatically by performing a sequence of Rietveld refinement with energy calculations with varying energy weights.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **refined structure.xsd** in the **refinement** folder.

Select **File | Save As...** from the menu bar to open the Save As dialog. Type in **pareto** as the filename and click the **Save** button.

Next define each atom as an individual motion group for an all-atom Pareto optimization calculation. This means that each atom is described by three translational parameters. You start by deleting the motion groups and torsions defined previously.

Press the **ALT** key and double-click on a motion group. All motion groups are selected. Press the **DELETE** key.

Repeat the same procedure to delete the torsions.

Select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu to select one entire molecule.

Open the **Reflex Powder Solve** dialog, select the **Structure Params** tab and click the **Create motion group(s) from selection as individual groups** button. Ensure that all of the refinement checkboxes are checked and that **Use Hydrogens** is switched on. Close the Reflex Powder Solve dialog.

Press **CTRL + D** to deselect everything.

Now you will use Pareto optimization to automatically calculate a set of possible optimal refinement solutions.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, set the **Refinement Type** to **Pareto optimization**. Click the **More...** button to open the Pareto Optimization Options dialog.

The number of points specify the total number of points to be calculated on a Pareto curve. The energy window describes the tolerance window above the global minimum within which realistic structure solutions can be expected. In this tutorial, you should use the default settings.

Close the **Pareto Optimization Options** dialog.

Specify the energy expression to be applied during the refinement process. It is recommended to select the same forcefield and charges that have been used to [optimize](#) the molecular geometries.

On the **Energy** tab, change the **Forcefield** to **COMPASS** and select **Forcefield assigned** from the **Charges** dropdown list.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click the **Refine** button and close the **Reflex Powder Refinement** dialog.

Close **Pareto.xsd** and click the **Yes** button when asked if you want to save the changes.

Note: Before you start a Pareto optimization, it is important that you choose an appropriate energy expression/forcefield and verify that it calculates the geometry and potential energy surface of the molecular fragments with sufficient accuracy.

Note: Pareto calculations are run as remote jobs.

Once the calculation starts, a new folder called `pareto Reflex Pareto` is created in the Project Explorer. The parameter settings for this job are automatically saved in a file called `pareto - Powder Diffraction`.

The Job Explorer informs you about the progress of the calculation. After some time, two new windows appear; a text document, `Status.txt`, and a chart document `pareto E vs Rwp.xcd`. These documents are updated regularly, as the job progresses.

Wait until the job finishes before proceeding.

Note: The first step of a Pareto optimization is a minimization of the potential energy of the crystal with fixed lattice parameters. This energy minimum provides the reference for the energy contribution to the combined figure of merit.

Next analyze the pareto optimization results.

Select **File | Save Project** from the menu bar and then **Window | Close All**.


In the **Project Explorer**, double-click on **pareto.txt** in the **pareto Reflex Pareto** folder.

The text file contains the values of all the settings used as input for the calculation, and a short summary of the calculation results.

Close **pareto.txt**.


In the **Project Explorer**, double-click on **pareto.xtd** followed by **pareto E vs. Rwp.xcd** in the **pareto Reflex Pareto** folder.

Select **Window | Tile Vertically**.

Choose the **Selection** tool  and click on any point in **pareto E vs. Rwp.xcd**.

You can see how the points on the chart relate to the trajectory frames. Alternatively, you can use the animation controls to select a trajectory frame and relate it to the corresponding graph point.

If the **Animation** toolbar is not displayed, select **View | Toolbars | Animation**.

Make **pareto.xtd** your active document. Click the **Animation Mode** arrow  and select **Options** from the dropdown list to open the Animation Options dialog. Type in **1** in the **Current frame** box and press the TAB key. Alternatively, use the spin controls to specify the frame number.

Next examine the optimized parameters for frame 1 and the weight of the energy contribution to the R_{comb} .

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, click **Load result settings** button.

Click the **More...** button for **Rietveld with energies**. Examine the **Weight** and click the **OK** button.

Repeat the same procedure for other frames in **pareto.xtd**, loading the results settings for each frame.

The *Weight* is different for each frame.



Close the **Animation Options** dialog and the **Reflex Powder Refinement** dialog.

Select **Window | Close All** and click the **No to All** button when asked if you want to save the changes.

The Pareto optimization suggests a best solution which is closest to the absolute optimum (minimum R_{wp} , minimum E). In the energy versus R_{wp} chart pareto E vs R_{wp} .xcd, this solution should have the shortest distance from the origin. It is saved automatically in the project at the completion of the Pareto optimization. You should examine the crystal structure.

In the **Project Explorer**, double-click on **pareto.xsd** in the **pareto Reflex Pareto** folder.

Open the **Display Style** dialog and select the **Lattice** tab, set the **Max** values for **A**, **B** and **C** to **2.00**.

Click the **Calculate Hydrogen Bonds** button  and then the **Calculate Close Contacts** button . Switch off the display of motion groups.

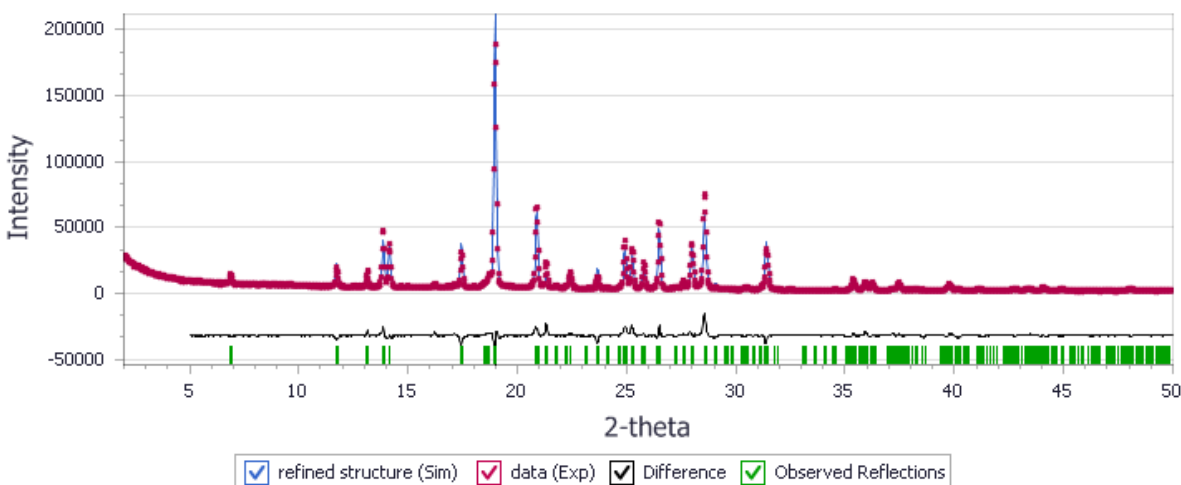
Close the **Display Style** dialog and the 3D Viewer for **pareto.xsd**, click the **No** button when asked if you want to save the changes.

Next, you should examine the comparison of the simulated and the experimental powder diffraction pattern.

In the **Project Explorer**, double-click on the Chart Document **pareto Reflex Pareto\pareto.xcd** and examine it.

The R_{wp} should be reduced to 11.2% compared to 14.2% obtained from regular Rietveld refinement. The overall intensity distribution of the experimental powder diffraction pattern is well reproduced. The inclusion of energy information into the Rietveld refinement process optimizing a R_{comb} allows for an improved structure solution.

Powder Refinement: $R_{wp} = 12.40\%$ $R_{wp}(w/o\ bck) = 21.63\%$
 $R_p = 9.49\%$




Comparison between the simulated powder pattern obtained by Rietveld refinement and experimental powder pattern.


Note: Pareto optimization only provides the set of optimum solutions. Although it suggests a "best solution", it by no means indicates the solution indeed is the best solution. The decision on which of the optimum solutions to select cannot be automated and has to be taken by the user according to specific criteria: is it more important in this particular case to have a good fit with the experimental pattern or is it critical that the energy is close to its minimum?

You should compare the crystal structure obtained from Rietveld with energies with that obtained from Rietveld refinement by overlaying the two structures.

Close **pareto.xcd**.

In the **Project Explorer**, double-click on **pareto.xsd** in the **refinement\pareto Reflex Pareto** folder. Press the **ALT** key and double-click on a motion group. All motion groups are selected. Press **DELETE** key.

Click the **Copy** button .

In the **Project Explorer**, right-click on project **preferred_orientation** and choose **New | 3D Atomistic Collection Document**. Click the **Paste** button .

In the **Project Explorer**, right-click on **3D Atomistic Collection.xod** and change the name of the document to **overlay.xod**.

Open the **Display Style** dialog, on the **Atom** tab, set **Coloring** to **Custom**. Choose **red** from the **Color** dialog and click the **OK** button. On the **Lattice** tab, set the **Color** to **red** as well.

Close **pareto.xsd** and click the **No** button when asked if you want to save the changes.

In the **Project Explorer**, double-click on **refined structure.xsd** in the **refinement** folder. Press the **ALT** key and double-click on a motion group to select all motion groups. Repeat this to delete all the torsions. **Copy** the entire document.


In the **Project Explorer**, double-click on **overlay.xod** and **Paste**.

On the **Display Style** dialog set the **Atom** and **Lattice** colors to **white**.

Close **refined structure.xsd** and click the **No** button when asked if you want to save the changes.

Expand the **overlay.xod** 3D Viewer by clicking the **Maximize**  icon. Click once in the 3D Viewer to deselect everything.


The two structures (**pareto.xsd** in red and **refined structure.xsd** in white) are indeed quite similar, with the differences mainly in the hydrogen positions. You should examine the hydrogen bonding scheme and contact contacts.

Double-click on one of the atoms in red to select all the molecular fragment for **pareto.xsd**. Click the **Calculate Hydrogen Bonds** button . Press **CTRL + D** to deselect everything.

Repeat the same procedure for the white **refined structure.xsd**.

The two structures have very similar hydrogen bonding schemes. Next examine the close contacts.

Press the **ALT** key and double-click on a hydrogen bond to select all the hydrogen bonds. Press the **DELETE** key.

Double-click on one of the atoms in red to select all the molecular fragment for **pareto.xsd**. Click the **Calculate Close Contacts** button . Press **CTRL + D** to deselect everything.

Repeat the same procedure for the white **refined structure.xsd**.

There should be fewer close contacts for the structure solution obtained by Rietveld with energies. The inclusion of energy contribution in this case provides more accurate atomic positions, for example the hydrogen atoms.

9. To interpret preferred orientation parameters

As an additional test of the correctness of the structure solution, it is advisable to check if the observed preferred orientation parameters can be related to the structural properties of the compound under investigation.

The powder diffraction pattern has been measured using a flat plate sample holder. For this kind of experimental setup, there is in general a simple relationship between the particle shape and the preferred orientation parameters. For a compound forming plate-like crystals, R_0 is smaller than one and the preferred orientation direction is perpendicular to the plates. For a compound forming needles, R_0 is larger than one and the preferred orientation direction is parallel to the needle axis.

In a previous section, an examination of the solved crystal structure showed that there is 1D hydrogen bonding parallel to the b-axis. Strong bonding along the b-axis is likely to cause fast growth in this direction and so, the compound under investigation can be expected to form needle-like crystals. Therefore, the direction of preferred orientation should be parallel to the b-axis, with $R_0 > 1$.


Close **overlay.xod** and click the **Yes** button when asked if you want to save the file as part of the project.

In the **Project Explorer**, double-click on **pareto.xsd** in the **refinement\pareto Reflex Pareto** folder.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, click the **Load result settings** button.

Select the **Sample** tab. Write down the preferred orientation parameters.

The strength of the preferred orientation is characterized by the parameter R_0 , which, in this case, should be about 2.6. As expected, R_0 is larger than 1. The preferred orientation direction is expressed in fractional coordinates a^* , b^* and c^* with respect to the reciprocal lattice. In order to interpret these values, you therefore have to find out what the reciprocal lattice looks like.

Make sure that **pareto.xsd** is the active document. Click the **Lattice Parameters** button  to open the Lattice Parameters dialog. Examine the lattice parameters.

The lattice parameters are approximately $a = 14.3 \text{ \AA}$, $b = 5.1 \text{ \AA}$, $c = 15.1 \text{ \AA}$ and $\beta = 117^\circ$. As the b-axis is about three times shorter than the other two axes, the b^* -axis of the reciprocal unit cell is about three times longer than the a^* -axis and the c^* -axis. Since the b^* -axis is always perpendicular to the a-c-plane, it is parallel to the b-direction in this example.

On the Sample tab, the absolute value of b^* should be much larger than the absolute values of a^* and the c^* . In addition, the b^* axis is much longer than the a^* - and the c^* - axes. Therefore, it follows that the preferred orientation direction is basically parallel to the b-axis of the unit cell. The preferred orientation parameters are thus in good agreement with the crystal structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.

It has to be mentioned that there is a twofold screw axis parallel to the b-direction in P 21/c. Therefore, the preferred orientation direction should either be parallel or perpendicular to the b-direction. The slight deviation from a completely parallel alignment is probably because the March-Dollase correction does not describe the true nature of the preferred orientation accurately enough.

When the March-Dollase correction is used, the intensity of reflections with k-vectors parallel to the preferred orientation direction are modified by a factor of R_0^{-3} . The intensity of reflections with k-vectors perpendicular to the preferred orientation direction changes by a factor of $R_0^{3/2}$. In the present case, this corresponds to a reduction of the scattering intensity parallel to the preferred orientation direction by a factor of 14 and an increase of the intensity perpendicular to the preferred orientation direction by a factor of 4. Certain intensity ratios are modified by as much as a factor of 56.

Select **File** | **Save Project** from the menu bar, followed by **Window** | **Close All**.

This is the end of the tutorial.

BIOVIA would like to thank P. G. Varlashkin, M. Sacchetti and J. Zhu from GlaxoSmithKline for supplying the experimental data.

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Toraya, H.; Marumo, F. *Mineral. J.*, **10**, 211 (1981).

Structure solution of the inorganic compound FIN31

Purpose: Illustrates how the Powder Solve tool can be used to solve the crystal structures of inorganic compounds.

Modules: Materials Visualizer, Reflex Plus, VAMP

Time: 🕒🕒🕒

Prerequisites: [Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus](#)

Introduction

In this tutorial, you will determine the crystal structure of the inorganic compound FIN31 ($\text{Ca}_5\text{F}(\text{PO}_4)_3$). FIN31 is one of several inorganic crystal structures that have been solved with Reflex Plus as part of a validation study.

This tutorial covers:

- [Getting started](#)
- [To index the diffraction pattern](#)
- [Pawley refinement](#)
- [To select the space group](#)
- [To prepare a starting model](#)
- [Structure solution](#)
- [Rietveld refinement](#)

Note: Later parts of this tutorial require the use of the VAMP module.


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **FIN31** as the project name, click the **OK** button.


The new project is created with *FIN31* listed in the Project Explorer. Now import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click on **fin31.3cam**.

2. To index the diffraction pattern

In this section, you will process the diffraction pattern and pick diffraction peaks automatically. Using the selected peaks, you will then determine the unit cell parameters with the indexing algorithm TREOR90.

The powder diffraction pattern has been measured using Copper $K\alpha_1$ and $K\alpha_2$ radiation. To facilitate the automatic peak search, you first subtract the background, smooth the powder diffraction pattern and strip off the $K\alpha_2$ diffraction peaks.

Click the **Reflex** button  on the **Modules** toolbar and select **Pattern Processing** from the dropdown list to open the Reflex Pattern Processing dialog.

On the **Pattern Preparation** tab, in the **Background** section, click the **Calculate** button and then the **Subtract** button.

This opens a new chart document, called fin31 (Background Removed).xcd.

On the **Pattern Processing** tab, in the **Smoothing** section, set the **Gaussian width** to **0.05** and click the **Smooth** button.



This opens a new chart document, called fin31 (Background Removed) (Smoothed).xcd.

On the **K alpha 2** tab, in the **$K\alpha_2$ stripping** section, click the **Strip** button. **Close** the Reflex Pattern Processing dialog.


Three new chart documents have now been created. The active document is FIN31 (Background Removed) (Smoothed) (Stripped).xcd. You can now proceed to the automatic peak picking.

Choose **Modules | Reflex | Powder Indexing** from the menu bar to open the Reflex Powder Indexing dialog. On the **Peaks** tab change the **Low amplitude cutoff** to **2** and click the **Search** button.

You should always inspect the result of the automatic peak search visually. In cases where $K\alpha_2$ stripping has been carried out, you also need to ensure that no peak markers have been attributed to minor residual features belonging to the $K\alpha_2$ satellites of strong $K\alpha_1$ peaks.

Use the **Zoom**  and **Translation**  tools, on the Chart Viewer toolbar, to examine the powder diffraction pattern in the range 15° to 50° .

See the Chart mouse and keyboard actions topic for more information about how to manipulate charts.

If changes are necessary, you can add and move peaks using the *Chart Viewer Marker Mode*  tool. However, in this case, no changes are required.

Now you are ready to index the powder diffraction pattern.

In the **Project Explorer**, rename **FIN31 (Background Removed) (Smoothed) (Stripped).xcd** to **fin31_index**.

Select the **Setup** tab on the Reflex Powder Indexing dialog. Choose **TREOR90** as the indexing **Program** and check all checkboxes in the **Crystal systems to test** section. The diffraction pattern has been measured using copper radiation so you do not have to change the default wavelength, in this case.

Click the **Index** button.

After TREOR90 has finished, a Study Table document containing the results of the indexing procedure is displayed. In the case of FIN31, the correct unit cell belongs to the hexagonal crystal system and has a volume of about 526 \AA^3 with $a = b \sim 9.4 \text{ \AA}$ and $c \sim 6.9 \text{ \AA}$.

Using the TREOR90 result, it is possible to generate a 3D model of an empty unit cell.

Click in the Study Table document with the indexing result to make it active. Click the **Create Cell** button on the Reflex Powder Indexing dialog and close the dialog.

A new 3D Atomistic document, called `fin31_index1.xsd` is created, containing an empty unit cell which matches the solution found by TREOR90.

In the **Project Explorer**, rename `fin31_index1.xsd` to **empty_cell**.

Choose **File | Save Project** from the menu bar.

3. Pawley refinement

The main purpose of Pawley refinement is to provide background parameters, profile parameters, cell parameters and the zero point shift for the structure solution step. In addition, it can be used to check the indexing results, since if the cell is incorrect there will usually be significant deviations between the simulated and the experimental powder patterns. The space group associated with the unit cell should be one with no systematic absences at this stage. So, by default, the lattice symmetry of this hexagonal unit cell is set to P3.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Setup** tab select **Pawley** from the refinement **Type** dropdown list.

The Pawley refinement proceeds in cycles. In each cycle, the peak intensities and background parameters are optimized first, while all other parameters remain fixed. In a second step, the peak intensities and background parameters are fixed and the remaining parameters are refined. By default, the number of cycles is set to 2. This value is usually too low to reach convergence in a single run so you should increase it.

On the **Setup** tab click the **More...** button for **Convergence quality** control to display the Refinement Convergence Options dialog. Change the **Number of cycles** from 2 to **5** and click the **OK** button.

The 2θ range has to be adjusted to match that of the powder diffraction pattern.

On the **Setup** tab, change the **2-Theta** range to **15°-85°**. When you have entered the new range, press the **TAB** key. Do not press ENTER, as this will start the Pawley refinement immediately.

On the **Exp. Data** tab select **Pattern 1** from the chart document `fin31.xcd`. Pattern 1 is the original data, Pattern 2 corresponds to the calculated background.

In general, the enhanced Pawley refinement method implemented in Reflex Plus is very stable and it is possible to refine all relevant parameters simultaneously. Using the Pseudo-Voigt profile function, you refine background parameters, the peak width parameters U, V, and W, the mixing parameters NA and NB, the zero point shift, and the lattice parameters.

On the **Pattern** tab, check the checkboxes for the refinement of the profile parameters **U**, **V**, **W** under FWHM, **NA** and **NB** under Profile parameters, and the **Zero point** under Line shift. The refinement of 20 background coefficients is switched on by default.

If `empty_cell.xsd` is not the active document, double-click on **empty_cell.xsd** in the Project Explorer.

On the **Lattice** tab, check the checkboxes for the refinement of all **cell parameters**.

Finally, you should modify the display options and start the Pawley refinement.

On the **Display** tab, check the **Display simulation/experiment difference** checkbox.

Click the **Refine** button on the Reflex Powder Refinement dialog.

As the Pawley refinement progresses, the cycle number and the current R_{wp} value are shown at the bottom of the Materials Visualizer window. After five cycles, the R_{wp} value should be about 7.8%. At the end of the calculation, a new chart document opens.

Examine the comparison of the simulated and the experimental powder patterns.

The agreement between the calculated and the experimental powder patterns should be quite good, confirming that the unit cell is correct. The final R_{wp} value is displayed at the top of the chart document. R_{wp} (w/o bck) is the weighted Rietveld parameter calculated after background subtraction.

To make sure that the refinement has converged, you should carry out a second run.

In the **Project Explorer**, double-click on **empty_cell.xsd** to make it the active document.

Click the **Refine** button on the Reflex Powder Refinement dialog.

After the second set of 5 cycles, the R_{wp} value should be about 7.75%.

Note: By default, Pawley refinement or Rietveld refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run synchronously** from the **Job Control** tab.

The Pawley refinement step is now finished and you should save the refined parameters.

Select **Modules | Reflex | Save Settings...** from the menu bar to open the Save Reflex Settings dialog. Enter **empty_cell** as the filename and click the **OK** button.

The settings document `empty_cell - Powder Diffraction` is added to the list of files in the Project Explorer. By double-clicking on this document, you can restore the refined parameters at a later stage.

Tip: If you right-click on `empty_cell - Powder Diffraction` in the Project Explorer and select *Powder Refinement* from the shortcut menu, the Reflex Powder Refinement dialog will be displayed with the settings used for this calculation.

Before you move on to the next section, you should save the project.

Choose **File | Save Project** from the menu bar.

4. To select the space group

You now have to identify the space group to which the crystal structure is likely to belong. Reflex provides functionality to estimate the likelihood for all space groups in a given crystal system, based on the intensities obtained by Pawley refinement ([Markvardsen et al., 2000](#)).

Make **empty_cell.xsd** the active document and open the **Reflex Powder Indexing** dialog. Select the **Space Groups** tab and click the **Search** button.

A study table document is generated in which all hexagonal and trigonal space groups are ranked according to their figure of merit. The highest figure of merit is shared by 3 space groups; P63/M, P63, and P6322. Under normal circumstances, it would be necessary to attempt structure solution for each space group until the crystal structure is solved. However, for the purposes of this tutorial you will only consider the correct space group, P63/M.


Now you should generate a 3D Atomistic document containing the unit cell with the correct space group settings.

Select the first row of the study table document **empty_cell.std**. Click the **Create Cell** button and close the dialog. Rename the new 3D Atomistic document **empty_cell_P63m_refined.xsd**.

You should repeat the Pawley refinement in the chosen space group.

Open the **Reflex Powder Refinement** dialog and click the **Refine** button. Close the dialog.

Finally, you should save the refined parameters and the project.

Select the **Reflex** button , then select **Save Settings...** from the dropdown list to open the **Save Reflex Settings** dialog. Enter **empty_cell_P63m** as the filename and click the **OK** button.

Choose **File | Save Project** from the menu bar.

5. To prepare a starting model

In this section, you will build a starting model for structure solution. First, you have to decide how many atoms you expect to find in the asymmetric unit and how these atoms are distributed over general and special positions.

Tip: If you make a mistake while sketching, you can undo your changes by choosing *Edit | Undo* from the Materials Studio menu bar.

At the end of the last section, you set the space group symmetry to P63/M and carried out a Pawley refinement in this space group. Now, you should make a copy of the empty unit cell. You will also change one of the options to make sure that atoms are not placed on special positions automatically.

In the **Project Explorer**, double-click on **empty_cell_P63m_refined.xsd** to make it the active document. Choose **File | Save As...** from the menu bar and save the file as **empty_cell_P63m**. The extension **.xsd** will be added automatically.

Choose **Build | Crystals | Rebuild Crystal...** from the menu bar to open the Rebuild Crystal dialog.

Select the **Options** tab and click on the **Ignore special positions** radio button.



Click the **Rebuild** button.

The chemical composition of FIN31 is $\text{Ca}_5\text{F}(\text{PO}_4)_3$ and its density is approximately 3.2 g/cm^3 . To work out how many formula units to place in the asymmetric unit, you should begin by adding one formula unit, then comparing the calculated and the experimental density.

Start with the Ca ions. First, generate a model containing a single Ca ion.

In the **Project Explorer**, right-click on the project name **FIN31** and choose **New | 3D Atomistic Document** from the shortcut menu.

Rename the new document **Ca**.

Select the **Sketch Atom**  tool and click the **Element used to sketch** arrow . Choose **Periodic Table...** from the dropdown list to display the Periodic Table dialog, select **Ca** and click the **OK** button.

Left-click once in the middle of the 3D Viewer for **Ca.xsd**, then press the **ESC** key.

Now, make five copies of the Ca ion in the empty P63/M unit cell.

Select **Edit | Copy** from the menu bar.

In the **Project Explorer**, double-click on **empty_cell_P63m.xsd** to make it the active document.

Select **Edit | Paste** from the menu bar, 5 times.


In the next step, you add a single F ion to the asymmetric unit.

Create a 3D Atomistic document containing a F instead of a Ca. Copy the F ion once into the P63/M unit cell.

Finally, place three PO_4 ions in the asymmetric unit. This step is a little more complicated, because you have to sketch the PO_4 ion before you can copy and paste it.

Create new **3D Atomistic** document called **PO4**.

Sketch a single **Phosphorus** atom. Change the **Sketch Atom to Use** from P to O. Click once in the 3D Viewer for **PO4.xsd** close to the P atom. Then click on the P atom. A bond is created between the P atom and the O atom. Repeat this three times.

On the Sketch toolbar, click the **Clean**  tool. Ensure that the PO₄ ion adopts a tetrahedral conformation.

To check the result of the sketching procedure, you should look at the PO₄ ion from different angles.

Use the **cursor keys** to rotate the model and ensure that **PO4.xsd** contains only a tetrahedral PO₄ ion.

Now you will use VAMP to optimize the geometry.

Select **Modules | VAMP | Calculation** from the menu bar to open the VAMP Calculation dialog. On the **Setup** tab change the **Task** from **Energy** to **Geometry Optimization** and the **Hamiltonian** to **NDDO MNDO/d**. Set the **Charge** to **-3**. Click the **Run** button and close the dialog.

A new folder, called **PO4 VAMP GeomOpt**, opens in the Project Explorer. The progress of the job during the computation is presented in the form of chart and text documents. The entire calculation takes about 3 minutes, depending on the speed of the processor in your computer. The optimized structure is located in the document **PO4.xsd** in the new folder.

Having optimized the PO₄ ion, you should copy it into the P63/M unit cell.

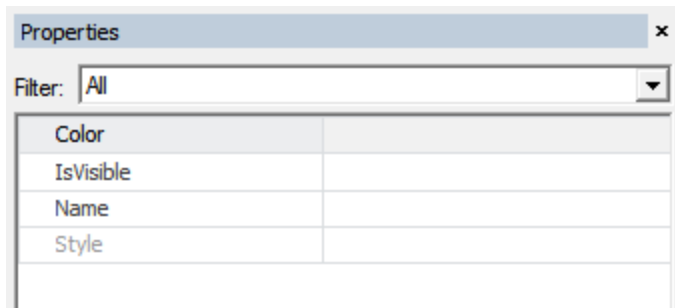
In the Project Explorer double-click on **PO4 VAMP GeomOpt/PO4.xsd** to make it the active document. Select **Edit | Copy** from the menu bar. Now double-click on **empty_cell_P63m.xsd** to make it the active document.

Select **Edit | Paste** from the menu bar, 3 times.

Note: In many cases, especially for small molecular fragments such as PO₄, it is sufficient to attempt structure solution using molecular fragments that have been optimized with the *Clean* tool alone. However, if you have access to modules that allow you to geometry optimize molecular fragments using classical or quantum calculations, such as Forcite or VAMP, you can increase your chances of successful structure solution by performing the pre-optimization step as outlined above on each individual molecular fragment in the unit cell.

Now examine the calculated density.

If the **Properties Explorer** is not already open, choose **View | Explorers | Properties Explorer** from the menu bar.



Properties Explorer

Ensure that no atoms are selected in **empty_cell_P63m.xsd**. Choose the **Symmetry System** filter and scroll down the list of properties until you find the **Density**.

With one formula unit in the asymmetric unit, the density is 19.2 g/cm^3 . This value is 6 times larger than the experimental density of about 3.2 g/cm^3 . As a consequence, the content of the asymmetric unit is $1/6$ of the formula unit: $5/6 \text{ Ca}$, $1/6 \text{ F}$ and $1/2 \text{ PO}_4$. As all these numbers are smaller than one, all ions must occupy special positions.

Note: Throughout this tutorial, it is assumed that the crystal structure is entirely ordered.

According to the International Tables for Crystallography, special positions in P63/M have a multiplicity of 2, 4 or 6, while the general position has a multiplicity of 12. If an atom occupies a special position of multiplicity m_s , the fraction of the atom in the asymmetric unit is m_s/m_g , where m_g is the multiplicity of the general position. Therefore, the multiplicities of 2, 4 and 6 in P63/M correspond to fractions of $1/6$, $1/3$ and $1/2$ ions in the asymmetric unit. Using these fractions, there are several ways of building the asymmetric unit:

Ion	Total content	Decomposition
Ca	$5/6$	$1/6, 1/6, 1/6, 1/6, 1/6$ (2,2,2,2,2)
-	-	$1/6, 1/6, 1/6, 1/3$ (2,2,2,4)
-	-	$1/6, 1/6, 1/2$ (2,2,6)
-	-	$1/2, 1/3$ (6,4)
F	$1/6$	$1/6$ (2)
PO_4	$1/2$	$1/6, 1/6, 1/6$ (2,2,2)
-	-	$1/3, 1/6$ (4,2)
-	-	$1/2$ (6)

Since there are only 4 special positions of multiplicity 2 in P63/M, it is not possible for there to be $5 \times 1/6$ Ca ions in the asymmetric unit. Furthermore, the F ion must be located on a special position with a multiplicity of 2. However, this still leaves several options for the Ca and PO_4 ions.

If there is more than one possibility, it is usually a good idea to try structure solution for the least complex choice first and then work through the list of possibilities in order of increasing complexity. In this case, the least complex choice is to place a single PO_4 ion on a special position with a multiplicity of 6 and to put two Ca ions on special positions with a multiplicity of 4 and 6, respectively.

There are two ways to take special positions into account during the structure solution search using Reflex Plus. One method is to place the ions on special positions when the starting model is prepared. For ions on special positions, only those rotations and translations that do not remove the ions from their special positions are allowed. This approach can be quite cumbersome when there are several non-equivalent possibilities.

Alternatively, you can place the ions on general positions and adjust their occupancies so that the total unit cell content is the same as if the ions were placed on special positions with an occupancy of 1.0. During the structure search, the ions should be moved onto the special positions by the global search algorithm, so as to obtain good agreement with the experimental data. In the final structure solution several symmetry copies of the ions will be superimposed, so that the total occupancy of the occupied special positions is one.

In this tutorial, you will use the second approach. So, based on the discussion above, you have to introduce into the asymmetric unit two Ca ions with occupancies of 1/2 and 1/3, one F ion with an occupancy of 1/6 and one PO₄ ion with an occupancy of 1/2.

First, delete all atoms in the 3D Atomistic document `empty_cell_P63m.xsd`.

Make sure that `empty_cell_P63m.xsd` is the active document.

Select all of the atoms in the 3D Viewer and press the **DELETE** key to delete all of the atoms.

In the next step, you put the first of the two Ca ions into the asymmetric unit. In order to tell Reflex Plus that it should optimize the position of the Ca ion during the structure search, you must define the Ca ion as a motion group. In addition, you have to set the occupancy of the Ca ion.

In the **Project Explorer**, double-click on `Ca.xsd` to make it the active document. Press the **CTRL + A** keys to select the Ca ion.

Open the **Reflex Powder Solve** dialog, on the **Structure Params** tab, in the **Motion groups** section, click the **Create** button.

In the **Properties Explorer**, select **Atom** from the **Filter** dropdown list. Double-click on **Occupancy** to open the Edit Occupancy dialog. Change the occupancy to **0.5** and click the **OK** button.

Copy the Ca atom and **paste** it into `empty_cell_P63m.xsd`.

Now add the second Ca ion.

In the **Project Explorer**, double-click on `Ca.xsd` to make it the active document.

In the **Properties Explorer**, change the **Occupancy** to **0.3333333**.

Copy the Ca atom and **paste** it into `empty_cell_P63m.xsd`.

You continue with the F ion.

In the **Project Explorer**, double-click on **F.xsd** to make it the active document.

Press the **CTRL + A** keys to select the F ion.

Use the **Reflex Powder Solve** dialog to create a **Motion group**.

In the **Properties Explorer**, change the occupancy of the F ion to **0.166666**.

Copy the F atom and **paste** it into **empty_cell_P63m.xsd**.

Finally, you add the PO_4 ion.

In the **Project Explorer**, double-click on **PO4 VAMP GeomOpt/PO4.xsd** to make it the active document.

Press the **CTRL + A** keys to select the molecule.

Use the **Reflex Powder Solve** dialog to create a **Motion group**.

In the **Properties Explorer**, change the occupancy to **0.5**. The change automatically applies to all selected atoms.

Copy the PO_4 molecule and **paste** it into **empty_cell_P63m.xsd**.

Before you move on to the next section, you should verify that the density of the starting model is correct. You should also change the name of the starting model and save the project.

Ensure that **empty_cell_P63m.xsd** is the active document. Press **CTRL + D** to deselect everything. In the **Properties Explorer**, select the **Symmetry System** filter and examine the **Density**.

The density should be 3.2 g/cm^3 .

Change the name of the starting model from **empty_cell_P63m.xsd** to **FIN31.xsd**.

Select **File | Save Project** from the Materials Studio menu bar.

6. Structure solution

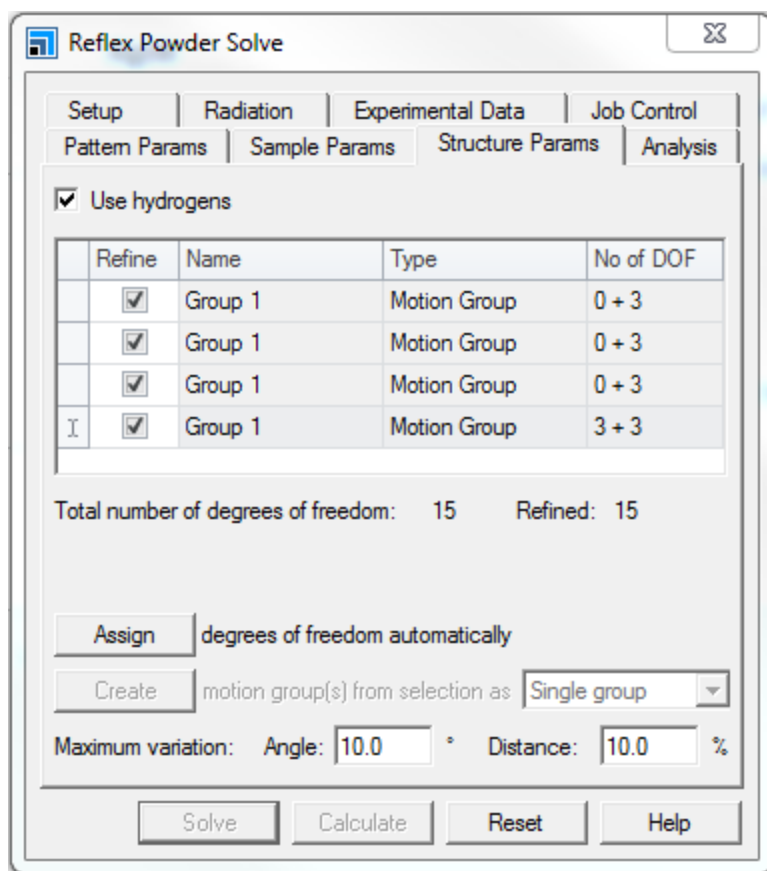
In this section, you will solve the crystal structure of FIN31.

To do this you must select the degrees of freedom that have to be optimized, decide on the global temperature factor, choose a computer to run your job on and select a global optimization algorithm.

First, make sure that all structural degrees of freedom are selected for optimization.

On the **Reflex Powder Solve** dialog, select the **Structure Params** tab and check all **Motion Groups** for refinement.

When you have done this, the *Structure Params* tab should look like the one shown below:



Reflex Powder Solve dialog, Structure Params tab with all of the Motion Groups selected for refinement.

Temperature factors are not optimized during the structure search. In general, it is a good idea to use a single global isotropic temperature factor for structure solution and to choose a value that is approximately right for the crystal structure under consideration. In the case of FIN31, the crystal structure has been measured at low temperature. So the average global isotropic temperature factor is quite small and can be neglected during structure solution.

On the **Sample Params** tab on the **Reflex Powder Solve** dialog, scroll down to the **Temperature factors** section. Set Applied to **None**.

Reflex Plus offers a choice of two global optimization algorithms, Monte Carlo simulated annealing and Monte Carlo parallel tempering.

Most simulation parameters are set automatically by default, but you have to decide on the number of cycles and the number of Monte Carlo steps.

As there is no guarantee that the crystal structure will be solved during the first cycle, you should always carry out several cycles. Only if the same solution is found in more than one cycle can you be reasonably sure that the global minimum has been reached.

By default, Reflex Plus estimates the required number of Monte Carlo steps based on the number of degrees of freedom. However, the estimate has been calibrated for organic compounds and tends to overestimate the number of steps required for the structure solution of inorganic compounds. So, for inorganic compounds, it is advisable to use a number of steps that is lower than the proposed number. However, if you choose a number that is too low, the structure will not be solved. It is therefore

essential to check that the same solution is found in several cycles. If not, you should repeat the structure solution with a larger number of steps.

On the **Setup** tab on the Reflex Powder Solve dialog, in the **Solve** section, select **Simulated Annealing** from the **Method** dropdown list. Set the **Number of cycles** to **5**. Make sure that **Automatic** is checked and examine the proposed **Number of steps**.

Uncheck **Automatic** and set the **Number of steps** to **300000**.

You are now ready to start the Powder Solve run.

Click the **Solve** button and close the dialog.

The Job Explorer informs you about the progress of the calculation. After some time, two chart documents should appear. While the calculation is running, you may wish to rearrange the open documents and close some of them.

Choose **File | Save Project** from the menu bar. Close all of the open documents apart from those starting with **FIN31 Reflex PSolve**. Choose **Window | Tile Vertically** from the menu bar.

Examine the output in the two new chart documents.

The length of time this calculation takes to complete depends on the configuration of your computer. Before you continue, you should wait for the calculation to finish.

The best crystal structure obtained at the end of several Monte Carlo simulated annealing cycles is not necessarily the right structure solution. The true crystal structure may have been missed because there were an insufficient number of cycles or Monte Carlo steps, or because the search was not carried out in the right space group.

It is also possible that the solution obtained is unrealistic because the geometries of the rigid bodies were not estimated accurately enough prior to structure solution. To decide whether or not the crystal structure has been solved, the results of the structure solution procedure have to be examined carefully.

To start with, you should examine the text output. Among other information, the text output contains the best R_{wp} value found in each cycle. If the lowest R_{wp} value is obtained in several cycles, you can be fairly confident that the global minimum has been found for the given choice of space group and degrees of freedom.

In the **Project Explorer**, double-click on the text document **FIN31 Reflex PSolve\FIN31.txt** and examine it.

The lowest R_{wp} value of about 9.68 % has been found several times.

The R_{wp} value is only a number and you should always compare the simulated and the experimental powder patterns visually. For the solution with the lowest R_{wp} value, the comparison between the simulated and the experimental patterns is saved in the chart document **FIN31 Reflex PSolve\FIN31 Solution.xcd**.

In the **Project Explorer**, double-click on the chart document **FIN31 Reflex PSolve\FIN31 Solution.xcd**. Examine the comparison between the experimental and the simulated powder diffraction patterns.

Over the full range of the powder diffraction pattern, the calculated peak intensities are in good agreement with the experimental peak intensities.

Finally, you should examine the best structure solution closely.

In the **Project Explorer**, double-click on the 3D Atomistic document **FIN31 Reflex PSolve\FIN31 Solution.xsd**. Use the tools on the **3D Viewer** toolbar to inspect the structure solution.

You can see that several symmetry copies of each ion overlap, as you would expect for the correct crystal structure. The chance of this happening accidentally is very small, so there is no doubt, at this stage, that the crystal structure has been solved.

7. Rietveld refinement

In this section, you will use Rietveld refinement to obtain a more accurate crystal structure. To start with, you should make a copy of the structure solution and delete the motion groups.

In the **Project Explorer**, double-click on the 3D Atomistic document **FIN31 Reflex PSolve\FIN31 Solution.xsd**. Choose **File | Save As...** from the menu bar and save the file as **FIN31_intermediate.xsd** at the top level of the project directory.

Choose the **Selection**  tool. Press and hold the **ALT** key, then double-click on a motion group (represented by gray ellipsoids) in **FIN31_intermediate.xsd**. Press the **DELETE** key to delete all of the motion groups.

You should now place all of the atoms exactly on the corresponding special positions.

Choose **Build | Crystals | Rebuild Crystal...** from the menu bar to open the Rebuild Crystal dialog.

Select the **Options** tab and choose to **Check for atoms on special positions, within 1.0 Å**.

Click the **Rebuild** button.

All atoms have been positioned exactly on the corresponding special positions.

When atoms are snapped to special positions their occupancies are not automatically updated. Therefore, you have to reset the occupancy of all the atoms to 1.0 manually.

Press **CTRL + A** to select everything.

In the **Properties Explorer**, select the **Atom** filter, scroll down the list of properties until you find the **Occupancy** and set it to **1.0**.

Make sure that **FIN31_intermediate.xsd** is the active document. Choose **File | Save As...** from the menu bar and save the file as **FIN31_refinement.xsd**.

You can now start the Rietveld refinement of the crystal structure. First, you refine only the atomic positions. To refine atomic coordinates, every atom must be defined as a motion group.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, in the **Refinement** section, set the **Type** to **Rietveld**.

Make sure that **FIN31_refinement.xsd** is the active document and press **CTRL + A** to select everything.

On the **Structure** tab select **Individual groups** from the dropdown list and click the **Create** button. Ensure that all 6 checkboxes are checked in the **Refine** column and examine the list of degrees of freedom.

Only 12 degrees of freedom are defined for the 7 inequivalent atoms in the asymmetric unit, so certain translations are symmetry forbidden for atoms on special positions.

Before you start the Rietveld refinement, you should make sure that no other parameters are refined. In addition, you want the comparison between the calculated and the experimental patterns to be displayed in a new chart document.

Select the **Pattern** tab and uncheck the checkboxes for the refinement of **U, V, W, NA, NB, Zero point** and **Background coefficients**.

Select the **Lattice** tab and make sure that the **lattice parameters** are not refined.

Select the **Display** tab, in the **View management** section, change **Chart view** from **Replace** to **New**.

Click the **Refine** button.

The resulting R_{wp} value should be about 8.81%.

Next you should refine some additional parameters, including a global isotropic temperature factor.

Make sure that **FIN31_refinement.xsd** is the active document.

On the **Pattern** tab, check the checkboxes for the refinement of **U, V, W, NA, NB, Zero point** and **Background coefficients**.

On the **Lattice** tab check on the refinement of **a, b, and c**. Check the **Keep fractional coordinates fixed during lattice changes** checkbox.

On the **Sample** tab, in the **Temperature factors** section, change **Applied** from **None** to **Global Isotropic** and check the **Global isotropic** checkbox for refinement.

On the **Display** tab, in the **View management** section, change **Chart view** from **New** to **Replace**.

Click the **Refine** button.

Examine the value of the Global isotropic temperature factor after refinement.

The R_{wp} value and the global isotropic temperature factor should be about 8.57% and 0.0045, respectively.

Finally, you should refine individual isotropic temperature factors for all of the atoms.

Make sure that **FIN31_refinement.xsd** is the active document.

Press **CTRL + A** to select everything.

On the **Sample** tab, in the **Temperature factors** section set Applied to **Atomic**.

Select the **Atoms** tab. All of the rows in the table are highlighted in blue because all of the atoms are selected in the corresponding 3D Viewer. In the first row, click on **None** and change the value to **Isotropic**. Check the Refine checkboxes to the left of the Temperature Factor column to refine all the isotropic temperature factors.

In the **Properties Explorer**, select the **Atom** filter. Double-click on **TemperatureFactor** to open the Atomic Temperature Factors dialog. Set the value of the isotropic atomic temperature factor to **0.0045**. The change applies automatically to all selected atoms.

Click the **Refine** button on the Reflex Powder Refinement dialog.

Adding the isotropic atomic temperature factors has slightly reduced the R_{wp} value, which is now around 8.54%. This value is very close to the R_{wp} factor of 7.75% obtained by Pawley refinement and it is not necessary to refine any further parameters at this point.

In Pawley refinement, all peak intensities are independent adjustable parameters and the R_{wp} values obtained therefore represent the lower limit for the R_{wp} values obtained by Rietveld refinement.

Now generate an HTML document that summarizes the results of the Rietveld refinement. The HTML document contains error bars for all refined parameters.

On the **Display** tab, in the **View management** section, check the **Generate HTML report** checkbox.

Make sure that **FIN31_refinement.xsd** is the active document.

Click the **Refine** button and close the dialog.

In the **Project Explorer**, double-click on the document **FIN31_refinement.htm**. Examine the HTML report.

Finally, you should visualize the thermal ellipsoids.

Make sure that **FIN31_refinement.xsd** is the active document.

Press and hold down the **ALT** key, then **double-click** on a motion group to select all motion groups. In the Properties Explorer, select the **Motion Group** filter and change **IsVisible** to **No**.

Press **CTRL + A** to select everything.

Open the Display Style dialog, select the **Temperature Factor** tab and click the **Add** button. Increase the **Scale factor** to **10** and close the dialog.

Make sure that **FIN31_refinement.xsd** is the active document. Press **CTRL + D** to deselect everything and examine the 3D Viewer.

Select **File | Save Project** from the menu bar.

You have successfully determined the crystal structure of FIN31.

This is the end of the tutorial.

References

Markvardsen, A. J., David, W. I. F., Johnson, J. C. and Shankland, K., "A probabilistic approach to space-group determination from powder diffraction data", *Acta Cryst.*, **A57**, 47-54, (2000).

Structure solution of 4-nitrophenylhexylurethane using a close-contact penalty

Purpose: Illustrates how to solve a crystal structure from a powder diffraction pattern using the close-contact penalty option in Reflex Plus.

Modules: Materials Visualizer, Reflex Plus, Forcite, COMPASS

Time: 🕒🕒🕒

Prerequisites: Using the Crystal Builder, [Indexing of 4-nitrophenylhexylurethane using X-Cell](#)

Background

Occasionally, the available powder diffraction data do not contain enough information for a successful structure solution. In such cases, additional chemical knowledge may be needed to determine the correct crystal packing. Typical examples include:

- Low quality powder patterns with broad, overlapping peaks
- Structures with a large number of degrees of freedom
- Strong preferred orientation of crystallites that reduces information in certain spatial directions
- High symmetry structures with only a small number of peaks in the powder pattern

In these instances, trying to determine the structure using just the powder data will typically result in a large number of solutions with low R_{wp} values. Some of these solutions (often those with the lowest R_{wp} factors) will be chemically unreasonable. For example, they may contain a large number of undesirable close contacts between structural fragments. To overcome this problem, Powder Solve allows you to add a close-contact penalty to the figure of merit. Using this new combined figure of merit during structure optimization removes configurations with bad contacts from the set of possible solutions very effectively. As a result, it may be possible to solve crystal structures in cases when the powder data alone do not contain enough information to locate the correct solution.

Introduction

In this tutorial, the crystal structure of 4-nitrophenylhexylurethane will be solved from powder diffraction data using a close-contact penalty and preferred orientation correction.

This tutorial covers:

- [Getting started](#)
- [To build the unit cell](#)
- [Pawley refinement](#)
- [To determine the space group automatically](#)
- [To attempt structure solution without preferred orientation correction or a close-contact penalty](#)
- [To attempt structure solution with preferred orientation correction, but without a close-contact penalty](#)
- [Structure solution using a combined figure of merit](#)
- [To analyze the solution](#)
- [To refine the solution](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **NPHU_cc** as the project name, click the **OK** button.

The new project is created with *NPHU_cc* listed in the Project Explorer. Next import the powder diffraction pattern and molecular structure of 4-nitrophenylhexylurethane.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the dropdown list to the right of the **File name** field. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click on **NPHU.xcd**.

Open the **Import Document** dialog again and navigate to **Examples\Reflex\Structures**. Choose **All Files (*.*)** from the dropdown list to the right of the **File name** field. Select **NPHU.xsd** and click **Open**.

2. Building the unit cell

In the tutorial [Indexing of 4-nitrophenylhexylurethane using X-Cell](#), the powder diffraction pattern of 4-nitrophenylhexylurethane was indexed. If you have an empty unit cell from that indexing result, you can use the model. Otherwise, you need to build an empty unit cell using the indexing information. X-Cell proposed $P2_1$ as the space group. You will confirm this later in the tutorial, but at this point, you should simply use the lowest symmetry monoclinic space group, $P2$.

Right-click on **NPHU_cc** in the Project Explorer and select **New | 3D Atomistic Document** from the shortcut menu. **Rename** the new document **cell.xsd**.

Select **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog. On the **Space Groups** tab, select space group number 3, **P2**. On the **Lattice Parameters** tab, enter the cell parameters obtained from the tutorial [Indexing of 4-nitrophenylhexylurethane using X-Cell](#): **a = 21.561 Å**, **b = 5.781 Å**, **c = 5.621 Å**, **$\beta = 96.781^\circ$** . Click the **Build** button.

3. Pawley refinement

Now you should determine the appropriate space group. The space group proposed by X-Cell is $P2_1$. You can use the automatic space group determination tool to confirm that this is the most probable space group and to see what other possibilities should be considered. The automatic space group determination tool requires previous Pawley refinement.

Make the model **cell.xsd** the active document. Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog. On the **Exp. Data** tab, select **NPHU.xcd**.

The peaks at 38.8 and 44.5° in the powder diffraction pattern of 4-nitrophenylhexylurethane are due to the aluminum sample holder. So they will not be included in the calculations.

To fit the peaks in the low angle range, which are strongly asymmetric, you need to apply the Finger-Cox-Jephcoat asymmetry correction to the peak profile function. This will increase the time required for the Pawley refinement to converge, so you will limit the angular range of the asymmetry correction to the low 2θ range.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

On the **Setup** tab, change the **Max. 2-Theta** value to **30°**.

On the **Pattern** tab, check the profile parameters **U**, **V**, **W**, **NA**, and **NB**, and the **Zero point** checkboxes. Select **Finger-Cox-Jephcoat** in the Asymmetry **Correction** dropdown field and set the **2-Theta limit** to **20**. Check the **H/L** and **S/L** parameters checkboxes. The refinement of **20 Background coefficients** is switched on by default.

On the **Lattice** tab, check on the refinement of all the cell parameters by checking the appropriate checkboxes.

On the **Display** tab, check the **Display simulation/experiment difference** checkbox and select **New** from the **Chart view** dropdown list.

Ensure that **cell.xsd** is the active document and click the **Refine** button and close the dialog.

The R_{wp} value at the end of the refinement should be about 14.7%.

4. To determine the space group automatically

You can now determine which monoclinic space groups are the most probable.

Select **File | Save Project** from the menu bar and **close** all the Viewers except **cell.xsd**.

Select **Modules | Reflex | Powder Indexing** from the menu bar to open the Reflex Powder Indexing dialog. Click the **Search space groups** button on the **Space Groups** tab.

A study table document, **cell.std**, containing all the monoclinic space groups ranked according to the figure of merit (FOM) is generated. Space groups with systematic absences not compatible with the experimental data have negative FOMs. Those without systematic absences have FOM = 0 and the most probable space groups have positive FOMs. In this case, the most likely ones are $P2_1$ and $P2_1/m$. The general position multiplicity is different for the two space groups. It is possible to eliminate one of them based on density considerations. The molecular weight of 4-nitrophenylhexylurethane is 266.296 g/mol and, according to the tutorial [Indexing of 4-nitrophenylhexylurethane using X-Cell](#), the cell volume is 700.630 Å³. A $P2_1$ cell, with two molecules in the unit cell, would have a density of 1.26 g/cm³. A $P2_1/m$ cell, with 4 molecules in the unit cell, would have an unrealistic density of 2.52 g/cm³. So Powder Solve should be run on the $P2_1$ cell.

Select the row in the study table document **cell.std** that contains details of the $P2_1$ unit cell. Click the **Create Cell** button and close the dialog.

A new 3D Atomistic document containing the empty $P2_1$ cell is created.

Right-click on this document in the Project Explorer and rename it **P21_cell.xsd**.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.


On the **Setup** tab, click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **3** and click the **OK** button. Click the **Refine** button.


The R_{wp} value at the end of the refinement should be about 14.6%.

Close the Reflex Powder Refinement dialog. Select **File | Save Project** from the menu bar and then **Window | Close All**.



5. To attempt structure solution without preferred orientation correction or a close-contact penalty

Initially, you should try to solve the structure using the diffraction data alone. Begin by attempting to solve the structure without refining the preferred orientation parameters.

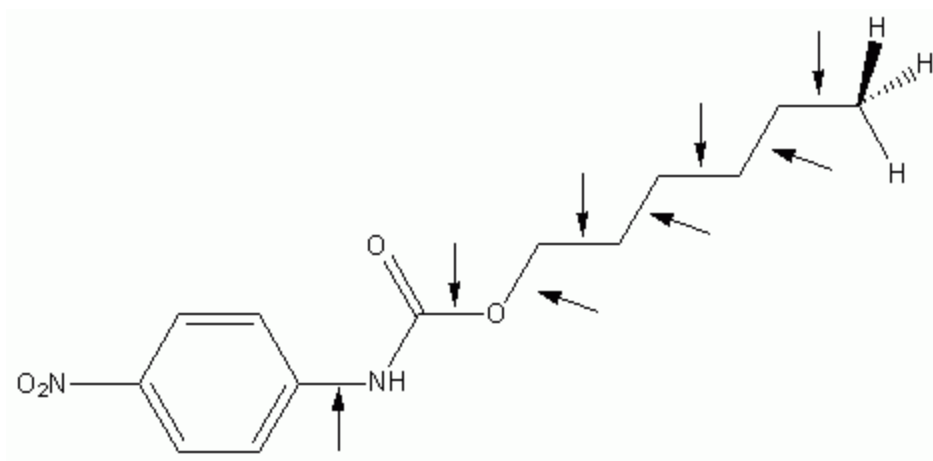
In the Project Explorer, double-click **NPHU.xsd** in the Project Explorer. Click the **Copy** button .

Open **P21_cell.xsd** and click the **Paste** button  to insert the optimized 4-nitrophenylhexylurethane molecular structure.

Because of the symmetry of the $P2_1$ space group, two copies of the molecule are automatically placed in the unit cell.


Magnify the structure using the **Zoom** tool , until you have a good view of one of the molecules in the unit cell. Click the **Measure/Change** arrow  and select **Torsion** from the dropdown list.

A number of flexible single bonds are identified in the figure below. Click on them in turn, starting from one end of the chain and working your way to the other.



Flexible single bonds in 4-nitrophenylhexylurethane

Now that the unit cell is set up, you can use Powder Solve to attempt to solve the crystal structure of 4-nitrophenylhexylurethane from the powder diffraction data.

Click the **3D Viewer Selection Mode** button  and select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu.

Open the **Reflex Powder Solve** dialog. On the **Structure Params** tab, click the **Create motion group (s) from selection as Single group** button to construct a motion group from the selected torsions. Click in **P21_cell.xsd** to deselect the structure.

Check all the checkboxes in the **Refine** column of the list except for that for C-C-C-H, enabling refinement of all the parameters except for the terminal bond to the methyl group, and ensure that the **Use hydrogens** checkbox is checked.

The C-C-C-H torsion is not included in the refinement at this stage because it can only influence the position of the methyl hydrogens. The position of the methyl hydrogens becomes important when intermolecular interactions are taken into account in the refinement. Since you will be attempting to solve the structure of 4-nitrophenylhexylurethane by applying a close-contact penalty in a subsequent section of this tutorial, the C-C-C-H torsion is being included, but not refined, at this stage simply for convenience.

On the **Setup** tab, change the **Number of cycles** to **5** and the global search **Method** to **Parallel Tempering**.

On the **Experimental Data** tab, select **NPHU.xcd**.

On the **Job Control** tab, choose **My Computer** as the **Gateway location**. Turn off the **Automatic Job description** option by unchecking the checkbox and enter **NPHUnoCCnoPO** as the **Job description**.

Select **File | Save Project** and **close** all the open documents. Open **NPHU.xcd** and then **P21_cell.xsd**. Click the **Solve** button and **close** the Reflex Powder Solve dialog.

Details of the new job will appear in the Job Explorer, informing you about the progress of the calculation. Two chart documents and a view of the unit cell are opened when the job starts and are periodically updated as it progresses. If you wish, you can close some or all of these documents while the calculation is running.

When the calculation is complete, details of the solutions are written to the file **NPHUnoCCnoPO.txt**.

In the Project Explorer, double-click **NPHUnoCCnoPO Reflex PSolve\NPHUnoCCnoPO.txt** to open it.

The lowest R_{wp} value reported is about 28%. Now examine the packing arrangement of the best solution, paying particular attention to the hydrogen bond patterns (if any) and close contacts.

Using the Project Explorer, open **NPHUnoCCnoPO Reflex PSolve\NPHUnoCCnoPO Solution.xsd**. Right-click on the structure and choose **Display Style** from the shortcut menu to open the Display Style dialog. On the **Lattice** tab, set the **Max** values for **A**, **B**, and **C** to **2.00** and close the dialog.

Now search the crystal structure for close contacts.

Choose **Build | Close Contacts** from the menu bar to open the Close Contact Calculation dialog. Click the **Calculate** button and close the dialog.

To make the crystal structure easier to view, you can switch off the display of the motion groups.

Hold down the **ALT** key and double-click on a motion group. All the motion groups are selected. If the Properties Explorer is not open, select **View | Explorers | Properties Explorer** from the menu bar. In the Properties Explorer, double-click on **IsVisible** to open the Edit IsVisible dialog. Click the **No/False** radio button and click the **OK** button.

The best solution has number of close contacts and voids.

6. To attempt structure solution with preferred orientation correction, but without a close-contact penalty

Now try to refine preferred orientation parameters during the global search.

Select **File | Save Project** from the menu bar and **Close** all the open documents apart from **P21_cell.xsd** and **NPHU.xcd**.

Open the **Reflex Powder Solve** dialog and make **P21_cell.xsd** the active document.

On the **Sample Params** tab, select **March-Dollase** from the dropdown list for **Preferred orientation** in the **Value** column. Check the boxes to refine all the preferred orientation parameters, **a***, **b***, **c***, and **R0**.

On the **Experimental Data** tab, select **NPHU.xcd**.

On the **Job Control** tab, ensure **My Computer** is the **Gateway location** and change the **Job description** to **NPHUnoCC**.

Click the **Solve** button and **close** the Reflex Powder Solve dialog.

As before, the new job will appear in the Job Explorer, where you can monitor the progress of the calculation. Various documents will be generated automatically and updated as the job progresses.

When the calculation is complete, **open** the folder **NPHUnoCC Reflex PSolve** in the Project Explorer and double-click on the text document **NPHUnoCC.txt**.

The lowest R_{wp} value reported should be about 19%. You should now examine the packing arrangement of the best solution, particularly any close contacts.

In the Project Explorer, double-click on **NPHUnoCC Reflex PSolve\NPHUnoCC Solution.xsd**. Open the **Display Style** dialog, on the **Lattice** tab, set the **Max** values for **A**, **B**, and **C** to **2.00** and close the dialog.

Click the **Calculate Close Contacts** button .

Switch off the display of the motion groups.

Once again, the structure exhibits several close contacts and voids. Therefore, it can be concluded that there is not enough information in the powder diffraction pattern to determine the correct crystal packing. In order to arrive at the correct structure, it will be necessary to introduce an additional chemical requirement in the form of a close-contact penalty.

7. Structure solution using a combined figure of merit

Obviously, the crystal structure of 4-nitrophenylhexylurethane will not contain overlapping atoms and this requirement can be incorporated into the optimization process by applying a close-contact penalty. This may allow the correct structure to be determined, even though the powder pattern alone does not contain enough information to distinguish it from other solutions.

Select **File | Save Project** from the menu bar and **close** all the open documents apart from **P21_cell.xsd** and **NPHU.xcd**.

Open the **Reflex Powder Solve** dialog and make **P21_cell.xsd** the active document.

On the **Sample Params** tab the preferred orientation parameters shown here are the best values found in the previous run. Change them back to the default values, **a* = 0, b* = 0, c* = 1, R0 = 1**.

On the **Structure Params** tab, check the appropriate checkbox in the **Refine** column of the list of parameters to include the previously neglected C-C-C-H torsion of the methyl group in the refinement.

On the **Setup** tab, check the **Apply close contact penalty** checkbox. Click the **More...** button to open the Powder Solve Options dialog. Change the **Radius scale factor** to **0.95** and click the **OK** button.

On the **Experimental Data** tab, select **NPHU.xcd**.

On the **Job Control** tab, ensure **My Computer** is the **Gateway location**. Enter **NPHUCC** as the **Job description**.

Click the **Solve** button and **close** the Reflex Powder Solve dialog.

The progress of the calculation can be followed using the Job Explorer.

When the calculation is complete, **Open** the folder **NPHUCC Reflex PSolve** in the Project Explorer and double-click on the text document **NPHUCC.txt**.

The lowest R_{wp} value of the best solution (lowest R_{comb}) should be about 17.5%

In the Project Explorer, double-click on **NPHUCC Reflex PSolve\NPHUCC Solution.xsd**. Open the **Display Style** dialog, on the **Lattice** tab, set the **Max** values for **A**, **B**, and **C** to **2.00** and close the dialog.

Click the **Calculate Close Contacts** button .

Switch off the display of the motion groups.


Looking at the best solution from the calculation using a close-contact penalty reveals that there are still too many close contacts for this structure to be viable.


Next investigate some of the other solutions that were found in the calculation. Each time a new structure is arrived at in the cycle of refinement, it is written to a trajectory file. The best solutions from each cycle of refinement can be extracted from this trajectory file.

Select **File | Save Project** from the menu bar and **close** all the open documents. Open the trajectory file **NPHUCC Reflex PSolve\NPHUCC.xtd**.

Open the **Reflex Powder Solve** dialog. On the **Analysis** tab, set the **X-axis property** to **Frame Number**, the **Y-axis property** to **R_{wp}**, and the **Graph style** to **Line**. Click the **Analyze** button and close the dialog.

This produces a plot of R_{wp} against frame number for all the solutions recorded in the trajectory file.

Make **NPHUCC.xtd** the active document and click the **Animation Mode** arrow , select **Options** from the dropdown list to open the Animation Options dialog. Check the **Recalculate atom visibility every frame** checkbox and close the dialog.

Make **NPHUCC.xcd** the active document and select the **Chart Viewer Selection Mode** tool  from the Chart Viewer toolbar. Examine the chart document to find the frame with the next lowest R_{wp} after the best solution. Click on the point representing this frame in the plot.

The trajectory document is updated with the structure found in this frame. You can now examine the structure for close contacts as you did previously for the best solution. Check the five frames with the lowest R_{wp} values and find the one with the fewest close contacts. The R_{wp} of this structure should be around 21%.

Now examine the hydrogen bonding in the selected structure.

Click the **Calculate Hydrogen Bonds** button .


The hydrogen bonds in the crystal are drawn as pale blue dotted lines. You should find that the hydrogen bonds overlay the close contacts, showing that the only close contacts in the structure are due to hydrogen bonds. You should also find that the alkyl chain adopts a low energy all-trans conformation. However, before you conclude that you have solved the crystal structure, you should perform some additional reality checks. This is always advisable and especially important in cases where the structure has been solved using a preferred orientation correction, which modifies the intensity ratios.

8. To analyze the solution

A straightforward way to check that a structure is chemically sensible is to verify that it is energetically stable. The simplest way to do this is to perform a forcefield minimization.

Make **NPHUCC.xtd** the active document and select **File | Export...** from the menu bar to open the Export dialog. Select **Materials Studio 3D Atomistic Files** from the **Save as type** dropdown list, name the new file **best_solution_to_verify.xsd**, and navigate to the **Documents** folder, at the same level as **P21_cell.xsd**. Click the **Save** button.

Select **File | Save Project** from the menu bar and then **Window | Close All**. Open **best_solution_to_verify.xsd**.

Click the **Forcite** button  and choose **Calculation** from the dropdown list to open the Forcite Calculation dialog.

Select **Geometry Optimization** from the **Task** dropdown list and click the **More...** button to open the Forcite Geometry Optimization dialog. Check the **Optimize Cell** checkbox and close the dialog.

On the **Energy** tab, select **COMPASS** from the **Forcefield** dropdown list. Ensure that **Ewald** is selected for both the **Electrostatic** and **van der Waals** summation methods.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click the **Run** button and close the dialog.

A new folder called **best_solution_to_verify Forcite GeomOpt** is created in the Project Explorer. The calculation should take less than one minute to complete. When the job is complete, the minimized structure is saved in the document **best_solution_to_verify.xsd** and the results of the calculation are contained in the text file **best_solution_to_verify.out**, both of which are in the new folder. You can verify that the optimized structure is very close to the Powder Solve solution. Therefore, it can be concluded that the packing arrangement found by Powder Solve is stable.

Now check that the observed preferred orientation parameters are consistent with the structural properties of the solution.

The lattice parameters are approximately $a = 21.6 \text{ \AA}$, $b = 5.8 \text{ \AA}$, $c = 5.6 \text{ \AA}$, and $\beta = 96.8^\circ$. With one axis four times longer than the other two, a plate-like morphology can be expected with the smallest crystal dimension being more or less parallel to the a axis. The preferred orientation correction for compounds forming plate-like crystals is expected to have $R0 < 1$ in a direction perpendicular to the plates.

In the Project Explorer, double-click on **NPHUCC - Powder Solve** in the **NPHUCC Reflex PSolve** folder. Select the **Sample Params** tab and verify that the preferred orientation parameters are in good agreement with the crystal structure.

9. To refine the solution

It has been established that the amount of information contained in the powder pattern is insufficient to find the right packing arrangement. Therefore, it can be expected that a Rietveld refinement alone will not be sufficient to refine the crystal structure. In this case, you have verified that COMPASS is suitable to optimize the crystal structure. Consequently, COMPASS can also be used to refine it. To do this, you should start by optimizing the molecular conformation in the crystal environment while keeping the cell parameters fixed.

Select **File | Save Project** from the menu bar and **close** all the open documents.

In the Project Explorer, double-click on **best_solution_to_verify.xsd** (the structure you exported from the trajectory document rather than the forcefield-minimized structure produced by Forcite that has the same filename, but is saved in the `best_solution_to_verify Forcite GeomOpt` folder) and make a copy of it by selecting **File | Save As...** from the menu bar. Rename the copy **best_solution_refining.xsd** and **Save** it in the **Documents** folder.

Open the **Forcite Calculation** dialog and click the **More...** button. On the Forcite Geometry Optimization dialog uncheck the **Optimize cell** checkbox and close the dialog. Click the **Run** button and close the Forcite Calculation dialog.

A new folder called `best_solution_refining Forcite GeomOpt` is created in the Project Explorer. The calculation should take less than five minutes to complete. When the job is complete, the minimized structure is saved in the document `best_solution_refining.xsd` in the new folder. If you inspect the refined structure you will find that it is basically the same as what you started with, except that the alkyl chain is closer to a perfect all-trans conformation.

You can now use Rietveld refinement to further refine the structure. After optimization with the COMPASS forcefield, you can assume that the molecular conformation is close to its final structure. Thus, you can keep it fixed during the Rietveld refinement. Begin by loading the Pawley refinement parameters.

Select **File | Save Project** from the menu bar and **close** all the open documents except **best_solution_refining.xsd**.

In the Project Explorer, right-click on **NPHUCC - Powder Solve** in the **NPHUCC Reflex PSolve** folder and select **Powder Refinement** to open the Reflex Powder Refinement dialog. Click the **Calculate** button.

The Pawley R_{wp} factor should be 14.6%, as it was at the beginning of the calculation.

On the **Setup** tab, change the **Type** from Pawley to **Rietveld**. Click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **10** and click the **OK** button.

On the **Pattern** tab, uncheck the refinement parameters **H/L** and **S/L**.

Select the **Lattice** tab and make sure that all the cell parameters checkboxes are checked. Check the **Keep fractional coordinates fixed during lattice changes** checkbox.

On the **Sample** tab, change the **Temperature factors** to **Global Isotropic** and check the appropriate checkbox to refine them.

On the **Display** tab, select **New** from the **Chart view** dropdown list.

On the **Structure** tab, deselect all the torsions, leaving only the refinement of the motion group position switched on, so that all the checkboxes except the first one are unchecked. Click the **Refine** button and close the dialog.

The final R_{wp} factor should be around 21%. The structure is in good agreement with the reported single crystal structure ([Yakimanski et al., 1997](#)).

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Yakimanski, A. V.; Kolb, U.; Matveeva, G. N.; Voigt-Martin, I. G.; Tenkovtsev, A. V. "The Use of Structure Analysis Methods in Combination with Semi-Empirical Quantum-Chemical Calculations for the Estimation of Quadratic Nonlinear Optical Coefficients of Organic Crystals", *Acta Crystallogr., Sect. A*, **53**, 603-614 (1997).

BIOVIA would like to thank Dr Ute Kolb of the University of Mainz, Germany, for supplying the experimental powder diffraction pattern for NPHU.

Sorption tutorials

The following tutorials illustrate how to utilize Sorption's capabilities.

- [Predicting the loading of CH₄ in zeolite MFI with Sorption](#)
- [Predicting the loading of ions in Al-substituted zeolite MFI](#)

Predicting the loading of CH₄ in zeolite MFI with Sorption

Purpose: Illustrates how to use Sorption to compute a loading curve for a molecule in a zeolite framework.

Modules: Materials Visualizer, Sorption

Time: 

Prerequisites: Project management Visualizer Tutorial

Background

Sorption is used to simulate sorption of small molecules, called sorbates (guest molecules), into porous 3D frameworks (hosts). The frameworks are typically microporous inorganic structures such as zeolites and aluminophosphates. Characterizing the behavior of these materials has important application in the fields of catalysis and separations technology.

The Sorption module has been designed to be used by experimental scientists, as well as computational chemists. Output-analysis features, such as automatic calculation and display of isotherms, make it easy to directly compare Sorption data with bench results.

Introduction

In this tutorial, you will learn how to use Sorption to calculate a loading curve for a small molecule, CH₄, in a framework, zeolite MFI. A loading curve is a series of fixed pressure (grand canonical ensemble) calculations performed over a series of fugacities.

This tutorial covers:

- [Getting started](#)
- [To set up the calculation](#)
- [To run the calculation](#)
- [To analyze the results](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CH4_MFI** as the project name.

The new project is created with *CH4_MFI* listed in the Project Explorer. You will begin by importing the structures you will need.

Select **File | Import...** from the menu bar or click the **Import** button  to open the Import Document dialog. Navigate to **Structures/organics** and select **methane.msi**, then click the **Open** button.


Open the **Import Document** dialog again and navigate to **Structures/zeolites**, select **MFI.msi** and click the **Open** button.

Sorption calculations require P1 crystal structures (those without any symmetry) as inserting the guest molecules will break any symmetry that is present. You will change the symmetry of MFI to P1.

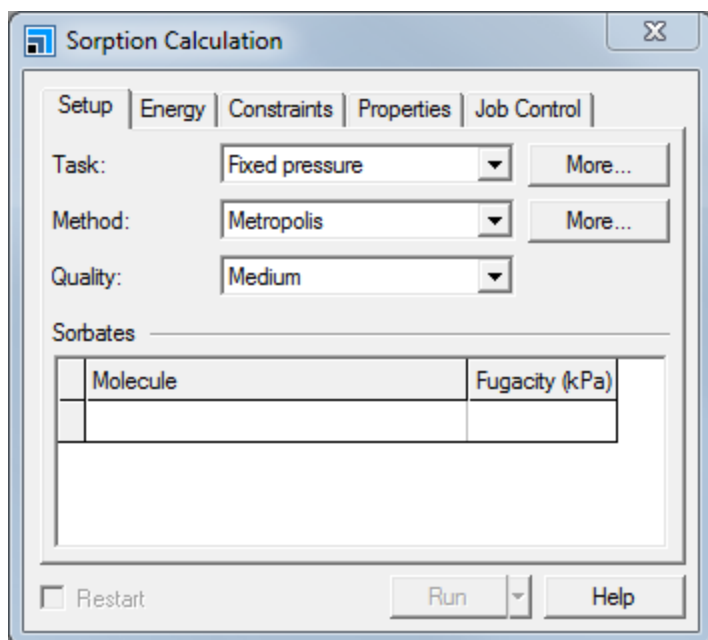
Ensure that **MFI.xsd** is the active document and select **Build | Symmetry | Make P1** from the menu bar.

2. To set up the calculation

Now you are ready to set the parameters for the calculation.

Click the **Sorption Tools** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the Sorption Calculation dialog.



Sorption Calculation dialog, Setup tab

Select **Adsorption isotherm** as the **Task** and **Metropolis** for the **Method**. Set the **Quality** to **Coarse**.

In the **Sorbates** section, click on first cell in the **Molecule** column and select **methane.xsd** from the dropdown list.

Note: The **Coarse** option is used so that this tutorial runs quickly. A realistic statistical analysis requires the **Medium** or **Fine** setting.

You need to set the upper and lower fugacities at which calculations will be performed and the number of intervals between them. In this example you will use a lower fugacity of 1 atm (101.325 kPa) and an upper fugacity of 10 atm (1013.25 kPa).

Click in the cell for the **Start** column of the **Sorbates** grid and enter a value of **101.33** kPa, enter a value of **1013** kPa in the **End** column.

Click the **More...** button for the **Task** to open the Sorption Isotherm dialog. Set the **Fugacity steps** to **9** and check the **Logarithmic** checkbox. Ensure that the **Temperature** is set to **298** K.

Close the Sorption Isotherm dialog.

Next you will select the forcefield options that will be used in the calculation.

On the **Energy** tab of the Sorption Calculation dialog, choose **COMPASS** as the **Forcefield** and set the **Charges** to **Forcefield assigned**.

Set the **Quality** of the energy calculation to **Medium**. Ensure that **Ewald & Group** is set as the **Electrostatic** summation method and that the **van der Waals** summation method is set to **Atom based**.

Finally, make sure that the appropriate properties calculations have been requested.

On the **Properties** tab of the Sorption Calculation dialog, ensure that the checkboxes are checked for **Energy distribution**, **Density field**, and **Energy field**.

Set the **Sample interval** to **50**.

Set the **Grid resolution** to **Medium**, which will automatically set the **Grid interval** to **0.4 Å**.

3. To run the calculation

Now set the job control options and start the calculations.

On the **Job Control** tab of the Sorption Calculation dialog, select an appropriate server for the **Gateway location**.

Click the **Run** button and **close** the dialog.

A new folder, called **MFI Sorption Isotherm**, is created in the Project Explorer. As the job progresses, updates are presented in both chart and text documents. The calculation should take 5-10 minutes, depending on the speed of the processor in your computer.

Sorption will perform a fixed pressure calculation at 10 different values of fugacity ranging from 101 kPa to 1013 kPa. Sorption returns the following graphs for each fugacity, which can be used to monitor the status of the calculation.

- MFI Etotal.xcd displays the value of energy at each Monte Carlo move. The total energy and various components are displayed.
- MFI Energy.xcd displays an energy distribution histogram.
- MFI Loading.xcd displays the instantaneous and average loading (number of molecules per unit cell) at each step.

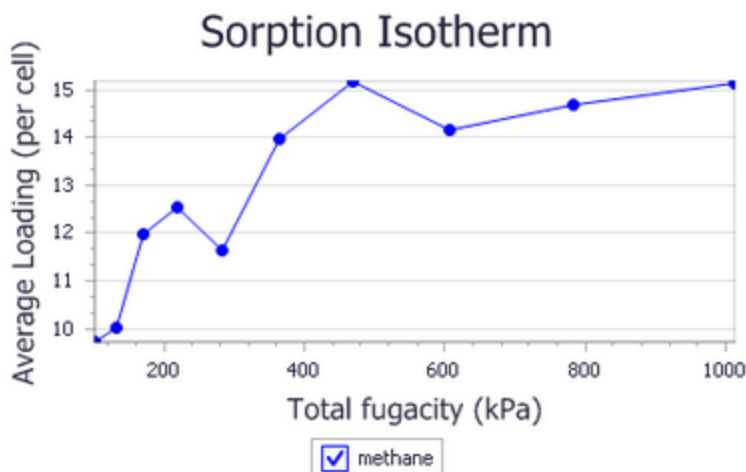
When sufficient Monte-Carlo steps accumulate, each of the graphs listed above should converge on a final value. When the requested number of steps have been executed, the program restarts at the next value of fugacity.

Note: The temporary documents, Status.txt, MFI Energy.xcd, MFI Etotal.xcd, MFI Loading.xcd and MFI.xsd, are only relevant at run time and should be disregarded once the job has completed. The output documents, MFI.txt, MFI.std and MFI Isotherm.xcd contain the final results of the Sorption job.

4. To analyze the results

Click the **OK** button to close the Job Completed dialog.

Locate the output folder for the Sorption job, **MFI Sorption Isotherm**, in the Project Explorer and open the adsorption isotherm results file, **MFI Isotherm.xcd**.



Adsorption isotherm for CH₄ in MFI computed by Sorption

The adsorption isotherm generated in this tutorial is not very smooth because it was generated using coarse settings. A smoother and more realistic curve would be obtained with finer grained settings.

Note: Your results may not look exactly like the images in the tutorial due to the random nature of Monte-Carlo calculations, but they should be qualitatively similar.

The adsorption isotherm displays the adsorption in molecules per cell at each fugacity. In a typical case, the curve will rise toward a saturation point value beyond which no more molecules can be adsorbed.

Tip: The field values are returned for every fugacity. The MFI.xsd 3D Atomistic document in the *Project Explorer* contains the results from the final fugacity.

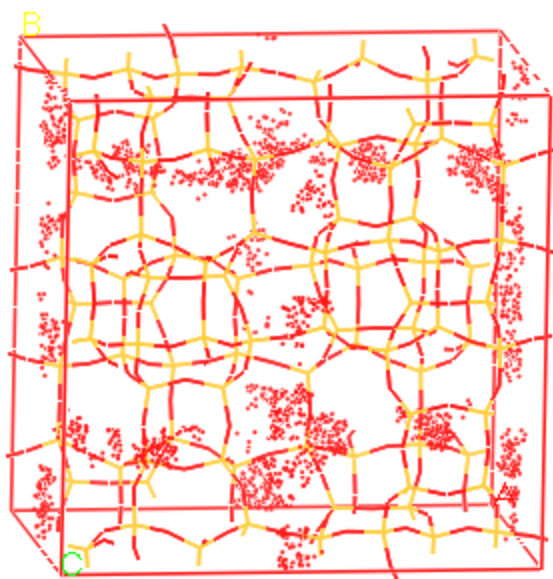
Next you will examine the density and energy fields returned by Sorption.

Double-click on the **MFI.std** study table document in the Project Explorer.

The total energy, fugacity, and energy components are included in the study table for each interval on the loading curve.

Locate the entry in the third row of the study table and double-click on the structure **MFI_structure_3**.

A *Detail View* similar to the one below will be displayed.



Density field for CH₄ in MFI computed by Sorption


The red output field represents a density distribution of CH₄ molecules in the MFI lattice framework. The density distribution is represented on a grid with resolution 0.4 Å. Results from the Monte-Carlo calculation are binned onto this grid. Regardless of the number of steps in the calculation, the amount of data displayed will be constant.

Tip: You can change the resolution of the grid at run time by setting a different sample interval on the *Properties* tab.

You will now change the volumetric representation of the results to get a better insight into the location of energy "hot spots" in the cell.

Select **View | Toolbars | Volume Visualization** from the menu bar to display the Volume Visualization toolbar.

There are two fields in the *Detail View*, a density field and an energy field. You will begin by selecting the density field.


Click the **Volumetric Selection** button  on the **Volume Visualization** toolbar to open the Volumetric Selection dialog. Ensure that the **methane-Density** checkbox is checked.

Now you will change the way that the field is displayed.


Right-click in the Detail View of **MFI_structure_3** and choose **Display Style** from the shortcut menu to open the Display Style dialog.

On the **Field** tab choose **Color by field values** in the **Coloring** section.

The field changes from a uniform red to a range of colors that represent the different density values.

Tip: To see the values associated with each color, click the *Color Maps* button  on the *Volume Visualization* toolbar.

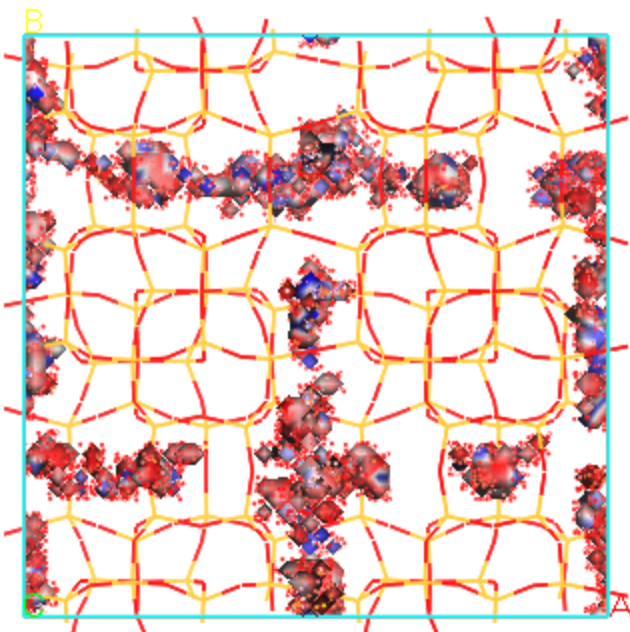
Now you will generate a display that combines the energy and density distribution information.

Select a display style of **Empty** on the **Field** tab of the Display Style dialog. Click the **Create Isosurfaces** button  on the **Volume Visualization** toolbar to open the Choose Fields To Isosurface dialog. Select **methane-Density of MFI** and click the **OK** button to generate an isodensity surface.

When the isosurface appears, click on it once to select it.

On the **Isosurface** tab of the Display Style dialog set the **Isovalue** to **0.02**. Select **methane-Potential of MFI** from the **Mapped field** dropdown list.

You have created a surface of constant density and colored it by the potential energy. In this display, dark blue areas have the lowest energy and dark red the highest energy. You can use this analysis to look for favorable binding sites in the lattice framework.



Isodensity surface colored by potential for CH_4 in MFI

This is the end of the tutorial.

Predicting the loading of ions in Al-substituted zeolite MFI

Purpose: Illustrates how to use Sorption to locate the positions of extra-framework cations in a zeolite.

Modules: Materials Visualizer, Sorption

Time: 🕒 🕒

Prerequisites: [Predicting the loading of CH₄ in zeolite MFI with Sorption](#)

Background

Sorption is used to simulate sorption of small molecules, called sorbates (guest molecules), into porous 3D frameworks (hosts). The frameworks are typically microporous inorganic structures such as zeolites and aluminophosphates. In most active forms of zeolites some Si atoms have been replaced by Al atoms. There must be enough extra-framework cations to balance the charge of the Al atoms.

The Sorption module can perform calculations on ionic systems, and this can be used to predict the locations of the cations. However, assigning charges to the system can be problematic.

Introduction

In this tutorial, you will learn how to use Sorption to calculate the positions of Na cations in zeolite MFI.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures](#)
- [To set up the calculation](#)
- [To run the calculation](#)
- [To analyze the results](#)


Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Al_MFI** as the project name.

The new project is created with *Al_MFI* listed in the Project Explorer. You will begin by importing the structures you will need.

Select **File | Import...** from the menu bar or click the **Import** button  to open the Import Document dialog. Navigate to **Structures/zeolites**, select **MFI.msi** and click the **Open** button.

Sorption calculations require P1 crystal structures (those without any symmetry) as inserting the guest molecules will break any symmetry that is present. You will change the symmetry of MFI to P1.

Select **Build | Symmetry | Make P1** from the menu bar.

2. To prepare the structures

You need to replace five of the Si atoms with Al, for purposes of the tutorial, you can select any 5 at random. In a realistic zeolite, however, no two Al atoms should be bonded to the same oxygen atom.

Select any **5 Si** atoms in the MFI structure, then choose **Modify | Modify Element | Periodic Table...** from the menu bar to open the Periodic Table dialog. Select **Al** and click the **OK** button. Click anywhere in the 3D Viewer to deselect the five new Al atoms.


The selected Si atoms will be changed to Al atoms, colored pink in the 3D Viewer.


Tip: It is easier to select individual atoms if you change the display style to *Ball and Stick*.

Finally, you will need to create a document that contains the extra-framework Na cation that will be used to balance the charges on the Al.

Select **File | New...** from the menu bar to open the New Document dialog. Select **3D Atomistic** and click the **OK** button.

You will add a single Sodium atom to this document.

Click the **Sketch Atom** button  on the **Sketch** toolbar and then the **Element used to sketch** button. Select **Periodic Table...**, choose **Na** and click the **OK** button.


Click anywhere in the 3D Viewer to add a new Na atom. Click the **3D Viewer Selection Mode** button  on the **3D Viewer** toolbar to exit sketch mode.

The new document with the Na atom has a default name of `3D Atomistic.xsd`, you will rename this document to Na atom.

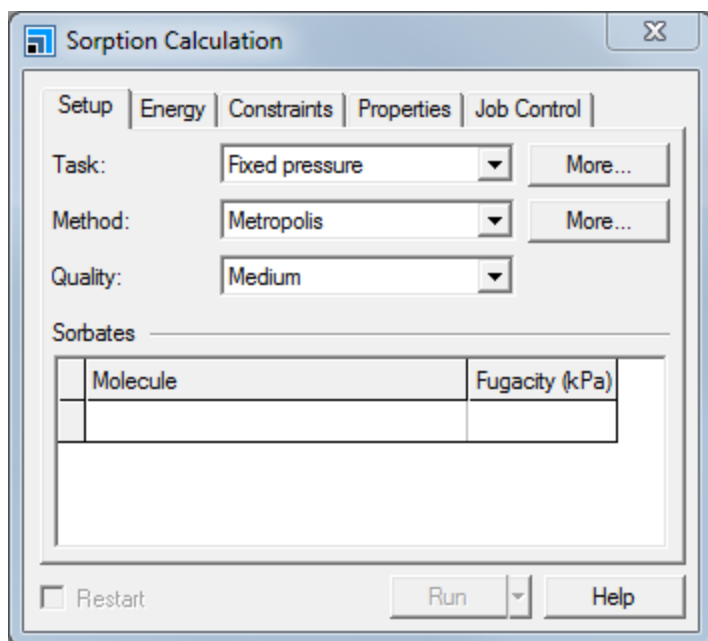
Rename the new document **Na atom.xsd**.

3. To set up the calculation

Now you are ready to set the parameters for the calculation.

Ensure that **MFI.xsd** is the active document. Click the **Sorption** button  on the **Modules** toolbar and choose **Calculation** from the dropdown list.

This opens the Sorption Calculation dialog.



Sorption Calculation dialog, Setup tab

Select **Locate** as the **Task** and **Metropolis** for the **Method**, set the **Quality** to **Coarse**.

Click the **More...** button for the task, to open the Sorption Locate dialog. Ensure that the **Automated temperature control** and **Adjust step sizes** checkboxes are checked. Select **Return lowest energy frames**, and set the **Number of frames** to **10**. Close the Sorption Locate dialog.

In the **Sorbates** section of the Sorption Calculation dialog, click in the top cell in the **Molecule** column and select **Na atom.xsd** from the dropdown list. Enter **5** for the **Loading**.

Note: The **Coarse** option is used so that this tutorial is not time consuming. A realistic statistical analysis would require the **Medium** or the **Fine** setting.

Next you will select the forcefield options that will be used in the calculation. At this stage you will also assign atomic charges to the atoms in the system. There are several ways that you can assign charges to atoms, but in this tutorial you will assign charges by hand to each atom type.

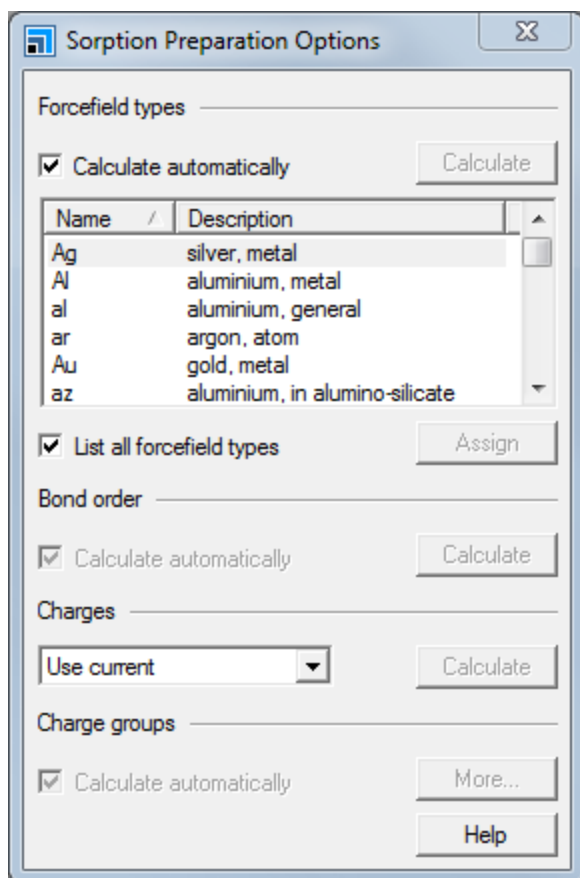
On the **Energy** tab of the Sorption Calculation dialog, select **cvff** from the **Forcefield** dropdown list.

Select **Use current** from the **Charges** dropdown list and set the **Quality** to **Medium**.

Select **Ewald** from the **Electrostatic** dropdown list.

Note: The **Electrostatic** option must be set to **Ewald** for systems where the framework and sorbates are charged.

Click the **More...** button for the **Forcefield** to open the Sorption Preparation Options dialog.



Sorption Preparation Options tab

Before you can assign charges, you need to assign forcefield types.

Ensure that **MFI.xsd** is the active document. On the Sorption Preparation Options dialog **uncheck** the **Calculate automatically** checkbox and click the **Calculate** button.

Make **Na atom.xsd** the active document and click the **Calculate** button again. **Close** the Sorption Preparation Options dialog.

Tip: You can see which forcefield types were assigned by using the Label dialog.

Make **MFI.xsd** the active document. Hold down the **ALT** key and **double-click** one of the Si atoms.

All the Si atoms are selected.

Select **Modify | Charges** from the menu bar to open the Charges dialog. On the **Edit** tab select the **Set all charges to** radio button and enter **2.4**. Click the **Assign** button.

Repeat this procedure to assign charges of **1.4** to all **Al** atoms and charges of **-1.2** to all **O** atoms.

Make **Na atom.xsd** the active document and assign the Na atom a charge of **1.0**. **Close** the Charges dialog.

The charges you assigned are the ones used by the `cvff_aug` forcefield. They have been optimized for simulations of silicates, aluminosilicates, clays and aluminophosphates.

As a result of using these charges, note that the total charge for all the Si atoms is +218.4, for all O atoms it is -230.4 and for all the Al atoms the total charge is +7. The zeolite, therefore, has a total -5 charge. You have specified a loading of five Na atoms, each with a +1 charge, which will neutralize the total charge on the zeolite when they are added to the structure during the Sorption calculation.

4. To run the calculation

Now you will set the job control options and start the calculation.

On the **Job Control** tab of the Sorption Calculation dialog, select an appropriate server for the **Gateway location**.

Make sure that **MFI.xsd** is the active document.

Click the **Run** button and close the Sorption Calculation dialog.

A new folder, called **MFI Sorption Locate**, is created in the Project Explorer. As the job progresses, updates are presented in both chart and text documents.

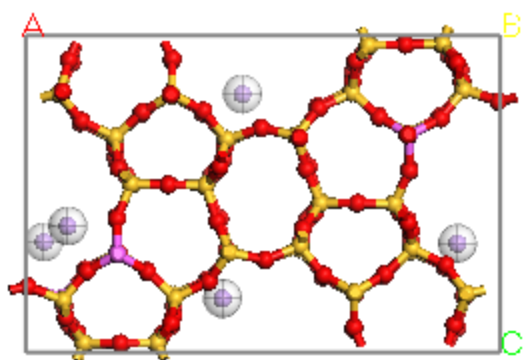
The following files are produced:

- **MFI.xsd** contains the minimum energy configuration of the sorbates and the framework.
- **MFI.txt** is the output file from the calculation. It contains information on the number and type of Monte Carlo moves.
- **MFI Low energy.xtd** is a trajectory file containing the lowest few configurations. The number of configurations can be specified as an input parameter to the Locate job.

Note: The file **MFI Low energy.xtd** is only produced when you select *Return lowest energy frames* on the *Sorption Locate* options dialog.

5. To analyze the results

Double-click on **MFI.xsd** in the **MFI Sorption Locate** folder in the Project Explorer.



Minimum energy configuration of Na in MFI computed by Sorption

The results of your job will be different depending up the location of the Al ions and on the random nature of the Monte-Carlo calculation. Note that the sorbates are displayed within a Motion Group to highlight their locations.

Double-click on **MFI Etototl.xcd** in the Project Explorer.

The total energy and energy components are plotted as a function of step. In a converged calculation, the total will converge to an asymptotic value. Because you used coarse settings for this tutorial, the energy may not have converged.

Examine again the final structure in MFI .xsd. As part of a scientific investigation, you would normally use this to perform subsequent calculations within Materials Studio. You could, for example, use this model to perform calculations of the loading of CH₄ as in the tutorial [Predicting the loading of CH₄ in zeolite MFI with Sorption](#). What effect do you think the presence of the Na cations will have on the loading?

You could also perform a geometry optimization with DMol³ or CASTEP to obtain a more accurate structure and energy.

This is the end of the tutorial.

Synthia tutorials

The following tutorial illustrates how to utilize Synthia's capabilities.

Predicting the properties of two random copolymers

Purpose: Illustrates how to use Synthia to predict properties for random copolymers.

Modules: Materials Visualizer, Synthia

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

The weight average molecular weight (M_w), the number average molecular weight (M_n), and the polydispersity of the system are important properties for characterizing a polymer. In dilute solutions of polymers, light-scattering experiments are one of several methods used to measure M_w . For dilute solutions of polymers, the rate of change of the refractive index with the concentration of the polymer, known as the specific refractive index increment (dn/dc), can be used to predict the optical constant, K_c . When K_c is divided by the excess Rayleigh ratio, ΔR , this gives a concentration-dependent function that can be extrapolated to a concentration of 0. When the concentration is 0, $K_c/\Delta R = 1/M_w$, thus giving the value of M_w (Young et al., 1991). The specific refractive index increments can be defined as:

$$\frac{dn}{dc} = \frac{n_p - n_s}{\rho_p}$$

where n_p is the refractive index of the polymer, n_s is the refractive index of the solvent, and ρ_p is the density of the polymer.

Synthia enables you to predict many properties of repeat units. Among these are the refractive index and the density, which you can then use to predict the specific refractive index increments.

Introduction

In this tutorial, you will build two copolymers, poly(*N*-benzyl methacrylamide-*co*-acrylamide) and poly(*N*-methyl methacrylamide-*co*-acrylamide). You will use Synthia to predict the density and refractive index for a range of concentrations from pure acrylamide to pure *N*-benzyl methacrylamide or pure *N*-methyl methacrylamide. Once you have these data, you will define a new function in the study table to predict dn/dc and plot this for the two copolymers. This work is based on results from a study by Bicerano (1994).

This tutorial covers:

- [Getting started](#)
- [To sketch the repeat units](#)
- [To define the structures as repeat units](#)
- [To define the copolymer](#)
- [To work with the study table](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

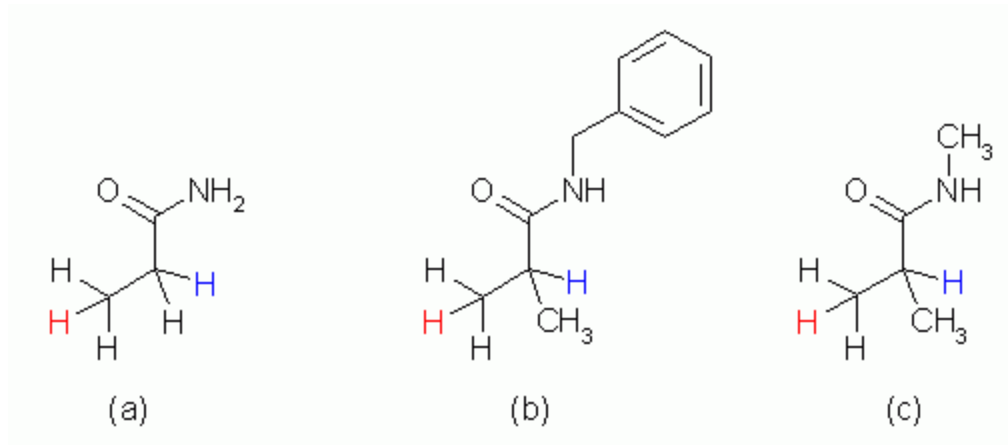
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Copolymer** as the project name, click the **OK** button.

The new project is created with *Copolymer* listed in the Project Explorer.


2. To sketch the repeat units

The first stage in this tutorial is to sketch the three repeat units that will be used to generate the copolymers.



Repeat units used to generate the copolymers: (a) acrylamide; (b) *N*-benzyl methacrylamide; (c) *N*-methyl methacrylamide

Start by sketching acrylamide.

Click the **New** arrow  on the toolbar and select **3D Atomistic Document** from the dropdown list. **Rename** the new document **acrylamide.xsd**.

Use the tools on the **Sketch** toolbar to construct acrylamide, as above.

Click the **Adjust Hydrogen** button  then the **Clean** button .

Next sketch the other two fragments.

Open two more 3D Atomistic documents. Sketch *N*-benzyl methacrylamide and *N*-methyl methacrylamide, adjust the number of hydrogen atoms, and clean the structures. Rename the documents **N-benzyl.xsd** and **N-methyl.xsd**.

You should now have three 3D Atomistic documents containing the structures of the three monomers.

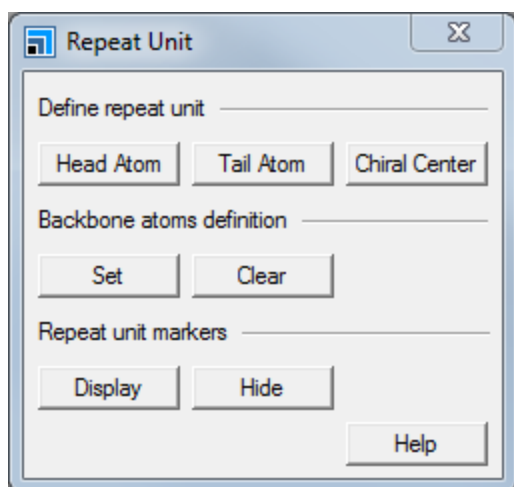
Tip: Calculations of the mechanical properties - bulk, shear, and Young's modulus, Poisson's ratio, shear yield stress, or brittle fracture stress - use the length of the repeat unit as a descriptor. Therefore, you should optimize the geometry of the repeat units using Forcite prior to performing Synthia calculations of these properties. All the calculations of other properties do not use the geometry of the structure and so optimization is not required.

3. To define the structures as repeat units

For Synthia to recognize the structures as repeat units, head and tail atoms must be defined. This is achieved using the Repeat Unit tool in the Polymer Builder functionality.


Ensure that **acrylamide.xsd** is the active document. Select **Build | Build Polymers | Repeat Unit** from the menu bar.

This opens the Repeat Unit dialog.



Repeat Unit dialog


The head/tail atoms are defined as hydrogen atoms attached to the two carbon atoms in the ethyl group (see the structures above).

Click the **3D Viewer Selection Mode** button  on the toolbar. Select the hydrogen shown in red in the figure above and click the **Head Atom** button on the Repeat Unit dialog. Select the hydrogen shown in blue as the tail atom and click the **Tail Atom** button. Repeat this process for the other two structures and close the Repeat Unit dialog.

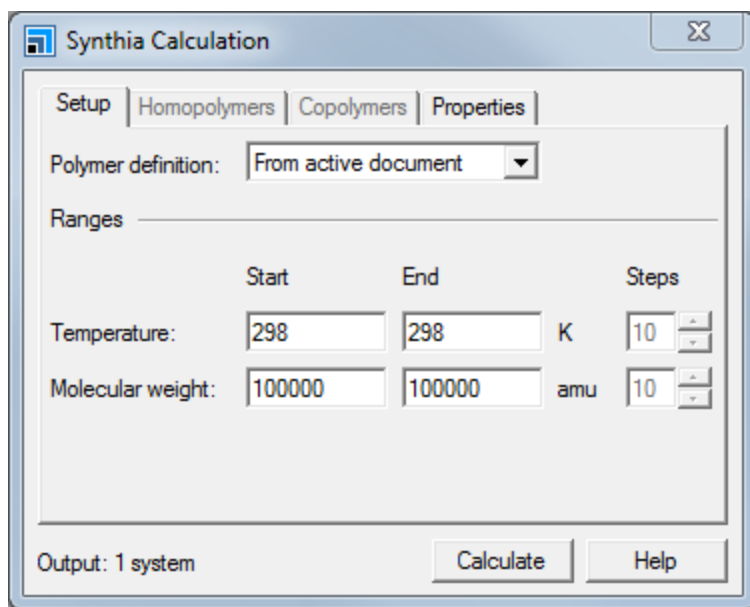
Select **File | Save Project** from the menu bar.

All of the structures are now identified as repeat units and can be used in a Synthia calculation.

4. To define the copolymer

Click the **Synthia** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | Synthia | Calculation** from the menu bar.

This opens the Synthia Calculation dialog.



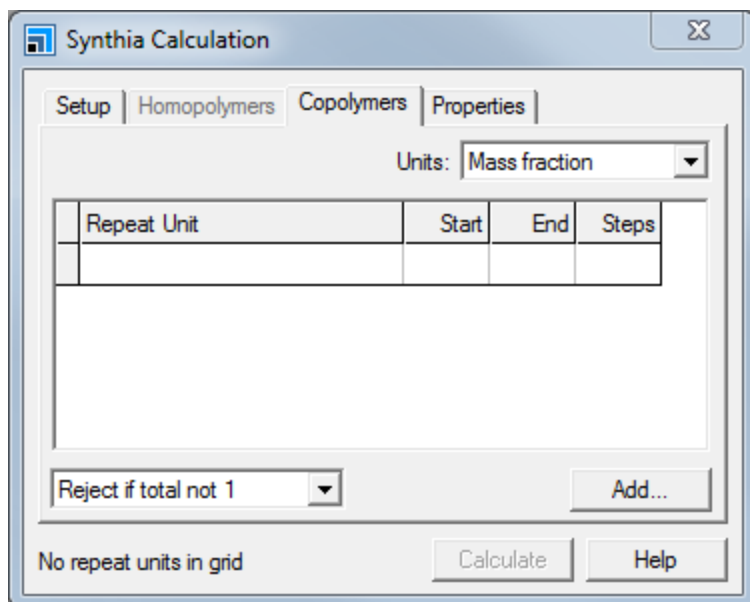
Synthia Calculation dialog, Setup tab

You have the option to calculate properties for the current repeat unit, select multiple homopolymers and calculate their properties, or generate one or more copolymers.

On the **Setup** tab, select **Random copolymers** from the **Polymer definition** dropdown list.

You are going to calculate the properties at 298 K and a constant molecular weight so you can move on to specify the copolymer.

Select the **Copolymers** tab.



Synthia Calculation dialog, Copolymers tab

You are going to define two copolymers. The first copolymer is acrylamide and *N*-benzyl methacrylamide. The second copolymer is acrylamide and *N*-methyl methacrylamide. You could define

two separate copolymers and run two calculations but, as they share acrylamide as a repeat unit, it is easier to define them all in one calculation.

The first step is to add the common repeat unit.

Click the **Add...** button to open the Add Repeat Unit dialog. Change the **Library** to **Current project**, select **acrylamide** and click the **OK** button.

The *Current project* filter shows all the structures in the current project. However, only structures defined as repeat units will activate the *OK* button.

Repeat units can be defined as sets and a set is displayed in braces, {}. If a set is defined, separate calculations will be performed for each unit in the set. This means you can generate more than one copolymer in the same calculation.

Click in the next empty cell in the **Repeat Unit** column to open the Add Repeat Unit dialog. Hold down the **CTRL** key and select **N-benzyl** and **N-methyl**, click the **OK** button.

The two repeat units are specified on the same line enclosed in braces, {}, meaning they are defined as a set.

For this example, you will vary the composition from pure acrylamide to pure *N*-benzyl methacrylamide or pure *N*-methyl methacrylamide. Therefore, the composition matrix should be edited to reflect this.

On the **Copolymers** tab, change the **Start** value from **1.0** to **0.0** in both rows.

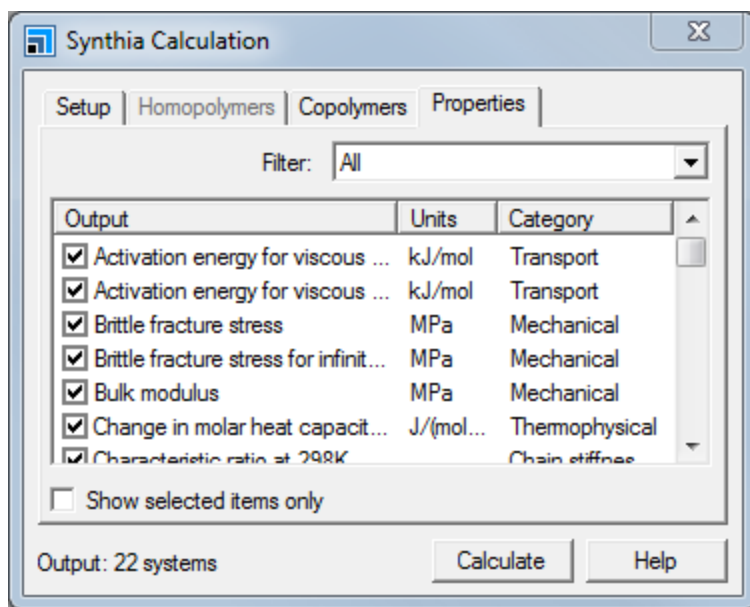
Finally, change the units from mass fraction to mole fraction.

Select **Mole fraction** from the **Units** dropdown list.

The number of calculations is shown at the bottom of the dialog and should now read *Output: 22 systems*.

You have now set up the copolymer calculation. The next step is to select the properties you wish to predict.

Select the **Properties** tab.



Synthia Calculation dialog, Properties tab

Initially, all the properties are selected. As the Synthia method uses underlying correlations to predict the properties, calculating all the properties does not take much more time than calculating only one. However, for this tutorial, you only need to calculate the refractive index and the density.

Select the first property in the list, hold down the **SHIFT** key and select the last property in the list. Uncheck any of the checkboxes.

This will deselect all the currently selected properties.

Check the **Density** (not *Density at 298K*) checkbox and check the **Refractive index** (not *Refractive index at 298K*) checkbox.

Tip: Click on any heading in the list of properties to sort the entries alphanumerically on that heading. Click again to toggle the sort order between descending and ascending.

The results of the calculation will be written to the currently selected folder; therefore, you should ensure that the root project folder is selected.

In the Project Explorer, click the project name (**Copolymer**). On the Synthia Calculation dialog, click the **Calculate** button and close the dialog.

The results of the calculation are displayed in a study table document called `Synthia.std`, which contains the results for both copolymers.


5. To work with the study table

The study table document contains different columns for the repeat units, their concentrations, the temperature, and the molecular weight. These are all the input variables into the Synthia calculation and are displayed in black text. The predicted properties, density and refractive index, are displayed in blue.


The two monomer units are currently displayed alternately in the study table. You can use the study table sorting tools to separate them into blocks.

Select column **C** and click the **Sort Ascending** button .

The results for *N*-benzyl methacrylamide are now displayed first and the results for *N*-methyl methacrylamide second.

Tip: If you wanted to separate the results entirely, you could select all the *N*-benzyl methacrylamide rows and use the *Filter* tool  to separate them into two worksheets on the same study table.

You can plot the properties directly from the study table.

Select column **D**. Hold down the **CTRL** key and select column **H**. Click the **Quick Plot** button .

A chart document called *Synthia Scatter plot.xcd* is displayed, which plots the refractive index against the mole fraction of *N*-benzyl and *N*-methyl methacrylamide.


Close all the open documents, except **Synthia.std** and **Synthia Scatter plot.xcd**. Select **Window | Tile Horizontally** from the menu bar to view the study table and the scatter plot simultaneously. Click on any point in the scatter plot.

Selecting points on the chart document highlights the corresponding rows in the study table.

To calculate the specific refractive index increment (dn/dc), you need to use both the refractive index and the density. The relationship being:

$$\frac{dn}{dc} = \frac{n_p - n_s}{\rho_p}$$

In this case, the refractive index of the solvent, water, is 1.33.

Ensure that **Synthia.std** is the active document. Click the **Define Function** button  on the toolbar to open the Define Function dialog.

In the **Expression** field, enter **(H-1.33)/G**. In the **Name** field, enter **Specific Refractive Index Increment**. In the **Description** field, enter **dn/dc**. Click the **OK** button.

A new column, column **I**, is automatically created and populated with the results of the calculation. You can now plot these against the comonomer mole fraction.

Select column **D** and column **I**. Click the **Quick Plot** button .

The following chart is displayed.

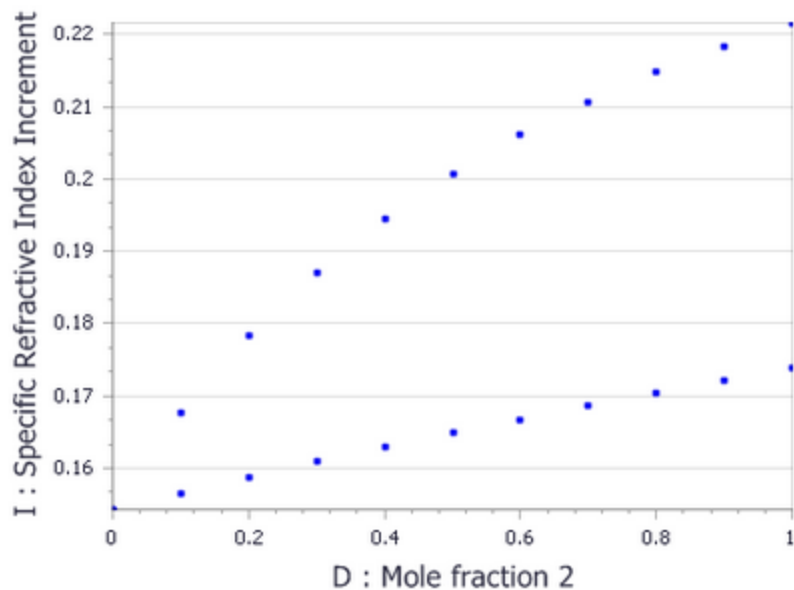


Chart of specific refractive index increment against mole fraction for *N*-benzyl methacrylamide (top line) and *N*-methyl methacrylamide (bottom line).

This is the end of the tutorial.

References

Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd Edition, Chapman and Hall: London (1991).

Bicerano, J. *Soil Sci.*, **158**, 255-266 (1994).

VAMP tutorials

The following tutorials illustrate how to utilize VAMP's capabilities.

- [Geometry Optimization and Transition State Calculation with VAMP](#)
- [Predicting the UV spectrum of cinnamate](#)

Geometry optimization and transition state calculation with VAMP

Purpose: Introduces the use of VAMP for predicting molecular structures, properties, and transition states of chemical reactions.

Modules: Materials Visualizer, VAMP

Time:  

Prerequisites: None

Background

VAMP is a semiempirical molecular orbital program that has been optimized to be highly numerically stable and fast so that most calculations can be run interactively on workstations and personal computers. It contains many enhancements in comparison with normal geometry optimization methods so that it even optimizes problematic systems successfully.

Other features of VAMP are transition state optimization, solvent models, and the calculation of many electronic properties.

Introduction

In this tutorial, you will learn how to use VAMP to optimize molecules, analyze the results, calculate molecular properties, and determine transition states of chemical reactions.

In the first part, you will optimize the structure of indigo, a classic pigment, and you will analyze several of its properties, derived from the calculated wavefunction.

In the second part of the tutorial, you will calculate the transition state of a chemical reaction leading to a heterocyclic organic compound.

This tutorial covers:

- [Getting started](#)
- [Optimizing the structure of indigo](#)
 - To prepare the structure for the optimization
 - To optimize the indigo structure
 - To analyze the VAMP output file and displaying electronic properties
- [Finding a transition state for the reaction of nitron and ethylene to form isoxazolidine](#)
 - To prepare the structures for the calculation
 - To calculate and confirming the transition state

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **indigo_VAMP** as the project name, click the **OK** button.

The new project is created with *indigo_VAMP* listed in the Project Explorer. You should create two folders for the different parts of the tutorial.

In the Project Explorer, right-click on the project root and select **New | Folder** from the shortcut menu. Right-click on the new folder and select **Rename** from the shortcut menu. Change the name of the folder to **Indigo**. Repeat these steps to create a second folder called **TS**.


Optimizing the structure of indigo

1. To prepare the structure for the optimization

In this section of the tutorial, you will build a single indigo molecule from the indigo crystal structure provided in the Materials Studio database.

In the Project Explorer, select the **Indigo** folder. Select **File | Import** from the menu bar to open the Import Document dialog. Navigate to the **Structures/molecular-crystals/pigments** folder and import the crystal structure of indigo, **indigo_1.msi**.


You have now imported the crystal structure of an indigo polymorph. From this crystal structure, you can obtain the structure of a single indigo molecule.

Select **Build | Symmetry | Unbuild Crystal** from the menu bar. Click the **Recenter** button .

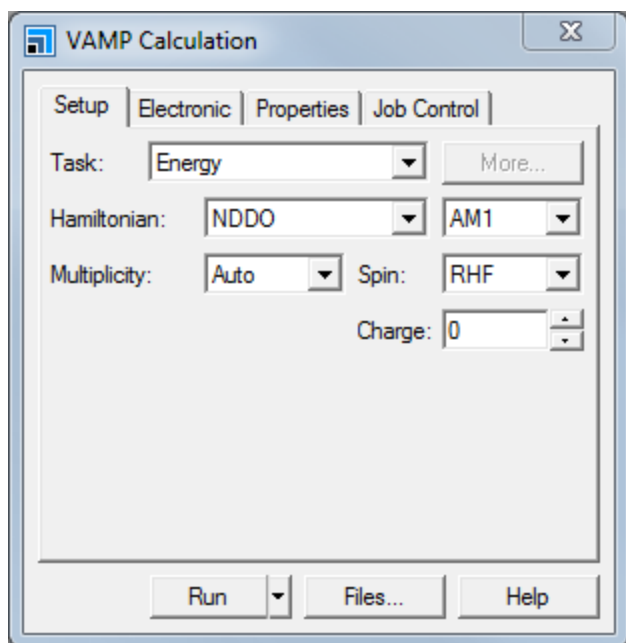
There should now be one indigo molecule centered in the 3D Viewer.

2. To optimize the indigo structure

Next, use the semiempirical VAMP program to optimize the geometry of the molecule.

Click the **VAMP** button  on the **Modules** toolbar, then select **Calculation** from the dropdown list or select **Modules | VAMP | Calculation** from the menu bar.

This opens the VAMP calculation dialog.



VAMP Calculation dialog, Setup tab

On the **Setup** tab, change the **Task** from Energy to **Geometry Optimization**. Make sure the **Hamiltonian** is set to **AM1**.

You have specified the calculation task and the semiempirical approximation to the Hamiltonian used in this calculation.

Click the **Run** button and close the dialog.

A new folder called `indigo_1 VAMP GeomOpt` opens in the Project Explorer. The progress of the job during computation is presented in the form of chart and text documents. The entire calculation takes about 30 seconds, depending on the speed of the processor in your computer.

3. To analyze the VAMP output file and displaying electronic properties

The optimized indigo structure is located in `indigo_1.xsd` in the new folder, while the VAMP text output of the computation is in the `indigo_1.out` document. In this section, you will examine the text output document and use the VAMP analysis tool to display isosurfaces.

VAMP calculates many properties, such as heats of formation, dipole moments, static polarizabilities, and ^{13}C chemical shifts, by default. The results for these properties can be viewed in the text output file.

Double-click on `indigo_1.out` in the `indigo_1 VAMP GeomOpt` folder. Press **CTRL + F** and search for **Heat**. Click the **Find Next** button until you reach the part of the document that looks like this:

```
* Heat of formation      =          38.942625 Kcal/mol

* Electronic energy     =        -20000.056110 eV
* Core-core repulsion   =         16761.585834 eV
* Total energy          =         -3238.470275 eV

* Gradient norm         =           0.332340
```

```
* RMS force           =           0.035032
* Ionization potential =           8.365898 eV
*                     =           48 filled levels
* Molecular weight    =           262.267
```


The heat of formation for indigo, as calculated by VAMP, is approximately 39 kcal mol⁻¹. Examples of other properties displayed are the total electronic and the total nuclear repulsion energies. The sum of these two energies gives the total energy.

The next two lines contain two convergence criteria, the gradient norm, and the root-mean-square force on the atoms. Default convergence criterion for the gradient norm is 0.4 kcal/mol/Å. The output shows that the convergence criterion is satisfied. Finally the ionization potential, the number of filled molecular orbitals and the molecular weight of indigo are listed.

Press **CTRL + F** and search for **Mulliken**. Click the **Find Next** button until you reach **Mulliken atomic charges**.

Below this line the net atomic charges resulting from a Mulliken analysis are displayed. If you scroll down further in the output file you find other properties displayed such as dipole moments, static polarizabilities, bond orders, electron populations, and ¹³C chemical shifts. The last two lines of the output report the successful completion of the calculation and the total run time.

Now you will make use of the VAMP Analysis tool to display several properties on the screen.

Double-click on **indigo_1.xsd** in the **indigo_1 VAMP GeomOpt** folder. Click the **VAMP** button  on the **Modules** toolbar and select **Analysis** from the dropdown list.

This opens the VAMP Analysis dialog. There are several different properties you can display using the VAMP Analysis tool. Initially, you are going to view the electron density as an isosurface.

Click the **Import** button.

Tip: You can improve the quality of the isosurface by changing the grid settings from the Analysis dialog. However, increasing the grid quality will affect the speed with which graphical objects are manipulated.

The total charge density is displayed. The Materials Visualizer has different tools for controlling how you view objects such as isosurfaces and these are located on the Display Style dialog. One of these tools allows you to control the transparency of isosurfaces.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Select the **Isosurface** tab and drag the **Transparency** slider to the right.

The isosurface becomes more transparent, revealing the molecule.

On the **Atom** tab change the display style to **Ball and stick**.


The atoms and bonds of the molecule are now displayed as balls and sticks. Once you have an isosurface displayed, you can map different properties onto it, such as the electrostatic potential. To do this, you must add the electrostatic potential field data to the 3D Atomistic document.

On the VAMP Analysis dialog select **Potentials** and click the **Import** button.

On the **Isosurface** tab of the Display Style dialog and change the mapped field from <none> to **VAMP electrostatic potential of indigo_1**.

The electrostatic potential is mapped onto the total charge density isosurface using color to represent the variation. Mapping the electrostatic potential in this manner gives you an insight into the charge distribution over the molecule.

You can remove the isosurface by either selecting it and pressing the DELETE key or by using the Volumetric Selection tool.

Click the **Volumetric Selection** button  on the **Volume Visualization** toolbar. Expand the **VAMP total electron density** node and select **Isosurface1**. Press the **DELETE** key and close the dialog.

The isosurface is removed, but the field data remains. You can also use VAMP to examine the orbitals of indigo.

On the **VAMP Analysis** dialog select **Orbitals**.

A list of all the calculated orbitals and their respective energy eigenvalues is displayed in the grid.

Change the **Filter** from All to **Minimal**.

Now only the three nearest eigenvalues on both sides of the highest occupied molecular orbital (HOMO) are listed. If you had performed a spin-polarized calculation, you could also list all spin-up or all spin-down orbitals.

Select **HOMO** from the orbital list and click the **Import** button.

The HOMO of indigo is displayed on the screen.

Click on the isosurface and press the **DELETE** key to remove it.

You can also apply the charges that VAMP calculates to the structure in the 3D Atomistic document.

Select **Population analysis** on the VAMP Analysis dialog and click the **Assign Coulson charges to structure** button. Right-click in the 3D Viewer and select **Label** from the shortcut menu to open the Label dialog. Set the **Object type** to **Atom**, select **Charge** from the **Properties**, and click the **Apply** button.

Now the partial atomic charges as calculated by the Coulson method are displayed on the molecule. You can also choose to display the Mulliken charges by changing the charge type to **Mulliken** on the VAMP Analysis dialog and pressing the *Assign chosen charges to structure* button.

On the Label dialog, click the **Remove** button.

Click the **Assign Mayer bond orders to structure** button on the VAMP Analysis dialog and close the dialog.

On the Label dialog, change the **Object type** to **Bond** and select **BondOrder** from the list of **Properties**. Click the **Apply** button and close the dialog.

The bonds in the molecule are updated from the VAMP calculation. Before you continue to the second part of this tutorial, you should save the project and close all the documents.

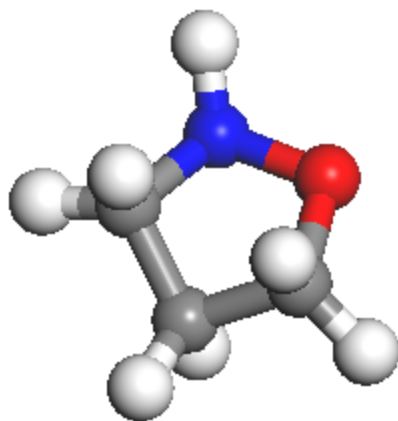
Select **File | Save Project**, then **Window | Close All** from the menu bar.

Finding a transition state for the reaction of nitrene and ethylene to form isoxazolidine

In the second part of the tutorial, you are going to use VAMP to find a transition state for a 1,3-dipolar cycloaddition reaction of nitrene and ethylene, which forms the heterocyclic compound isoxazolidine. 1,3-Dipolar cycloadditions provide an important synthetic route to functionalized five-membered heterocyclic systems, including those commonly found in natural products. A detailed understanding of the transition state is essential for predicting the regiochemistry of the reaction products.

1. To prepare the structures for the calculation

In this section you will prepare the structures for the transition state optimization starting from the product, isoxazolidine.





Structure of isoxazolidine

In the Project Explorer, right-click on the **TS** folder and select **New | 3D Atomistic Document** from the shortcut menu.

Click the **Sketch Ring** arrow  and select **5 Member**. Click once in the 3D Viewer.

A five-membered carbon ring is displayed in the new 3D Atomistic document.

Change the appropriate atoms to **Nitrogen** and **Oxygen**. Click the **Adjust Hydrogen** button  and the **Clean** button .

In the Project Explorer, right-click on the **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Enter the name **isoxazolidine**.

Now you can use VAMP to optimize the structure of the isoxazolidine product.

Open the **VAMP Calculation** dialog.

On the **Setup** tab, change the **Task** to **Geometry Optimization** and ensure that the **Hamiltonian** selected is **AM1**.

Click the **Run** button and close the dialog.

A new folder, called **isoxazolidine VAMP GeomOpt**, is created in the Project Explorer. Examine the text output file.

Double-click on **isoxazolidine.out** in the **isoxazolidine VAMP GeomOpt** folder. Press **CTRL + F** and search for **Heat**. Click the **Find Next** button until you reach the part of the document that looks like this:

```
* Heat of formation      =          -8.894573 Kcal/mol

* Electronic energy     =          -3533.525022 eV
* Core-core repulsion   =           2526.879750 eV
* Total energy          =          -1006.645272 eV


* Gradient norm        =              0.348646
* RMS force             =              0.058108

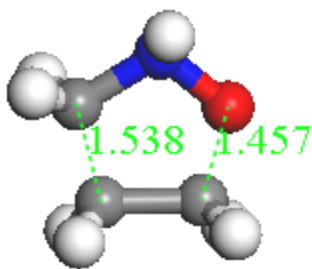
* Ionization potential =              9.816158 eV
*                      =             15 filled levels
* Molecular weight     =              73.094
```

Now that you have built the isoxazolidine product, you can break two bonds to form the two reactant structures.

Ensure that the original (unoptimized) **isoxazolidine.xsd** structure is the active document. Select the $\text{CH}_2\text{-CH}_2$ bond adjacent to the $\text{CH}_2\text{-N}$ bond. Hold down the **SHIFT** key and select the **C-O** bond. Press the **DELETE** key.

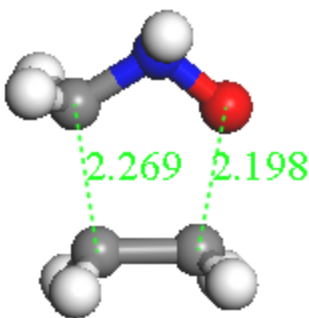
Now you are going to use the *Measure/Change* tool to calculate the lengths of the bonds you have just removed.

Click the **Measure/Change** arrow  and select **Distance** from the dropdown list. Select the atoms that were connected by the bonds you just deleted.



Distance monitors are displayed in green and both distances should be about 1.5 Å. To set up the starting structure for the calculation, you need to separate the two fragments.

Choose the **Selection Mode** tool. Select the oxygen atom, right-click, and choose **Select Fragment** from the shortcut menu. Hold down the **SHIFT** and **ALT** keys and use the right mouse button to separate the fragments until they are approximately 2.2 Å apart.



Tip: If you have a three-button mouse or a mouse with a wheel, you can use the middle mouse button and the SHIFT key to translate selected objects.

2. To calculate and confirm the transition state

Next, use the VAMP Calculation dialog to optimize the transition state and the vibrational modes of the structure.

Open the **VAMP Calculation** dialog.

Change the **Task** to **TS Optimization** and the **Hamiltonian** to **AM1**. Click the **More...** button to open the VAMP TS Optimization dialog. Change the **Method** to **Powell** and close the dialog.

On the **Properties** tab check the **Frequency** checkbox.

You have specified the approximate Hamiltonian and the calculation task. In this example, you will use the Powell algorithm for the transition state search. On the *Properties* tab, you selected *Frequency*, so that a normal mode analysis will be performed. This means that you can verify the transition state by animating the imaginary normal mode associated with the reaction coordinate.

Click the **Run** button and close the dialog.

The result of the transition state search is returned. Values of $r_{\text{C-C}} = 2.15 \text{ \AA}$ and $r_{\text{O-C}} = 2.04 \text{ \AA}$ are obtained. These are very close to earlier Hartree-Fock results ($r_{\text{C-C}} = 2.19$, $r_{\text{O-C}} = 2.04 \text{ \AA}$) obtained by Sosa et al.

(1994). However, the same authors, obtained another transition state ($r_{C-C} = 2.34$, $r_{O-C} = 2.24$ Å) using local density functional theory, in accordance with earlier MCSCF calculations (Hehre et al., 1969).

Finally, calculate the normal modes at the transition state and animate the reaction mode.

Ensure that the **isoxazolidine VAMP TSOpt/isoxazolidine.xsd** optimized transition state structure is the active document. Select **Tools | Vibrational Analysis** from the menu bar to open the Vibrational Analysis dialog. Click the **Calculate** button.

A list of frequencies, or eigenvalues, is displayed in the *Analysis* tab, one of which is negative. The presence of a large single negative eigenvalue indicates that this is the transition state.

Highlight the negative mode and click the **Animation** button and close the dialog.

The normal mode associated with this negative frequency is animated. This is the reaction mode.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Hehre, W. J.; Stewart, R. F.; Pople, J. J. *Chem. Phys.*, **51**, 2657 (1969).

Sosa, C.; Andzelm, J. *Int. J. Quantum Chem.*, **49**, 511 (1994).

Predicting the UV spectrum of cinnamate

Purpose: Illustrates how to use VAMP to perform geometry optimization and to calculate optical spectra.

Modules: Materials Visualizer, VAMP

Time: 🕒 🕒

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

VAMP is a semiempirical molecular orbital program that has been optimized to be highly numerically stable and fast, so that most calculations can be run interactively on workstations and personal computers. It contains many enhancements in comparison to normal geometry optimization methods so that it even optimizes problematic systems successfully. Other features of VAMP include transition state optimization, solvent models, the calculation of many electronic properties, and the prediction of optical spectra.

Introduction

In this tutorial, you will learn how to use VAMP to calculate UV/vis optical spectra.

First you will optimize the structure of 2-ethylhexyl-p-methoxycinnamate (cinnamate), a classic sunscreen molecule, and then you will calculate its UV spectrum.

This tutorial covers:

- [Getting started](#)
- [Optimizing the structure of cinnamate](#)
 - To prepare the structure for optimization
 - To perform the optimization
- [Calculating the UV spectrum of cinnamate](#)
 - To prepare the input file for the calculation
 - To calculate the UV spectrum and analyze the output

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **cinnamate** as the project name, click the **OK** button.

The new project is created with *cinnamate* listed in the Project Explorer.

Optimizing the structure of cinnamate

1. To prepare the structure for optimization

In this section of the tutorial, you will build a single cinnamate molecule (shown below) using the tools provided in the Materials Visualizer.

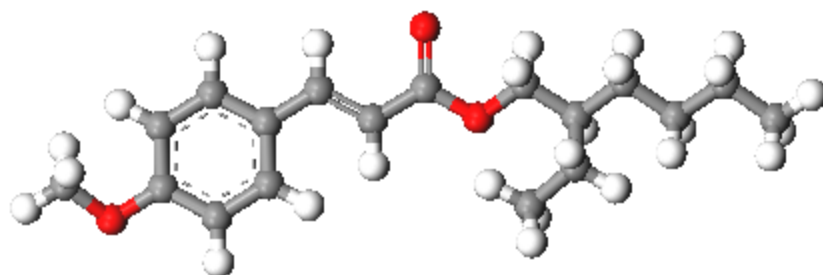



Figure 1. Structure of cinnamate

Begin by creating a new 3D Atomistic document.

Select **File | New...** from the menu bar to open the New Document dialog. Select **3D Atomistic** and click the **OK** button.

In the **Project Explorer**, right-click on **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Rename the document to **cinnamate** and press the **ENTER** key.



Now sketch the cinnamate structure, starting with the aromatic ring.

Click the **Sketch Ring** arrow button  on the **Sketch** toolbar and select **6 Member** from the dropdown list. Hold down the **ALT** key and click once in the **cinnamate.xsd** 3D Viewer.

A 6 membered aromatic ring appears in the document. Now, sketch the oxymethane substituent.

Add the side chains as shown in [Figure 1](#), ensure that you change the appropriate atoms to **Oxygen** to form the ester and methoxy groups. Make sure that you place the double bonds correctly.

When the basic structure of the cinnamate molecule is complete, finish off by adding the hydrogen atoms and cleaning the structure.


Click the **Adjust Hydrogen** button  and the **Clean** button  on the **Sketch** toolbar.

Before continuing you should save the project.

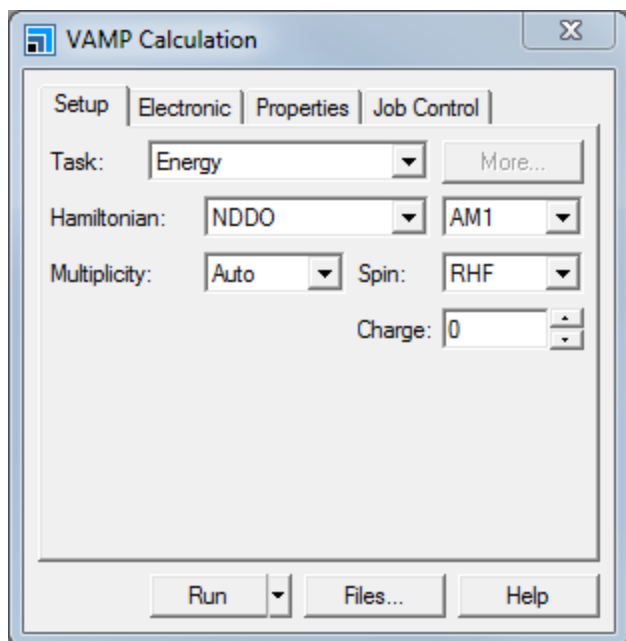
Select **File | Save Project** from the menu bar.

2. To perform the optimization

In this step, you will use the semiempirical VAMP program to optimize the geometry of the cinnamate molecule.

Click the **VAMP** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the VAMP calculation dialog.



VAMP Calculation dialog, Setup tab

First, specify the task you wish to perform and the semiempirical approximation to the Hamiltonian that will be used in the calculation.

On the **Setup** tab, select **Geometry Optimization** from the **Task** dropdown list.

Click the **More...** button to display the VAMP Geometry Optimization dialog. Select **Fine** from the **Quality** dropdown list and close the dialog.

On the **Electronic** tab of the VAMP Calculation dialog select **Fine** from the **SCF quality** dropdown list. Click the **More...** button to display the VAMP Electronic Options dialog. Set the **Max. SCF cycles** to **500** and close the dialog.

Now start the geometry optimization.

Click the **Run** button on the VAMP Calculation dialog.

A new folder, called `cinnamate VAMP GeomOpt`, is created in the *Project Explorer*. As the job progresses, updates are presented in both chart and text documents. The calculation should take a few minutes, depending on the speed of the processor in your computer.

When the job is complete, the optimized cinnamate structure can be found in `cinnamate.xsd` in the new folder and textual output from the run is contained in the file, `cinnamate.out`.

Click the **OK** button to close the Job Completed dialog.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

To calculate the UV spectrum of cinnamate

This section of the tutorial illustrates how to use VAMP to calculate the UV spectrum of cinnamate.

1. To set up the UV spectrum calculation

Ensure that the optimized cinnamate structure is active.

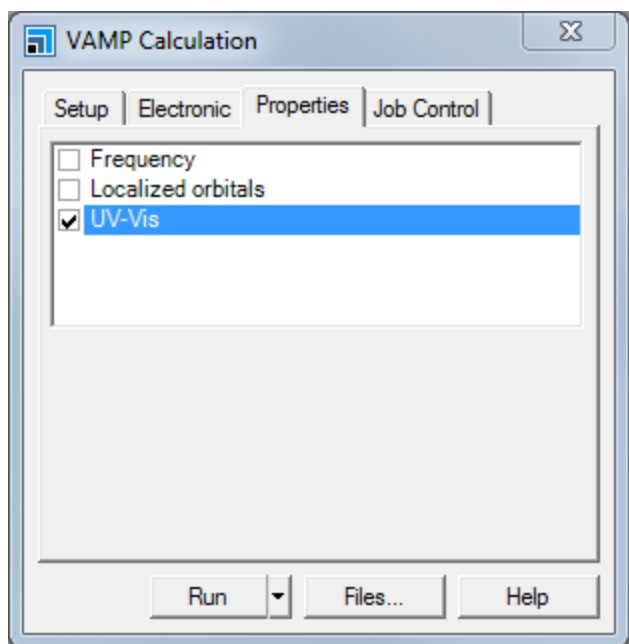
In the **Project Explorer**, double-click on **cinnamate.xsd** in the **cinnamate VAMP GeomOpt** folder.

Now you can prepare the VAMP input file required for the calculation.

On the **Setup** tab of the VAMP Calculation dialog, select **Energy** from the **Task** dropdown list.

On the **Electronic** tab select **Full** from the **CI type** dropdown list. Click the **More...** button to open the VAMP Electronic Options dialog and set the **Total CI orbitals** to **6**. Check the **Ignore degenerate orbitals** checkbox and close the dialog.

On the **Properties** tab check the **UV-Vis** checkbox.



VAMP Calculation dialog, Properties tab

Now the input file is ready, you can start the calculation.


Click the **Run** button on the VAMP Calculation dialog and close the dialog.

The calculation begins. It should take around a minute, depending on the speed of the processor in your computer.

Click the **OK** button to close the Job Completed dialog.

2. To analyze the UV spectrum

The output from the calculation is written to the file **cinnamate.out** in the **cinnamate VAMP Energy** folder.

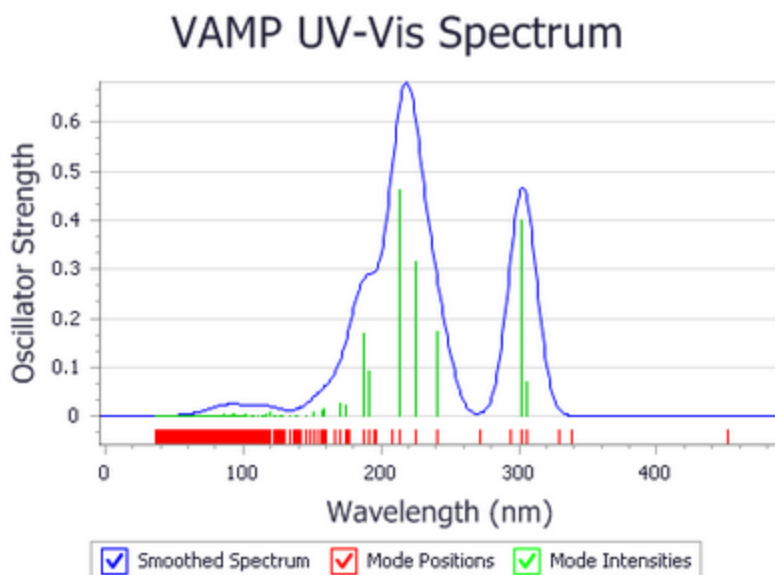
Click the **VAMP** button  on the **Modules** toolbar and select **Analysis** from the dropdown list to open the VAMP Analysis dialog.

Double-click on **cinnamate.xsd** in the **cinnamate VAMP Energy** folder in the **Project Explorer**.

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.

Select **Electronic levels** in the VAMP Analysis dialog and click the **View spectrum** button.

A graph is displayed in a new Chart Viewer.



VAMP simulated spectrum for cinnamate

The green lines on the graph represent the positions and non-zero intensities of the absorption frequencies computed by VAMP. The short red lines show the positions of all computed transitions, even forbidden transitions. Notice that there is a significant number of forbidden transitions. The smooth blue line indicates a simulated spectrum based on the computed frequencies and intensities. This is achieved by broadening the computed results with a Gaussian or Lorentzian function.

Double-click on **cinnamate.xsd** in the **cinnamate VAMP Energy** folder in the **Project Explorer**.

On the VAMP Analysis dialog, select **Electronic levels** and click the **View electronic energy levels** button.

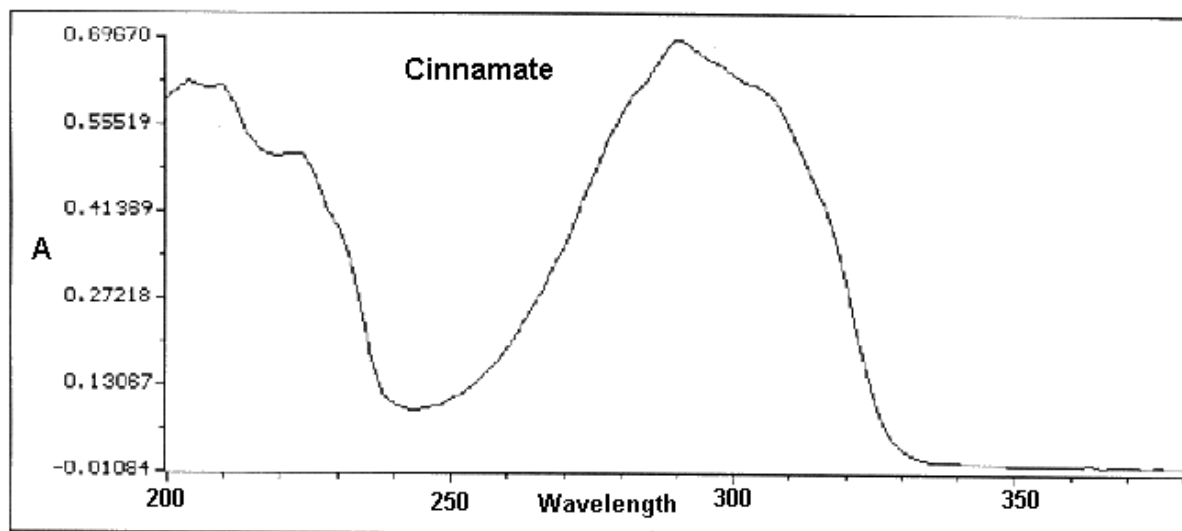
A table is displayed in a new Study Table Viewer

	A	B	C	D
	Level Energy (eV)	Excitation wavelength (nm)	Oscillator Strength	Multiplicity
1	-0.56567200	0.00000000	Ground State	Singlet
2	2.70172700	458.89159300	Forbidden	Triplet
3	3.64493400	340.14330100	Forbidden	Triplet
4	3.73524300	331.91947400	Forbidden	Triplet
5	4.01644400	308.68101200	0.02501300	Singlet
6	4.08373200	303.59486000	0.44910300	Singlet
7	4.20481000	294.85281900	Forbidden	Triplet
8	4.33294800	286.13315600	Forbidden	Triplet
9	5.08321200	243.90089200	0.13738400	Singlet
10	5.45586500	227.24168700	0.25750800	Singlet

Computed VAMP frequencies and intensities

The table provides values for the energy (in eV), the excitation wavelength (in nm), the multiplicity (spin arrangement), and the oscillator strength (transition dipole moment) of each electronic state.

The spectrum contains two maxima, at about 210 nm and 300 nm. Compare this with the experimentally derived spectrum shown below:



Experimental spectrum of cinnamate

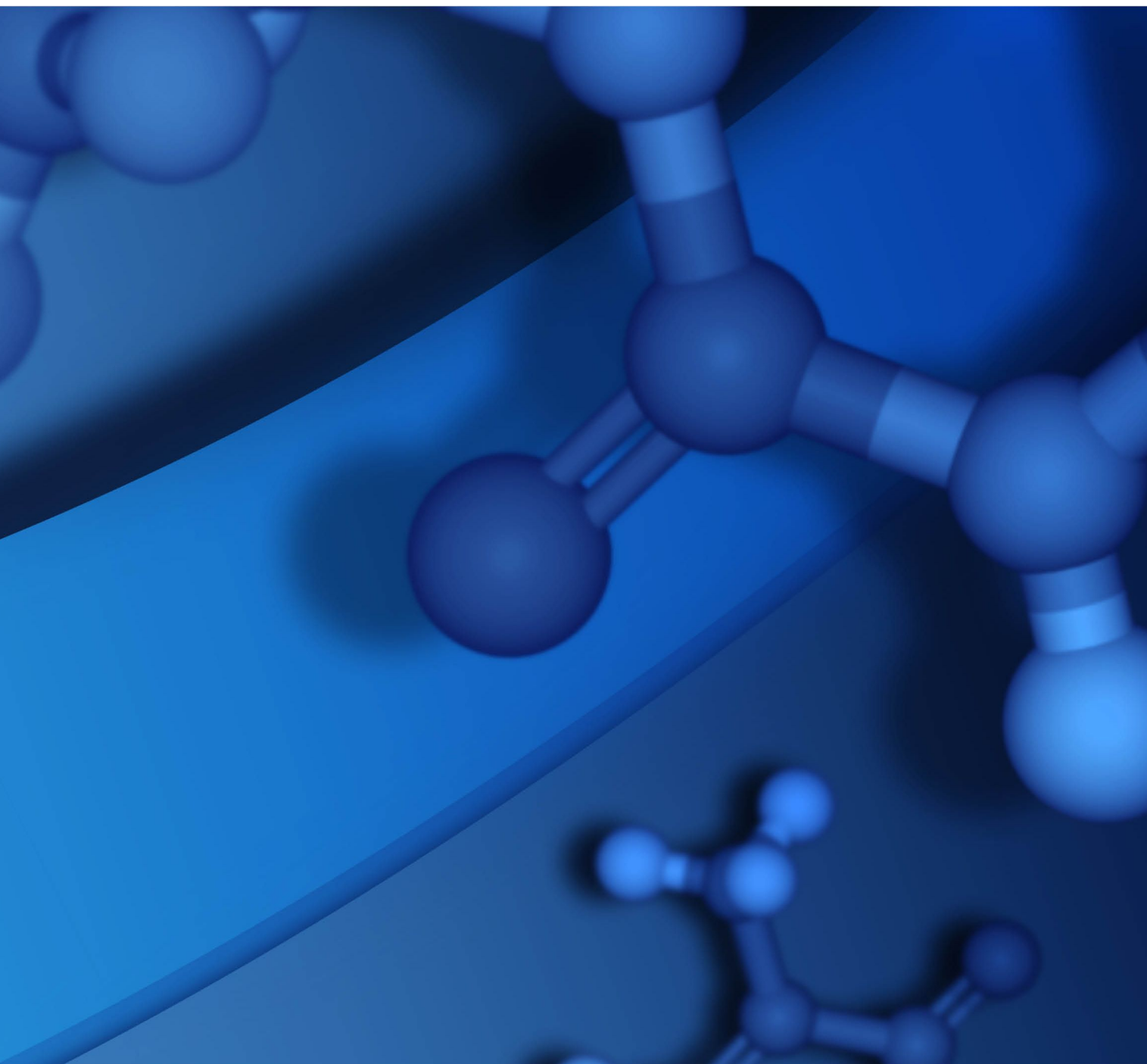
The theoretical peaks agree with the experimental ones, to within 20 nm. Optical spectra depend strongly on the structure of the system as well as solvent effects and this probably accounts for the discrepancies. A better starting geometry could be obtained by performing ab initio calculations using DMol³. Solvent effects can be simulated by setting the solvation scheme to COSMO or SCRF on the *Electronic* tab of the VAMP Calculation dialog.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

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CASTEP

Introduction

CASTEP is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science. CASTEP employs the density functional theory plane-wave pseudopotential method, which allows you to perform first-principles quantum mechanics calculations that explore the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites.

Typical applications involve studies of surface chemistry, structural properties, band structure, density of states, and optical properties. CASTEP can also be used to study the spatial distribution of the charge density and wavefunctions of a system.

In addition, you can use CASTEP to calculate the full tensor of second-order elastic constants and related mechanical properties of a crystal (Poisson coefficient, Lamé constants, bulk modulus). The transition-state searching tools in CASTEP enable you to study chemical reactions in either the gas phase or on the surface of a material using linear synchronous transit/quadratic synchronous transit technology. These tools can also be used to investigate bulk and surface diffusion processes.

CASTEP can be used effectively to study properties of both point defects (vacancies, interstitials, and substitutional impurities) and extended defects (for example grain boundaries and dislocations) in semiconductors and other materials.

Furthermore, the vibrational properties of solids (phonon dispersion, total and projected density of phonon states, thermodynamic properties) can be calculated with CASTEP using either the linear response methodology or the finite displacements technique. The results can be used in various ways, for instance, to investigate the vibrational properties of adsorbates on surfaces, to interpret experimental neutron spectroscopy data or vibrational spectra, to study phase stability at high temperatures and pressures, and so on. The linear response method can also be used to calculate the response of a material to an applied electric field - polarizability for molecules and dielectric permittivity in solids - and to predict IR spectra.

CASTEP can be used to calculate the properties required to analyze the results of solid-state NMR experiments, that is, chemical shifts and electric field gradients on atoms of interest. A detailed review of the CASTEP NMR formalism and numerous examples of practical applications are discussed in Bonhomme et al. (2012).

The CASTEP STM analysis tool allows you to model scanning tunneling microscopy images at different bias voltages in order to solve the surface structures based on the experimental STM images.

In all publications arising from your use of CASTEP, please cite:

Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. "First principles methods using CASTEP", *Zeitschrift fuer Kristallographie*, **220 (5-6)**, 567-570 (2005).

Additional Information

For additional information about BIOVIA Materials Studio and other Dassault Systèmes software applications, visit the Dassault Systèmes Customer Support site:

<https://www.3ds.com/support/>

Tasks in CASTEP

The CASTEP module allows you to perform first-principles quantum mechanical calculations in order to explore the properties of crystals and surfaces in the solid state. CASTEP can currently perform several different tasks:

- Single-point energy calculation
- Geometry optimization
- Molecular dynamics
- Elastic constants calculation
- Transition state search
- Transition state confirmation
- Properties

Each of these calculations can be set up so that it generates specified chemical and physical properties. An additional task, known as a properties calculation, allows you to restart a completed job to compute additional properties that were not calculated as part of the original run.

There are a number of steps involved in running a CASTEP calculation, which can be grouped as follows:

- **Structure definition:** A periodic 3D Atomistic document containing the system of interest must be specified. There are a number of ways to prepare a structure:
 - Periodic structures can be built using the tools available in the Materials Visualizer for building crystals, surfaces, and single-wall nanotubes.
 - Existing structures can be modified using the Materials Visualizer sketching tools
 - Structures can be imported from an existing structure file

In the case of a transition-state search, a 3D Atomistic Trajectory document containing a reaction sequence is required as the input document. You should define the structures of the reactants and the products in two separate 3D Atomistic documents using the methods listed above and then use the Reaction Preview tool to generate the trajectory.

Note: CASTEP can only be used to perform calculations on 3D periodic structures. If you wish to study a molecular system using CASTEP, you will need to [construct a supercell](#) to use as the input structure.

Note: CASTEP cannot handle structures containing pi-system objects. Such objects should be removed from the document prior to running a CASTEP calculation.

Note: CASTEP performance can be greatly increased if the symmetry of the structure is taken into account. CASTEP offers an option of finding and using the symmetry automatically if the input structure is described as having a P1 symmetry. This option is particularly relevant for calculations on molecular crystals and crystal surfaces, since these structures are typically created as P1 (or p1) systems. Automatic conversion to a higher symmetry structure will honor all atomic properties that are relevant to the current CASTEP settings, such as constraints and electronic configuration.

Tip: The time required for a CASTEP calculation increases with the cube of the number of atoms in the system. Therefore, it is recommended that you use the smallest primitive cell description of your system whenever possible. Select *Build | Symmetry | Primitive Cell* from the menu bar to convert to a primitive cell.

- **Calculation setup:** Once a suitable 3D structure document has been defined, then it is necessary to select the type of calculation to be performed and set the associated parameters. For example, in the case of a dynamics calculation, these parameters include the ensemble and its settings, the temperature, and the number and length of the time steps. Finally, the server on which the calculation is to be run should be selected and the job initiated.
- **Analysis of the results:** When the calculation is complete, the files related to that job are returned to the client and, where appropriate, displayed in the Project Explorer. Some further processing of these files may be required to obtain observables such as optical properties. The tools on the [CASTEP Analysis dialog](#) may be used to visualize the results of the calculation.

To select a CASTEP task

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the [Setup](#) tab.
3. Select the required CASTEP task from the *Task* dropdown list.

CASTEP Energy task

The CASTEP [Energy](#) task allows you to calculate the total energy of the specified 3D periodic system, as well its physical properties.

In addition to the total energy, the forces on atoms are reported at the end of the calculation. A charge density file is also created, allowing you to visualize the spatial distribution of the charge density using the Materials Visualizer. The electronic energies at the Monkhorst-Pack k-points used in the calculation are also reported, so that you can generate a density of states chart during CASTEP analysis.

The [Energy](#) task is useful for studying the electronic properties of systems for which reliable structural information is available. It can also be used to calculate an equation of state (that is, a pressure-volume and/or energy-volume dependence) for high-symmetry systems with no internal degrees of freedom, as long as the *Stress* property is specified.

Note: In systems with internal degrees of freedom, the equation of state can be obtained using the [Geometry Optimization](#) task.

The default unit of energy in CASTEP is the electron-Volt (eV). The relationship between eV and other popular energy units are found in [Mohr et al., 2008](#):

1 eV	0.0367493254 Ha	23.0605 kcal/mole	96.4853 kJ/mole
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CASTEP Geometry Optimization task

The CASTEP [Geometry Optimization](#) task allows you to refine the geometry of a 3D periodic system to obtain a stable structure or polymorph. This is done by performing an iterative process in which the coordinates of the atoms and possibly the cell parameters are adjusted so that the total energy of the structure is minimized.

CASTEP geometry optimization is based on reducing the magnitude of calculated forces and stresses until they become smaller than defined convergence tolerances. It is also possible to specify an external stress tensor to model the behavior of the system under tension, compression, shear, and so on. In these cases the internal stress tensor is iterated until it becomes equal to the applied external stress.

The process of geometry optimization generally results in a model structure that closely resembles the real structure.

The accuracy of the lattice parameters calculated using CASTEP is illustrated in [Figure 1 \(Milman et al., 2000\)](#).

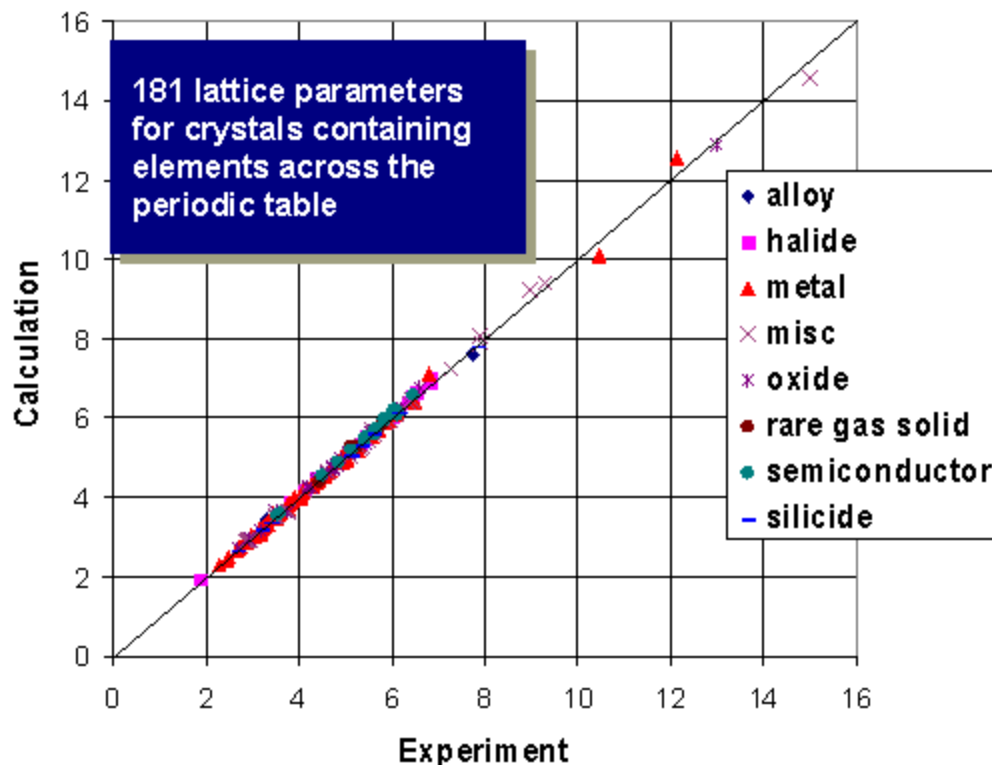


Figure 1. Experimental vs. CASTEP calculated lattice parameters

Equation of state calculation

Geometry optimization under applied hydrostatic pressure can be used to determine the bulk modulus of a material, B , and its pressure derivative, $B'=dB/dP$. The procedure involves calculating a theoretical equation of state, EOS, which describes the dependence of the cell volume on the external hydrostatic pressure. The methodology is very similar to the real experiment: the external pressure is fixed using the [Minimizer](#) tab on the Geometry Optimization dialog and the cell volume at that pressure is found by carrying out geometry optimization with CASTEP.

The subsequent analysis of the P-V dataset is exactly the same as in experimental studies (see [Winkler, 1999](#) for more details). An analytical expression is chosen to describe the EOS and its parameters are fitted to the calculated datapoints. The most popular form of EOS is the [third order Birch-Murnaghan equation](#):

$$P = \frac{3}{2}B \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] * \left\{ 1 + \frac{3}{4}(4 - B') \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}$$

Where:

V_0 is the equilibrium volume

A detailed comparative study of various analytical forms of EOS was performed by Cohen et al. ([2000](#)).

Note: The values of B and B' obtained from such fitting experiments depend on the pressure range used in the calculations. Experimental values obtained using a diamond anvil cell are usually in the range 0-30 GPa, so this is the range recommended for theoretical studies. It is also important to avoid using negative values of pressure in such studies. In addition the pressure values used to create the P-V dataset should not be uniform. More accurate sampling of the low-pressure region is required to obtain an accurate value of the bulk modulus.

Geometry optimization methods

By default, CASTEP uses the [BFGS geometry optimization](#) method. This method usually provides the fastest way of finding the lowest energy structure and this is the only scheme that supports cell optimization in CASTEP.

The [Damped molecular dynamics](#) method is an alternative that can be as effective as BFGS for systems with a flat potential energy surface, for example molecular crystals or molecules on surfaces.

The [TPSD geometry optimization](#) algorithm is a viable alternative for systems where the potential energy surface deviates significantly from the quadratic form. TPSD offers robust convergence and is particularly recommended when user-supplied constraints on lattice parameters are applied during cell optimization (for example, when optimizing a solid-solid interface in a direction perpendicular to the interface plane).

CASTEP Dynamics task

The CASTEP [Dynamics](#) task allows you to simulate how the atoms in a 3D periodic structure will move under the influence of computed forces.

Before performing a CASTEP dynamics calculation you can select the thermodynamic ensemble and associated parameters and define the simulation time, temperature, and pressure.

Selecting the thermodynamic ensemble

Integrating Newton's equations of motion allows you to explore the constant-energy surface (NVE dynamics) of a system. However, most natural phenomena occur under conditions where a system exchanges heat with the environment. These conditions can be simulated using NVT ensembles (either the deterministic Nosé ensemble or the stochastic Langevin ensemble).

External pressure can be incorporated into the dynamics calculation by using either the NPH (constant enthalpy) or the NPT (constant temperature) ensemble.

Defining the time step

An important parameter in the integration algorithm is the time step. To make the best use of the computer time, a large time step should be used. However, if the time step is too large it may lead to instability and inaccuracy in the integration process. Typically, this is manifested as a systematic drift in the constant of motion.

Note: Quantum-mechanical molecular dynamics calculations usually require a smaller time step than forcefield based dynamics applications. However, this is less of an issue in CASTEP because [wavefunction and density extrapolation](#) are used.

Constraints during dynamics

CASTEP supports [constraints](#) during molecular dynamics simulations. However, you can only apply some of the more basic constraints through the Materials Studio interface:

- The center of mass can be fixed.
- Individual atom positions can be fixed.
- Bonds lengths can be fixed.

CASTEP Elastic Constants task

The CASTEP [Elastic Constants](#) task allows you to run a set of CASTEP calculations which provides all of the information necessary to obtain the full 6×6 tensor of elastic constants for a 3D periodic structure with any symmetry.

CASTEP automatically generates the set of distorted structures that is required by symmetry to produce the full set of elastic constants, then submits jobs for the ideal structure and for all the distorted structures.

The actual calculation of elastic constants, based on the values of initial strains and calculated stresses, is performed at the [Analysis stage](#).

The accuracy of the elastic constants, especially of the shear constants, depends strongly on the quality of the SCF calculation and in particular, on the quality of the Brillouin zone sampling and the degree of convergence of wavefunctions. Therefore, you should use the [Fine](#) setting for SCF tolerance and for k-point sampling and a [Fine](#) derived FFT grid.

It is not necessary to perform geometry optimization before calculating elastic constants, so you can generate C_{ij} data for the experimentally observed structure. However, more consistent results are obtained if you perform full geometry optimization, including cell optimization and then calculate the elastic constants for the structure which corresponds to the theoretical ground state.

Note: Elastic Debye temperature and averaged sound velocity are not reported if the calculated elastic constants do not produce physically meaningful sound velocities in some directions (for example, if certain C_{ij} values or their combinations are negative when they should be positive). This can happen for low quality calculations or for calculations that were not preceded by a geometry optimization (including optimization of the lattice parameters).

CASTEP minimizes internal coordinates for each distorted structure while keeping the lattice parameters fixed. It is possible to use either the BFGS or the damped MD geometry optimization method. To select a different method you have to select the [Geometry Optimization](#) task, change the relevant setting and then return to the [Elastic Constants](#) task.

Note: As part of the [Elastic Constants](#) task, CASTEP performs a single point energy calculation for the undistorted structure. This allows you to analyze electronic and volumetric properties. The energy and stress from this calculation are not used to evaluate the elastic constants.

CASTEP Transition State Search task

The CASTEP [TS Search](#) task allows you to optimize a transition state.

When a 3D periodic molecular or crystal structure is built, it usually needs to be refined to bring it to a stable geometry. The refinement process is known as optimization. It is an iterative procedure in which the coordinates of the atoms are adjusted so that the energy of the structure is brought to a stationary point, that is, one in which the forces on the atoms are zero. A transition state is a stationary point that is an energy maximum in one direction (the direction of the reaction coordinate) and an energy minimum in all other directions.

During the course of chemical reaction, the total energy naturally changes. Starting from the reactants, the energy increases to a maximum and then decreases to the energy of the products. The maximum

energy along the reaction pathway is known as the activation energy. The structure corresponding to this energy is called the transition state.

The [TS Search](#) task is particularly useful for predicting barriers to chemical reactions and determining reaction pathways. It can be also used to find diffusion barriers for either solid state diffusion or surface diffusion. The reactants and products can either be optimized separately before running a TS Search or as part of this task. In the latter case partition functions for reactant, product, and transition state can also be calculated. This information can be used to calculate the reaction rate coefficient.

Synchronous transit methods

CASTEP transition state searches are performed using synchronous transit methods. These work best when reasonable structures for the reactants and products exist, but the location of the transition state is unknown.

Starting from reactants and products, the synchronous transit methods interpolate a reaction pathway to find a transition state. The Linear Synchronous Transit (LST) method performs a single interpolation to a maximum energy. The Quadratic Synchronous Transit (QST) method alternates searches for an energy maximum with constrained minimizations in order to refine the transition state to a high degree. The options available through CASTEP include:

- [LST Maximum](#) performs a single LST maximization, bracketing the maximum between the reactants and product. This is the quickest but least accurate of the options. The TS structure determined by this method generally requires further refinement.
- [LST/Optimization](#) performs an LST maximization, followed by an energy minimization in directions conjugate to the reaction pathway. This yields a structure lower in energy and closer to the true TS than a simple LST. Minimization steps continue until an energy minimum is reached or the number of conjugate directions is exhausted.
- [Halgren-Lipscomb](#) is a kind of limited LST/Optimization, and is designed to reproduce the algorithm popularized by Halgren and Lipscomb. After determining the LST maximum, this method performs a conjugate gradient minimization, but only in a single direction.
- [Complete LST/QST](#) begins by performing an LST/Optimization calculation. The TS approximation obtained in that way is used to perform a QST maximization. From that point, another conjugate gradient minimization is performed. The cycle is repeated until a stationary point is located or the number of allowed QST steps is exhausted.

A complete description of the algorithms used is given in [Govind et al. \(2003\)](#).

CASTEP TS Confirmation task

The TS Confirmation tool verifies that a TS calculated by an [LST or QST search](#) connects the reactant and product as expected. See [Setting up a TS confirmation calculation](#) for more details on the mechanics of this method. Materials Studio automatically determines the reactant, TS and product from the given LST or QST trajectory document.

Use the controls on the [CASTEP TS Confirmation](#) dialog to specify the convergence criteria for each individual geometry optimization (microiteration), and to specify the number of frames to use in the TS confirmation trajectory.

The output of a TS confirmation calculation is another trajectory document. This one follows the Intrinsic Reaction Path (IRP) as discussed in Reaction pathways. Each successive refinement to the pathway is displayed as a graph in Materials Studio. Use the chart selection tools to choose any point on the graphs and display the corresponding geometry.

In most cases, no minima will be found on the IRP other than your reactant and product. If so, the TS confirmation calculation verifies that the TS does connect your presumed reactant and product.

On the other hand, any other minima located by the TS confirmation are the structures that are actually connected by the TS. These are identified with an asterisk (*). You should perform a geometry optimization to refine the geometry of these minima. Select the structures as described in the [Displaying trajectory and chart data](#) topic.

You can generate a detailed map of the entire reaction by repeating TS Search and TS Confirmation for all minima on the IRP.

CASTEP Properties

The CASTEP [Properties](#) task allows you to compute electronic, structural, and vibrational properties after the completion of a single-point energy, geometry optimization, or dynamics run on a 3D periodic system.

Note: In order to calculate properties using the CASTEP [Properties](#) task, the results files from a suitable simulation must be present in the current project.

You can also use the [Properties](#) tab on the CASTEP Calculation dialog to [request](#) that such properties be calculated as part of a CASTEP run. You can view the results using the [CASTEP Analysis dialog](#).

The properties that can be generated by CASTEP are:

- **Band structure:** Electronic eigenvalues along high symmetry directions in the Brillouin zone are calculated non-self-consistently for both valence and conduction bands, using electronic charge densities and potentials generated during the simulation.
- **Core level spectroscopy:** Electronic energies on the Monkhorst-Pack mesh of k-points and the matrix elements for electronic interband transitions are calculated, either with or without core holes.
- **Density of states:** Electronic eigenvalues on a fine Monkhorst-Pack grid are calculated non-self-consistently for both valence and conduction bands, using electronic charge densities and potentials generated during the simulation.
- **Electron density difference:** The electron density difference with respect to either a linear combination of the atomic densities or a linear combination of the densities of sets of atoms contained in the structure is calculated.
- **Electron localization function:** A simple measure of electron localization in atomic and molecular systems.
- **Electronic excitations (TD-DFT):** Electronic excitations for molecules in a box calculated using the time-dependent density functional theory (TD-DFT).
- **NMR:** Chemical shielding tensors and electric field gradients are calculated.

Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

- **Optical properties:** Matrix elements for [electronic interband transitions](#) are calculated. The CASTEP Analysis dialog can be used to [generate grid and chart documents](#) containing measurable optical properties.
- **Orbitals:** Information about electronic wavefunctions is provided. This allows you to visualize 3D distribution of various electronic states (orbitals). This information is required also for visualization of STM profiles.
- **Phonons:** For phonon dispersion runs, phonon frequencies and eigenvectors along high symmetry directions in the Brillouin zone are calculated. In the case of phonon density of states calculations, phonon frequencies and eigenvectors are computed on a Monkhorst-Pack grid. This information is required during analysis to display total and projected (partial) phonon densities of states. It is also used to calculate thermodynamic properties including atomic displacement parameters, which allow

assignment of temperature factors during analysis.

Note: Phonon calculations take into account existing fixed atom constraints, regardless of the overall *Task* setting. Such fixed atoms are excluded from the calculation of vibrational properties, which corresponds to the "partial Hessian" approach.

Tip: You must check the *Fix fractional position* checkbox on the *Atom* tab of the Edit Constraints dialog, accessible from the *Modify* menu.

- **Polarizability, IR and Raman spectra:** The optical ($\omega = \infty$) and dc ($\omega = 0$) dielectric permittivity or the optical ($\omega = \infty$) and static ($\omega = 0$) molecular polarizability, along with infrared or Raman intensities (response to an electric field in the infrared range) are calculated. Permittivity is relevant for solid materials, while polarizability and infrared intensities are relevant to molecules prepared using the [supercell approach](#).
- **Population analysis:** [Mulliken analysis](#) and [Hirshfeld charge analysis](#) is performed. Mulliken bond populations and angular momentum-resolved atomic charges (as well as magnetic moments for spin-polarized calculations) are calculated. Optionally, the weights required for partial density of states (PDOS) calculations are generated. Hirshfeld atomic charges are produced.
- **Stress:** The stress tensor is calculated and written to a `seedname.castep` file. This information is useful if, for example, you perform a geometry optimization run in which cell parameters are fixed and you want to check how far the lattice is from equilibrium. For instance, a supercell study of a point defect should be carried out with the fixed cell that corresponds to the theoretical ground state of the given system. The value of the stress after geometry optimization gives an indication of the magnitude of the elastic effects associated with the supercell approximation.

Modeling disorder in solids

Many crystal structures possess static positional disorder. Materials Studio allows you to model disorder by defining mixture atoms.

Mixture atoms

Atomic sites in a disordered crystal can be described in terms of a hybrid atom, which consists of two or more element types. The relative concentrations can be set for any number of atoms, where the total concentration must be 100%. The mixture atoms description is the most often used representation of solid solutions, metallic alloys, disordered minerals, and so on.

Technical limitations

Current implementation of the molecular dynamics (MD) algorithms in CASTEP is not yet compatible with the [virtual crystal approximation](#) (VCA) formalism, which is used to model disorder in solids. None of the MD schemes (NVE, NPT, and so on) work for disordered crystals in the current version.

The following properties are unavailable for disordered systems:

- Population analysis
- Vibrational properties (phonon dispersion, phonon density of states)
- Optical properties

In addition, geometry optimization based on damped MD is not available (since MD itself is not allowed).

Atom occupancy cannot be used with the current CASTEP implementation of the virtual crystal approximation (VCA). Partial atom occupancy can be considered as a special case of a mixture atom, where one part of the mixture is an atom of "nothing". This case is not supported for a number of technical and fundamental reasons.

The limitations listed above fall into three categories:

- Properties that are ill-defined or do not make sense at all for mixture atoms (population analysis, vibrational properties).
- Features where the calculations might be possible, but which require more theoretical work (optics, partial atomic occupancies).
- Features that are blocked for purely technical reasons (molecular dynamics).

These limitations are imposed by the user interface; if you attempt a run using a combination of settings which is not allowed, a message box explaining why the run cannot be carried out will be displayed when you select *Run* or *Save Files*.

Setting up CASTEP calculations

The topics in this section describe how to set up CASTEP calculations of various types, as well as the ways in which the job control facility can be used.

There are a number of options that are understood by CASTEP which are not currently accessible through the Materials Studio interface. Such options can be utilized by manually editing the CASTEP input files. Information about how to do this is also presented in this section.

An important concept that affects a large number of settings exposed in CASTEP is that of a calculation quality. The *Quality* setting on the Setup tab of the [CASTEP Calculation](#) dialog provides a shortcut for setting up a balance between the accuracy and speed of calculations. The range of values from [Coarse](#) to [Ultra-fine](#) allows you to increase the accuracy gradually by imposing more strict tolerances, improving accuracy of reciprocal space sampling, and increasing the number of basis functions. Nevertheless there are cases where there is no need to systematically change the quality settings and a fast qualitative description is sufficient. The [Express](#) quality setting is provided to allow many simple cases to get reasonable results quickly. Please note that these settings cannot be translated into the [Coarse - Ultra-fine](#) accuracy scale. This setting is especially useful for semiconductors and insulators and can be fairly accurate for nonmagnetic metals. The study of magnetic metallic systems requires more accurate calculation settings than those defined by the [Express](#) quality setting.

Note: CASTEP does not support all possible permutations of electronic settings for all possible properties requests. In cases where the input settings are contradictory the Materials Studio client will display messages explaining the problem. However, sometimes the combinations selected during the setup of a CASTEP calculation are impossible to satisfy. The main source of such contradictions is in the type of pseudopotentials used. For example, NMR calculations and core level spectroscopy calculations require the use of on-the-fly generated (OTFG) pseudopotentials for at least some elements. On the other hand, nonlocal exchange-correlation functionals (for example B3LYP) or linear response phonon calculations are limited to norm-conserving pseudopotentials. It is therefore impossible to use the same settings for requesting, for example, phonon dispersion using linear response and core level spectra, or to calculate band structures with B3LYP and request NMR chemical shifts.

Tip: Accurate calculations for 3D periodic systems may require a large number of k-points if the lattice has a strongly skewed unit cell (for example, some cell angles are very small). In such cases it might be beneficial for the speed of calculations to convert the structure to reduced (Niggli) cell representation using the Redefine Lattice dialog.

Setting electronic options

Electronic options must be set for [Energy](#), [Geometry Optimization](#), [Dynamics](#), [Elastic Constants](#), and [TS Search](#) calculations. The settings used for [Properties](#) calculations are copied from the input files of the

calculation that is to be restarted and are unaffected by any changes made through the interface.

The basic controls used to define the calculations are available on the [Setup](#) and [Electronic](#) tabs of the CASTEP Calculation dialog. The important settings that you might need to modify are:

- [Quality](#) - determines how accurate and how expensive the calculation will be
- [System parameters](#) - describe the charge and spin state of the system
- [Exchange-correlation functional](#) - determines the level of the DFT description
- [Pseudopotentials](#) - affect both the accuracy and the cost of the calculation
- [Basis set](#) - specifies the quality of the plane wave basis set
- [k-points](#) - determine the accuracy of the Brillouin zone sampling
- [SCF](#) - specifies the scheme that is to be used for electronic minimization

Setting the quality of a calculation

An important concept that affects a large number of settings exposed in CASTEP is that of a calculation quality. The *Quality* setting on the Setup tab of the [CASTEP Calculation](#) dialog provides a shortcut for setting up a balance between the accuracy and speed of calculations. To help you select appropriate values for CASTEP parameters, four predefined parameter sets are available. The predefined sets vary in quality from [Coarse](#), suitable for quick approximate calculations, to [Ultra-fine](#), for calculations where high precision is required.

CASTEP formalism lends itself naturally to a systematic convergence study by means of increasing the size of the basis set, accuracy of Brillouin zone sampling, and so on. Nevertheless there are cases for which there is no need to systematically change the quality settings and a fast qualitative description is sufficient. The [Express](#) quality setting is provided to allow you to obtain reasonable results quickly in many simple cases. This setting can be an order of magnitude faster than the [Fine](#) setting, while producing results that are sufficiently accurate for exploratory studies, for investigation of qualitative trends in a high-throughput context for example. The [Express](#) setting is especially useful for semiconductors and insulators and can be fairly accurate for nonmagnetic metals. The study of magnetic metallic systems usually requires more accurate calculation settings than those defined by the [Express](#) quality setting.

Note: The [Express](#) setting cannot be translated into the [Coarse - Ultra-fine](#) accuracy scale.

To help you select appropriate values for CASTEP parameters, four predefined parameter sets are available. The predefined sets vary in quality from [Coarse](#), suitable for quick approximate calculations, to [Ultra-fine](#), for calculations where high precision is required.

To select a quality

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the [Setup](#) tab.
3. Choose a *Quality* setting from the dropdown list to select one of the four predefined parameter sets.

When you choose a *Quality* setting, the parameters are set according to the task and the system.

Quality	Express	Coarse	Medium	Fine	Ultra-Fine
Energy tolerances per	Cell	Atom	Atom	Atom	Atom
SCF tolerance (eV/atom)		1.0×10^{-5}	2.0×10^{-6}	1.0×10^{-6}	5.0×10^{-7}
SCF tolerance (eV/cell)	0.0001				

Quality	Express	Coarse	Medium	Fine	Ultra-Fine
SCF Convergence window	2	3	3	3	3
k-points separation (metals) (\AA^{-1})	0.07	0.07	0.05	0.04	0.04
k-points separation (insulators) (\AA^{-1})	0.1	0.1	0.08	0.07	0.07
Energy cutoff	Fine	Coarse	Medium	Fine	1.1 × Fine
FFT Grid Density	Standard	Standard	Standard	Fine	Precise
Apply finite basis set correction	1	1	1	1.2	1.5
Augmentation density scaling factor	Never	Smart	Smart	Smart	Smart

The values of the *Energy cutoff* that correspond to the [Coarse](#), [Medium](#), and [Fine](#) settings are element specific and are taken from the pseudopotential files stored in the database. These values were determined from convergence tests for single atoms and diatomic molecules and they roughly correspond to total energy convergences of 2, 0.3, and 0.1 eV atom⁻¹, respectively. The highest value for the selected quality setting among the elements present in the 3D structure document is accepted.

The *Quality* setting also affects the values of the convergence tolerances for tasks such as [geometry optimization](#), [elastic constants calculations](#), and [transition-state searching](#).

Note: The values of force, stress, and displacement tolerances for the [Geometry Optimization](#) and [Elastic Constants](#) tasks are set to 100 for [ExpressQuality](#). This preset value instructs CASTEP to ignore these tolerances and consider only the energy tolerance as a convergence criterion.

Geometry optimization

Quality	Express	Coarse	Medium	Fine	Ultra-fine
Energy tolerance (eV/atom)		5.0e-5	2.0e-5	1.0e-5	5.0e-6
Energy tolerance (eV/cell)	0.001				
Max. force tolerance (eV/ \AA)	100	0.1	0.05	0.03	0.01
Max. stress tolerance (GPa)	100	0.2	0.1	0.05	0.02
Max. displacement tolerance (\AA)	100	5.0e-3	2.0e-3	1.0e-3	5.0e-4
BFGS Use line search	No	Yes	Yes	Yes	Yes

Note: The values of force, stress, and displacement tolerances are set to 100 for [ExpressQuality](#). This preset value instructs CASTEP to ignore these tolerances and consider only the energy tolerance as a convergence criterion.

The individual tolerances may need to be adjusted in some cases:

- The *Max. force* tolerance can be reduced for molecular systems (isolated molecules, molecules on surfaces, molecular crystals, and so on)
- The *Max. stress* tolerance is generally expressed as a fraction of the bulk modulus of the material, so it should be smaller for soft materials. However, in practice, cell optimization of soft substances (for example, molecular crystals) is difficult and might not be stable enough to impose very stringent convergence criteria.

Elastic constants

Quality	Express	Coarse	Medium	Fine	Ultra-fine
Energy tolerance (eV/atom)		1.0e-5	4.0e-6	2.0e-6	1.0e-6
Energy tolerance (eV/cell)	0.001				
Max. force tolerance (eV/Å)	100	0.02	0.01	0.006	0.002
Max. displacement tolerance (Å)	100	1.0e-3	4.0e-4	2.0e-4	1.0e-4

Note: The values of force, and displacement tolerances are set to 100 for [ExpressQuality](#). This preset value instructs CASTEP to ignore these tolerances and consider only the energy tolerance as a convergence criterion.

Note: These tolerances are five times more strict than the ones used for the [Geometry Optimization](#) task.

TS Search

Quality	Express	Coarse	Medium	Fine	Ultra-fine
RMS convergence (eV/Å)	0.1	0.5	0.25	0.05	0.01

Setting system parameters

System charge

CASTEP allows you to perform calculations on charged systems. This is useful for studies of, for example, charged defects in semiconductors ([Milman et al., 1993](#) and [Hakala et al., 2000](#)).

Note: [Makov-Payne](#) corrections, which improve the convergence of the total energy with respect to the supercell size in charged periodic systems, are not implemented in this version of CASTEP. This means that the results obtained for charged systems with small unit cells are less reliable.

To set system charge

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the [Setup](#) tab.
3. Specify the system charge in the *Charge* field.

Spin polarization

Magnetic systems can be studied by carrying out spin-polarized DFT calculations with CASTEP. This setting is recommended for transition metal oxides, certain inorganic surface studies, and metallic systems containing magnetic elements (Fe, Co, Mn, Ni).

Spin-polarized CASTEP calculations are normally carried out with a variable magnetic moment. This procedure, however, does not guarantee finding the lowest energy state. DFT solutions can converge to a variety of local minima, so that the metastable states are found. The most commonly obtained solutions correspond to high spin and low spin states. The state generated by CASTEP depends on the initial magnetic configuration, since the solution is likely to converge to the nearest local minimum rather than to the global minimum.

There are two ways of defining the initial magnetic configuration: either specify the total magnetic moment per unit cell, which gets uniformly distributed over the space, or provide detailed information on the absolute values and direction (up or down) of the spins for each atom in the unit cell. The former

method can be used for relatively simple systems where only two solutions are expected (magnetic and non-magnetic). The latter method, which specifies the spin state of the atoms in the system, is more general and gives much more flexibility. It is possible to set up ferromagnetic, ferrimagnetic, or antiferromagnetic calculations to get different starting spin arrangements.

To set up a spin-polarized calculation with a uniformly distributed initial magnetic moment

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the *Setup* tab.
3. Check the *Spin polarized* checkbox and uncheck the *Use formal spin as initial* checkbox.
4. Specify an *Initial spin* value.
5. To optimize the spin value, select the [Electronic](#) tab and click the *More...* button to access the CASTEP Electronic Options dialog.
6. Select the [SCF](#) tab.
7. Uncheck the *Fix occupancy* checkbox and check the *Optimize total spin* checkbox.

To set up a spin-polarized calculation with a specified ordering of atomic moments

Note: Initial magnetic moments on atoms are treated correctly by CASTEP only when the density mixing scheme is used for electronic structure minimization. CASTEP will ignore atomic information and will use the uniformly distributed magnetic moment for the all bands or EDFT minimizers. The value of the total moment is determined by the sum of formal spins in the system.

1. Set formal spins for the atoms.
2. After setting the formal spins, find and impose the symmetry of the system.
3. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
4. Select the *Setup* tab.
5. Check the *Spin polarized* and *Use formal spin as initial* checkboxes.
6. Select the *Electronic* tab and click the *More...* button to access the CASTEP Electronic Options dialog.
7. Select the *SCF* tab.
8. Select *Density mixing* as the *Electronic minimizer* setting.
9. Uncheck the *Fix occupancy* checkbox and check the *Optimize total spin* checkbox.

It is important to include a sufficient number of empty bands when optimizing the spin state. The default number of empty bands is 4, which means that the maximum accessible increase in the spin value is 8. A calculation that started with the low spin state will be extremely slow if the actual minimum found by CASTEP corresponds to the high spin state (although this is not the case when a calculation starts with high spin and converges to low spin).

Note: CASTEP might fail to converge the SCF if the number of empty bands is insufficient to accommodate the high spin state, especially in a calculation with variable occupation numbers (metallic systems).

Electric fields

An external electric field can be applied to the system. This causes a force to act on each atom which is proportional to the charge on that atom. This can be used to calculate the polarizability of a dielectric material.

To apply an electric field

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the *Electronic* tab and click the *More...* button to access the CASTEP Electronic Options dialog.
3. Select the *Potentials* tab.
4. Specify the strength of the *Electric field* to apply.
5. Enter the *Field direction* in lattice vectors (A B C).

Setting the exchange-correlation functional

CASTEP supports one local exchange-correlation functional, [LDA](#), three gradient-corrected exchange-correlation functionals, [GGA](#), and a set of [nonlocal functionals](#) for the self-consistent total energy calculations.

LDA functional

[CA-PZ](#) is the only local ([LDA](#)) functional available in CASTEP. It is based on the [Ceperley and Alder \(1980\)](#) data as parameterized by [Perdew and Zunger \(1981\)](#).

GGA functionals

[GGA functionals](#) provide a better overall description of the electronic subsystem than the LDA functionals. The LDA description tends to overbind atoms, so that the bond lengths and the cell volume are usually underestimated by a few percent and the bulk modulus is correspondingly overestimated. GGA corrects this error but may underbind instead, leading to slightly long bond lengths.

[PBE](#) ([Perdew et al., 1996](#)) is the default exchange-correlation functional. It is recommended, especially, for studies of molecules interacting with metal surfaces, although it is also fairly reliable for bulk calculations. The [PW91](#) ([Perdew et al., 1992](#)) functional should be used for comparisons with literature data, as it is the most widely used GGA functional. The results obtained with the PW91 functional should be very similar to those obtained with PBE. Another nonlocal functional, [RPBE](#) ([Hammer et al., 1999](#)), is a revised form of the PBE functional designed to improve the description of metallic surfaces. One of the latest GGA potentials, WC, is due to [Wu and Cohen \(2006\)](#). The authors claim significant improvements for lattice constants, crystal structures, and metal surface energies over the most popular Perdew-Burke-Ernzerhof (PBE) GGA. Another recent functional, PBEsol, has been developed specifically to improve the description of exchange in solids, resulting in better structures and energetics for densely packed solids and their surfaces ([Perdew et al., 2008](#)).

Nonlocal exchange-correlation functionals

[Nonlocal exchange-correlation functionals](#) result from the generalized Kohn-Sham procedure ([Seidl et al., 1996](#)) and are intended to improve on the description of band gaps in insulators and semiconductors compared with [LDA](#) or [GGA](#) calculations. This additional accuracy comes at the price of more time consuming calculations.

Several approximations for nonlocal exchange-correlation functionals are available:

- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

The recommended functionals are [sX-LDA](#), [PBE0](#), [B3LYP](#) and [HSE06](#); the rest are supported mostly for testing against other packages that implement Hartree-Fock schemes for solids.

Note: There are limitations on the use of this approach: nonlocal exchange can only be used for insulators using the all-bands minimizer (not density mixing) with the [Energy](#), [Geometry Optimization](#), and [TS Search](#) tasks (without cell optimization). It is not compatible with stress, NMR, phonon or polarizability calculations. The formalism cannot be used with mixture atoms or ultrasoft potentials. Note that stress calculations, and hence cell optimization and the [Elastic Constants](#) task, are supported for screened exchange versions, sX and sX-LDA, and for the HSE family of functionals.

To select the exchange-correlation functional

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Select the *Setup* tab.
3. Choose a local ([LDA](#)), a gradient corrected ([GGA](#)) or nonlocal functional from the first dropdown list for the *Functional*.
4. Select the specific functional from the second dropdown list.

Setting up pseudopotentials

Ultrasoft and norm-conserving pseudopotentials

CASTEP uses on-the-fly generated ultrasoft pseudopotentials (USP) by default. These are generally more accurate and more efficient than norm-conserving pseudopotentials (NCP).

USP implementation allows CASTEP calculations to be run with a lower energy cutoff than their NCP counterparts producing a clear advantage in terms of the calculation time. However, USP formalism is more complex and becomes close to intractable for such complex concepts as linear response implementation for phonons or NMR properties, or for nonlocal exchange-correlation functionals. As a result, there is a number of tasks and properties that CASTEP can address only with norm-conserving potentials.

There are two types of pseudopotentials available in Materials Studio: tabulated and generated on-the-fly.

Pseudopotentials generated on the fly

CASTEP server code allows you to generate pseudopotentials on the fly, that is, you can provide the parameters which govern the generation rather than a tabulated file from the database. This approach has a number of advantages; for example, the same exchange-correlation functional is used in the atomic and solid state calculations; it is possible to generate "softer" or "harder" potentials by changing the core radius; it is possible to study excited configurations with a core hole, and so on.

The latest set of OTFG settings introduced in Materials Studio 8.0 has been developed in order to minimize the error with respect to fully converged all-electron DFT calculations. The error achieved by this set is 0.5 meV/atom which puts CASTEP among the most accurate pseudopotential codes available. A full definition of the test framework and the meaning of the error is given by Lejaeghere et al. ([2014](#)) and on the website of the [Delta project](#). The files that correspond to this set have an `_80` suffix. Some of these files have been subsequently improved to eliminate ghost states. The recommended set of OTFG settings includes files with an `_2017R2` (ultrasoft) or an `_2017R2ncp` (norm-conserving) suffix.

Note: It is not recommended to use PW91 exchange-correlation functional when requesting on the fly generation of pseudopotentials; PBE, RPBE, WC, BLYP, or PBESOL are better options when a GGA functional is required.

This scheme has been validated for all elements of the Periodic Table, the results of the tests are included in the files themselves. It is possible to create customized versions of the pseudopotential

generation settings, but it is recommended to test the resulting potentials thoroughly for convergence and transferability by performing calculations for a variety of systems and at different energy cutoffs. The details of the format of the [settings file for on the fly generation](#) are provided.

On the fly generation of pseudopotentials involves solution of the electronic structure of an atom and a pseudoatom, this step can be done either in a non-relativistic (Schroedinger) framework or using one of the available scalar relativistic approaches (Koelling-Harmon or ZORA). It is important to use a scalar relativistic treatment for improved accuracy of calculations for heavy elements.

Note: J-coupling can only be computed using the Schroedinger or ZORA approach.

Note: CASTEP NMR calculations can be performed only by using on the fly generation scheme, since the available potentials in the database do not contain sufficient information about all-electron projectors.

Tabulated pseudopotentials

Tabulated USP files in the database have a `.usp` or `.uspc` extension, tabulated norm-conserving files have a `.recpot` extension.

Note: Different tabulated ultrasoft potentials should be used for LDA and GGA exchange-correlation functionals. The naming convention in the database is `<element name>_<ID>.usp[CC]` for LDA functionals and `<element name>_<ID>PBE.usp[CC]` for GGA functionals. By default, Material Studio tries to find the best fit of the potentials to the exchange-correlation potentials, although this behavior can be overridden.

The database of NCPs available in Materials Studio is rather old and in some cases might contain potentials that have not been tested sufficiently. An alternative to using this database is to generate NCPs using the open source software package Opium, the Optimized Pseudopotential Interface / Unification Module (<http://opium.sourceforge.net/>). This package allows you to generate files in `.recpot` format using the latest pseudopotential generation technology.

Besides changing the global selection of pseudopotentials, it is possible to change the individual selections for each element according to the selected value of the [exchange-correlation functional](#).

Tip: Individual selections are also useful for elements such as oxygen and silicon where additional *soft* versions of the USPs are available. These require a smaller energy cutoff but may be less transferable than the standard potentials.

Nonlinear core corrected pseudopotentials

USPs with nonlinear core correction (NLCC) are provided for some elements, most notably transition metals. These potential files have a `.uspc` extension. In some cases, NLCC potentials are more accurate than the corresponding non-corrected USPs and others they provide a cheaper and less accurate alternative to the non-corrected USPs.

You can distinguish between these two cases by comparing the *Valence* values displayed on the *Potentials* tab of the *CASTEP Electronic Options* dialog.

For example, `Mn_00.usp` and `Mn_00.uspc` both use seven valence electrons. This means that the NLCC version is more accurate (and it is therefore the default potential for Mn). On the other hand, `Cr_00.usp` uses 14 valence electrons, while `Cr_00.uspc` uses only six. This means that `Cr_00.usp` treats semicore *s* and *p* states explicitly as valence states and is thus more accurate than the NLCC version.

To change global pseudopotential selection

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Set the *Pseudopotentials* option to either [Ultrasoft](#) or [Norm-conserving](#) using the dropdown list.

To change pseudopotential selection for a given element

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Click the *More...* button to open the *CASTEP Electronic Options* dialog.
4. Select the *Potentials* tab.
5. Set the *Pseudopotential* for each element from the dropdown list which appears in the appropriate grid cell when it is edited (for example, for Mg the following pseudopotentials would be available *Mg_00.usp*, *Mg_00PBE.usp*, *Mg_00PW91.usp*, *Mg_00.recpot*).
6. Click the *View* button to display the selected pseudopotential scheme.

Pseudopotential database

Pseudopotentials are stored as ASCII text files in the folder `share\Resources\Quantum\CASTEP\Potentials`. The headers of these files contain useful information about:

- Recommended cutoff energies for different convergence levels
- Pseudopotential generation data (core radii, electronic configuration, exchange-correlation potential, and so on)
- Convergence testing (energy and forces on atoms for a simple system as a function of the energy cutoff)
- Scientific testing (lattice constants and molecular bond lengths compared to experiment)

This information might be useful when deciding which potential to use, or when writing up the results of a calculation. In addition, core radii can be used as a guide to selecting a real-space transformation radius.

Setting up the basis set

Energy cutoff

The basis set, as defined by the energy cutoff value, is one of the most important parameters that determine the accuracy (and the cost) of a CASTEP calculation. The easiest way to set this value is by using the *Energy cutoff* option on the *Electronic* tab of the *Calculation* dialog. If you use this method, the cutoff value which is optimal for a given level of the total energy convergence will be determined, based on the information in the pseudopotential data files.

Alternatively, you can specify a custom energy cutoff value on the *Basis* tab of the *Electronic Options* dialog. Custom energy cutoffs may be required in a number of cases, for instance, when modeling a molecule-surface interaction, for example CO on a Pt surface. In such situations, the protocol for the calculation of the binding energy includes separate CASTEP runs for the isolated molecule, the clean Pt surface and finally the CO-Pt complex. The basis sets for the systems containing oxygen will be determined by the convergence properties of the oxygen potential, the hardest element out of O, C, and Pt. In order to achieve maximum error cancellation, it is necessary to set the energy cutoff for the clean Pt surface calculation to the same value as in the other two runs. Therefore, an automatic selection of the energy cutoff is not totally appropriate in this case.

To change the energy cutoff quality

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Set the *Energy cutoff* quality using the dropdown list.
4. The energy cutoff value that corresponds to the selected quality is displayed next to the dropdown list.

To set a specific energy cutoff value

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Click the *More...* button to access the *Electronic Options* dialog.
4. Select the *Basis* tab.
5. Check the *Use custom energy cutoff* option.
6. Modify the energy cutoff value.

FFT grid

The size of the FFT grid which is used to represent wavefunctions, charge density and potentials is determined by the energy cutoff value and the reciprocal lattice vectors.

The ideal FFT value is determined by the requirement that there be no wrap-around error in the representation of wavefunctions and potentials ([Payne et al., 1992](#)).

This value corresponds to the maximum G-vector of the FFT grid, G_{\max} , which is exactly twice the radius of the reciprocal space sphere determined by the energy cutoff E_{cut} .

However, it is possible to use smaller FFT values and still obtain accurate answers even though some wrap-around error will be present. By default CASTEP uses a grid that corresponds to 3/4 of the ideal grid size. This setting can be changed using the *Derived grid* option on the *Basis* tab of the *Electronic Options* dialog. The actual values of the FFT grid are then displayed in the *Divisions* text boxes on the same dialog.

Note: Ultrasoft potentials require a better FFT grid in order to represent the augmentation density accurately. The PW91 exchange-correlation functional also requires a better grid, to represent gradient-dependent terms in the potential.

Therefore, CASTEP derives a finer FFT grid in both of these cases, compared with other exchange-correlation functionals or norm-conserving potentials.

The table below shows the factor by which the actual grid differs from the ideal one depending on (i) *Derived grid* setting and (ii) the use of either the PW91 functional or ultrasoft pseudopotentials.

	Standard	Fine	Precise
No USP, no PW91	0.75	0.875	1.0
Either USP or PW91	0.875	1.0	1.15

Tip: Use the **Fine** setting (or better) for high-accuracy calculations, especially when the cell optimization is required.

To change the FFT grid quality

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Electronic* tab.
3. Click the *More...* button to access the *Electronic Options* dialog.
4. Select the *Basis* tab.
5. Set the *Derived grid* quality from the dropdown list.
6. The FFT grid values that corresponds to the selected quality are displayed below the dropdown list.

Finite basis set corrections

It is recommended that you apply a finite basis set correction to the total energy and to the stress tensor when stress is calculated, including geometry optimization runs with variable cell parameters and NPT/NPH molecular dynamics calculations. The *Apply finite basis set correction* setting corresponding to this is [Smart](#).

Note: Variable cell CASTEP calculations can be carried out in two modes, either fixed basis set quality (that is, fixed energy cutoff), or fixed basis set size (fixed number of plane waves). Finite basis set correction is required only in the former case, and this is accounted for automatically when the [Smart](#) setting is used.

CASTEP calculates the correction by determining the total energy at a number of cutoff energies, then evaluating the derivative required in the correction term, numerically. It is normally sufficient to use three reference points in such calculations.

In some cases the value of the derivative may be known from a previous calculation. In such circumstances, the value can be input directly, using the [Manual Correction mode](#).

However, under normal circumstances, it is strongly recommended that the finite basis set correction settings are left at their default values. These are:

Apply correction: [Smart](#)

Correction mode: [Automatic](#)

Numerical differentiation: 3 points

Setting up k-points

The k-point set used in a calculation defines the accuracy of the Brillouin zone sampling. The Monkhorst-Pack k-points used in CASTEP are characterized by divisions along three reciprocal space axes and by an optional origin shift. However, the origin shift should not be used. Thus, the k-points setup procedure simply involves selecting three integer divisions.

The quality of the k-point set can be quantified in a number of ways; CASTEP uses the distance between the points in reciprocal space as a numerical measure. The simplest way to define the set is the following:

Simple way of setting the k-points

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Electronic](#) tab.
3. Choose the desired *k-point set* from dropdown list.

This method creates either a Monkhorst-Pack set of the selected quality ([Coarse](#), [Medium](#), or [Fine](#)) or instructs CASTEP to use only one Γ -point (the origin in reciprocal space).

Note: Explicit selection of Γ -point sampling is not recommended. CASTEP will automatically use this option if the cell is very large in real space, so that the Brillouin zone is small and no sampling is required.

In all other cases, the Γ -point is the least representative of all Brillouin zone points and using it as the only sampling point can distort the results severely.

Puska (2000) showed, for example, that there is a 1-2 eV error in the vacancy formation energy in silicon when the Γ -point is used for cells containing up to 128 atoms.

Finer control over k-point sets can be exercised by using the [k-points](#) tab on the [CASTEP Electronic Options](#) dialog. This tab allows you to enter the actual Monkhorst-Pack mesh parameters by selecting the [Custom grid parameters](#) option.

CASTEP automatically optimizes the mesh parameters according to the point group symmetry of the 3D model. For example, in a cubic crystal the even mesh parameters, N, will generate the set with as many k-points as the one with the odd mesh parameters, N-1. Since the former set provides better sampling, it will be selected automatically when either [Quality](#) or [k-point separation](#) is used to define the k-point set. [Custom grid parameters](#) is the only option which allows you to specify a suboptimal mesh with odd divisions.

The quality of the k-point sampling is particularly important for metallic systems, where rapid changes in electronic structure may occur along the energy band that crosses the Fermi level. Insulators or semiconductors, even when they are treated using variable occupation numbers for electronic states, are less sensitive to the quality of k-point sampling. The default settings used by CASTEP are designed to give accurate sampling for metallic systems. This means that you can get good results for insulators and semiconductors with a slightly less fine k-point mesh than the default.

Note: The total energy is not guaranteed to decrease as more k-points are added. Therefore, when carrying out convergence testing, you should strive to find a set of k-points such that further improvements do not alter the total energy beyond the tolerance level you require. However, the energy is not likely to converge smoothly and oscillations are to be expected.

Setting up SCF parameters

SCF settings determine the algorithm that CASTEP uses to find the ground state of the electronic subsystem, as well as the accuracy required. Most of these settings do not need to be changed by the user. For example, the SCF tolerance is controlled by the global *Quality* option on the *Setup* tab. It can also be modified using the *SCF tolerance* option on the *Electronic* tab, however this is not recommended.

Similarly, the maximum number of SCF cycles, which can be adjusted using *Max. SCF cycles* option on the *SCF* tab on the *CASTEP Electronic Options* dialog, need not be changed under normal circumstances.

The *Max. SCF cycles* setting determines how many SCF steps are taken by CASTEP before it moves atoms according to the task being performed (that is, [Geometry Optimization](#) or [Dynamics](#)).

Note: The CASTEP server automatically increases the number specified in the interface by a factor of three for metallic systems.

Electronic minimization algorithm

The algorithm that is used to solve the DFT equations is specified by the *Electronic minimizer* option on the *SCF* tab on the *CASTEP Electronic Options* dialog.

[Density mixing](#) is the recommended choice, in terms of both robustness and efficiency. It is 2-4 times faster for insulators than the conjugate-gradient based [All Bands/EDFT](#) scheme. The [Density mixing](#)

scheme is especially good for metallic systems, where speedups for metal surfaces compared to conjugate gradient schemes are in the region of 10-20.

The only case where density mixing may not improve performance is for molecule in a box calculations.

The default density mixing settings use Pulay mixing and conjugate-gradient minimization of each electronic state. You should only attempt to change these parameters if SCF convergence is very poor. Sometimes it helps to reduce the length of the DIIS history from the default value of 20 to a smaller value (5-7). It might also be helpful to decrease the mixing amplitude from the default value of 0.5 to 0.1-0.2.

Variable electronic states occupancies

By default CASTEP uses variable electronic occupancies, thus effectively treating all systems as metallic. This is recommended, as it speeds up density mixing optimization, even for systems with large band gaps. The number of empty bands should be sufficiently large to cater for nearly degenerate bands close to the Fermi level. This is relevant for transition or rare earth metal compounds, where narrow *d* or *f* bands can be pinned at the Fermi level.

If the number of bands used for such a system is insufficient, the SCF convergence will be very slow and probably oscillatory. Occupation numbers of the highest electronic states as reported in the `.castep` file are likely to be noticeably nonzero for at least some k-points.

SCF convergence with the [Density mixing](#) minimization scheme can sometimes be poor for metallic systems. If this is the case, the alternative [All Bands/EDFT](#) scheme, which is based on the ensemble density-functional theory ([Marzari et al., 1997](#)) offers a more robust alternative.

Tip: Slow SCF convergence is often indicative of an insufficient number of empty bands, especially in spin-polarized calculations. To check if this is the cause, inspect the occupancies of the highest energy electronic states. They should be very close to zero for all k-points in a calculation which is setup correctly.

Dipole corrections

By default CASTEP does not perform dipole corrections, however, for slab and single molecule systems with P1 symmetry either a [Self-consistent](#) or [Non self-consistent](#) dipole correction can be applied. The self-consistent scheme is based on the method suggested by [Neugebauer and Scheffler \(1992\)](#) where the correction potential is recalculated at each SCF step. The non self-consistent scheme is based on the approach of [Yeh and Berkowitz \(1999\)](#) where a dipole correction is added after the SCF has converged. In this scenario only the total energy and its gradients are corrected, not the electrostatic potential. As a result, this type of correction is not suitable for electrostatic potential studies such as workfunction calculations.

Dipole corrections can be essential in eliminating nonphysical electrostatic interactions between periodic images, improving accuracy of calculated adsorption energies for molecules on surfaces, for example.

Tip: It is recommended to use the [All Bands/EDFT](#) electronic minimization scheme when applying a self-consistent dipole correction to an elongated cell of a slab representing a metal surface; the [Density mixing](#) minimization scheme may fail to converge for such systems.

Setting up a geometry optimization

Geometry optimization is one of the tasks most often performed with CASTEP.

Convergence criteria

The accuracy of the calculation is controlled by the *Quality* option on the *Geometry Optimization* dialog.

For a detailed description of the quality settings please refer to the [Setting the quality of a calculation](#) topic.

Geometry optimization algorithm

The BFGS algorithm is the recommended algorithm for minimizing structures. The damped molecular dynamics approach is always slower and does not allow cell relaxation. The only case when damped dynamics may be appropriate is in systems with a very flat potential energy surface. BFGS can be extremely slow in such cases and can get stuck in a local minimum.

The [TPSD geometry optimization](#) algorithm is a viable alternative for systems where the potential energy surface deviates significantly from the quadratic form. TPSD offers robust convergence and is particularly recommended when user-supplied constraints on lattice parameters are applied during cell optimization (for example, when optimizing a solid-solid interface in a direction perpendicular to the interface plane).

Constraints

Geometry optimization in CASTEP obeys constraints on fractional atomic positions imposed using the Materials Visualizer. You can set such constraints using the Edit Constraints dialog, accessible from the *Modify* menu. Note that atoms must be completely fixed; CASTEP does not support partial constraints on the x, y, and z components of Cartesian atom positions.

Tip: At present, you must check the *Fix fractional position* checkbox on the *Atom* tab of the Edit Constraints dialog in order to apply fixed atom constraints in CASTEP. This has the effect of fixing both fractional and Cartesian positions in a fixed cell calculation, and fixing fractional positions in a variable cell run. In the current version of Materials Studio, checking the *Fix Cartesian position* checkbox has no effect on CASTEP calculations.

More general linear constraints in CASTEP can be specified manually by editing the `.cell` file.

Note: The default setting in CASTEP is to optimize atomic coordinates only. You must choose an option from the *Cell optimization* dropdown list on the [Minimizer](#) tab of the Geometry Optimization dialog if cell optimization is required.

Non-linear constraints

Geometry optimization using delocalized internals in CASTEP obeys constraints on interatomic distances, bonds, and/or torsions imposed using the Materials Visualizer. You can set such constraints using the Edit Constraints dialog, accessible from the *Modify* menu.

Notes:

- All non-linear constraints are only taken into account if you choose the delocalized internal minimizer, by checking the *Use delocalized internals* checkbox on the [Options](#) tab of the CASTEP Geometry Optimization dialog.
- The [Damped MD](#) algorithm for [geometry optimization](#) acknowledges only constrained bonds (distances) between atoms, all other constraints (torsions and angles) are ignored.
- Non-linear constraints cannot be applied in conjunction with symmetry constraints. Thus, if your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.
- Non-linear constraints cannot currently be applied to disordered systems.

Potential pitfalls

One of the most difficult parts of geometry optimization in CASTEP is cell optimization. It is important to ensure that you use a finite basis set correction in such calculations, and preferably a [fine](#) quality level.

The accuracy of the stresses which are used in the cell optimization algorithm are crucial for the success of geometry optimization. Certain systems, for example, rare-earth compounds with highly localized electronic states, require very stringent criteria for [SCF](#) convergence in order to converge the stress tensor. This is particularly true for the [Density mixing](#) minimizer.

If cell optimization fails with the following message in the output file:

```
"BFGS: Geometry optimization failed to converge after ... steps",
```

You should try one of the following:

- change electronic minimization algorithm to [All Bands/EDFT](#) scheme
- use a stricter [SCF tolerance](#)
- use a less strict [Max. stress](#) tolerance

Another potential pitfall is the use of the [Fixed Basis Size Cell optimization](#) setting when the starting geometry is very different from the final one. Finite basis set correction does depend on the cell variables, although this dependence is disregarded by the minimizer. In addition, the effective cutoff energy changes when the cell geometry is modified with the above setting (it is the number of plane waves that is kept fixed). If this change takes the $dE_{\text{tot}}/d(\ln E_{\text{cut}})$ function far away from the point that was used to evaluate the finite basis set correction, the results obtained will not be accurate. Therefore, you should compare the starting and final geometries and perform a completely new run starting from the final configuration if the difference between the two is large.

Tip: [Fixed Basis Quality](#) is a recommended setting for cell optimization. Even then it is a good idea to perform an additional geometry optimization calculation after successfully completing the first, particularly if there were noticeable changes in the geometry.

Setting up a molecular dynamics calculation

In most cases a dynamics calculation is preceded by structure minimization. It may also be desirable to perform minimizations after the calculation on several of the conformations that were generated.

Note: CASTEP dynamics calculations can be only performed for systems with P1 symmetry.

Defining the time step

A key parameter in the integration algorithms is the integration time step. A common rule-of-thumb used to pick the time step is that the highest frequency vibration should be sampled between 15 and 20 times in one cycle. For example, if the highest frequency is 20 THz, a typical optical mode frequency in an insulator, a time step of 2.5-3.3 fs is appropriate (period = 1/frequency = 50 fs). In water, the stretch frequencies are around 110 THz, indicating that a time step of 0.45-0.6 fs is required. You will probably be able to use a time step that samples the motion as few as 10 times in a cycle. However, you must check your choice of time step by monitoring energy conservation in the NVE ensemble. A thermostat in the NVT ensemble can completely mask inadequate integration.

Note: The *Time step* can be increased to about 4-5 fs when the extended Lagrangian formulation ([Steneteg 2010](#), [Niklasson, 2011](#)) is used.

To choose a time step

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Setup* tab.
3. Click the *More...* button to open the *Dynamics* dialog.
4. Select the *Dynamics* tab.
5. Set the *Time step* in the text box.

Note: Along with the related value *Number of steps*, *Time step* also determines the *Total simulation time*. Changes to the *Dynamics time* also affect the *Number of steps*.

Choosing an ensemble

You can control temperature of a CASTEP dynamics calculation, in order to simulate a system that exchanges heat with the environment. Under these conditions, the total energy of the system is no longer conserved and extended forms of molecular dynamics are required.

You can simulate several thermodynamics ensembles with a constant number of particles.

Ensemble	Conditions	Description
NVE	Constant-volume/constant-energy dynamics	The Newtonian equations of motion, which conserve the total energy, are used. The unit cell is fixed. The temperature is allowed to vary. Energy is the constant of motion - it can fluctuate slightly, but there should be no systematic drift.
NVT	Constant-volume/constant-temperature dynamics	The unit cell is fixed. A thermostat maintains a constant temperature. The dynamics are modified to allow the system to exchange heat with the environment at a controlled temperature. Several methods of scaling or controlling the temperature are available.
NPH	Constant-pressure/constant enthalpy dynamics	The size of the unit cell is allowed to vary with a barostat to maintain constant pressure. The enthalpy is a constant of the motion. The size of the unit cell is allowed to vary, while the temperature is also allowed to vary. The enthalpy, which is a constant of the motion, is not allowed to vary beyond a set value between dynamics steps.
NPT	Constant-pressure/constant-temperature dynamics	The size of the unit cell is allowed to vary with a barostat to maintain constant pressure. A thermostat maintains a constant temperature. Similar to NPH, except that temperature is controlled. Several methods of scaling or controlling the temperature are available.

To choose an ensemble

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the *Setup* tab.
3. Click the *More...* button to open the *Dynamics* dialog.
4. Select the *Dynamics* tab.
5. Select the required ensemble from the *Ensemble* list.
6. Select the *Options* tab to enter parameters for the selected ensemble.

Constraints

Molecular dynamics in CASTEP obeys constraints on atomic positions and/or interatomic distances (bonds) imposed through the Materials Visualizer. You can set such constraints using the Edit Constraints dialog, accessible from the *Modify* menu.

To fix atomic positions in CASTEP you must check the *Fix fractional position* checkbox on the *Atom* tab of the Edit Constraints dialog.

Setting up a transition state calculation

CASTEP transition-state searches are performed using synchronous transit methods. These work best in situations where the structures of the reactants and products are known, but the location of the transition state is not.

A transition-state search requires a trajectory document (for example, an `.arc` or `.xtc` file) as input. The reactants are taken from the first frame of the trajectory, and the products from the last frame. For quadratic synchronous transit (QST) calculations, the current frame is used for the QST mid-point. The trajectory files generated by any of the other transition state search methods may be used as input to a QST run.

Note: When a transition state search is performed on a periodic system the unit cell is fixed.

For a detailed description of the quality settings please refer to the [Setting the quality of a calculation](#) topic.

Note: Synchronous transit calculations are performed in Cartesian coordinates. There is no option to override this.

To set up a synchronous transit calculation

1. Begin by constructing two separate documents, one for the reactants and a second for the products.
2. Determine the correspondence between atoms in the two documents using the Find Equivalent Atoms tool. The synchronous transit method performs a geometric interpolation between the atomic coordinates of the atoms in the reactants and the atoms in the products. In order to accomplish this, it is necessary that the program understand which atom matches to which.
3. Generate a trajectory that converts reactants into products using the Reaction Preview tool. You can animate this document to check that the reactants are converted correctly to products. If you are satisfied with the match, proceed with the calculation. If not, use the Find Equivalent Atoms tool to edit the atom correspondence and try again.
4. Using the document that was created by the Reaction Preview tool, select your options for the *TS Search* calculation and submit the CASTEP calculation by clicking the *Run* button.

Tip: To optimize the reactant and product structures as part of the TS Search run, check the *Optimize reactants and products* checkbox on the [CASTEP Transition State Search](#) dialog.

Setting up a transition state confirmation calculation

The [LST and QST tools](#) locate a maximum energy structure along the reaction path, but this maximum may not, in fact, be the transition state that you are looking for. You can use the [TS confirmation tool](#) to confirm that the transition state found does indeed connect your presumed reactant and product.

A TS confirmation calculation requires three structures to proceed - the reactants, the products, and the transition state. The trajectory used as input for this calculation should contain reactants in the first frame and products in the last frame. Transition state structure is taken as the current frame of this trajectory, unless the current frame is either the first or the last - in which case the penultimate frame is

used as transition state. This is the frame where CASTEP TS Search calculations store the transition state determined in the synchronous transit search.

To perform a Transition State Confirmation

1. First perform a [TS Search](#) using LST or QST. The trajectory computed by this method is used as input to the TS Confirmation. Make sure this trajectory document is in focus when you set up the TS Confirmation.
2. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
3. Open the [Setup](#) tab.
4. Set the *Task* to [TS Confirmation](#).
5. If desired, set additional options by selecting the *More...* button to open the [CASTEP TS Confirmation dialog](#). Normally, the default options will yield adequate results.
6. Click the *Run* button.

Note: The *Max. images* is the *upper limit* for the number of frames. Structures that are too similar will be dropped during the calculation.

Users should be aware that TS Confirmation jobs can take a long time to complete. These jobs perform a series of geometry optimizations along the reaction pathway, requiring quite a lot of computer time.

Tip: At the end of the calculation, you can select any geometry on the reaction pathway using the [chart/trajectory tools](#) and perform subsequent calculations. In this way you could, for example, perform further geometry optimization on an interesting structure.

Setting up an elastic constants calculation

In most cases the calculation of elastic constants is preceded by full geometry optimization, including cell optimization. This means that elastic constants will be generated for the theoretical lattice constants. However, it is possible to skip this step and generate elastic constants for the experimental structure.

Elastic constants are evaluated by calculating the stress tensor for a number of distorted structures. Internal coordinates are optimized in each run, while keeping the lattice parameters fixed. The accuracy of the elastic constants depends to a great extent on the accuracy of the SCF part and also on the level of convergence of geometry optimizations for each distorted structure.

Note: Elastic Debye temperature and averaged sound velocity are not reported if the calculated elastic constants do not produce physically meaningful sound velocities in some directions (for example, if certain C_{ij} values or their combinations are negative when they should be positive). This can happen for low quality calculations or for calculations that were not preceded by a geometry optimization (including optimization of the lattice parameters).

Setting up strain patterns

CASTEP generates the strain patterns automatically, based on the lattice type of the structure. The maximum number of patterns required is six for a monoclinic structure, while one pattern is sufficient for cubic cells. Certain symmetries allow you to modify the patterns so that whenever possible, volume-conserving strains are generated.

The quality of the calculated values depends strongly on the amplitude of the applied distortions and the number of points that are used for each strain pattern. You should use at least four steps for each strain to obtain a statistically reliable linear fit of the stress-strain relationship. The maximum strain amplitude should be chosen so as to be (i) sufficiently low that the material stays within the linear

elasticity regime, and (ii) sufficiently high that the distortion generates stresses significantly higher than the error level of the CASTEP calculation (errors due to imperfect SCF convergence, for example).

To set up strain patterns

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Setup](#) tab.
3. Choose the [Elastic Constants](#) task.
4. Click the *More...* button to open the [CASTEP Elastic Constants](#) dialog.
5. Select the [Elastic Constants](#) tab.
6. Specify the *Number of steps for each strain* and *Maximum strain amplitude* in the appropriate text boxes.

Convergence criteria

The accuracy of the calculation is controlled by the *Quality* setting on the [Minimizer tab](#) of the CASTEP Geometry Optimization dialog.

For a detailed description of the quality settings please refer to the [Setting the quality of a calculation](#) topic.

To change the convergence tolerances

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Setup](#) tab.
3. Choose the [Elastic Constants](#) task.
4. Click the *More...* button to open the [CASTEP Elastic Constants](#) dialog.
5. Select the [Options](#) tab.
6. Specify the *Quality* using either the dropdown list or by providing individual convergence tolerances for the energy, maximum force and maximum displacement in the corresponding text boxes.

Note: For trigonal symmetry, the orientation standard where C lies along the z-axis and A is in the xz plane must be used. For further details on the lattice orientation standard and how to set it, see the [Viewing or changing the lattice parameters](#) topic.

Setting up an LDA+U calculation

CASTEP LDA+U calculations are only available in the spin-polarized mode, even if there is no magnetic solution. The majority of correlated systems are either ferrimagnetic or anti-ferromagnetic, so the initial spin moments must be carefully chosen (see [Changing atomic spin](#)). In some cases, a supercell must be constructed before beginning calculations.

Note: The LDA+U formalism is not compatible with NMR, phonon, or polarizability calculations. The formalism cannot be used with mixture atoms or real-space pseudopotentials.

To set up an LDA+U calculation

1. Either import a structure from a pre-existing file or construct a new molecule using the sketching tools in the Materials Visualizer.
2. Select *Modify | Electronic Configuration* from the menu bar to display the Hubbard U tab of the Electronic Configuration dialog.
3. Set the U values for the orbitals as desired (see Changing Hubbard U values for further guidance).

Note: Default effective Hubbard U values should be considered as guidelines only, as they are not universal and depend greatly on the chemical environment. The results obtained depend on the value of U as well as the atomic orbitals, so literature values are often inappropriate.

4. On the Spin tab set the *Formal spin* parameters for your system. Then close the Electronic Configuration dialog.
5. Choose *Modules | CASTEP | Calculation* from the menu bar.
6. Select the [Setup](#) tab.
7. Select a *Functional* from the dropdown list (see the [theory](#) section for more information on functionals).
8. Check the *Spin polarized* and *Use LDA+U* checkboxes.
9. Click the *Run* button.

The symmetry used in LDA+U calculations is often lower than the crystallographic symmetry, so the number of k-points needed is increased. More calculations are carried out at each step increasing computation times and requiring more steps to achieve convergence.

Tip: For cubic systems, converting to tetragonal or rhombohedral symmetry may improve performance.

Note: Sometimes the density mixing scheme may not converge. In such cases you should switch to an [EDFT minimizer](#) to improve results and set the option to [Optimize total spin after](#) 1 SCF step.

Note: The Hubbard U operator can be applied only to the states which have an LCAO projector in the pseudopotential. If there is no projector for any orbital with nonzero U value, CASTEP will return the following error message:

Hubbard U is requested for the states which do not have LCAO projectors. Please check HUBBARD_U block in the cell file.

If you think that the states to which you want to apply Hubbard U are really important, you could use a different pseudopotential (on-the-fly generated potentials are likely to have more projectors than other pseudopotentials).

Setting up a core hole calculation

Calculations with core holes are designed to describe the electronic structure of a system containing highly excited ions with a hole in a core shell. Such calculations can be relevant to the description of such excitations and relaxations of these excited states.

Core holes can be used in any CASTEP calculation, however they are most relevant to the generation of core level spectroscopy results. It is not recommended to carry out geometry optimizations in the presence of core holes.

Note: CASTEP calculations using core holes are only available for atoms using on-the-fly generated pseudopotentials (OTFG).

To set up a core hole calculation

1. Either import a structure from a pre-existing file or construct a new structure using the sketching and crystal building tools in the Materials Visualizer.
2. Extend the crystal lattice using the Supercell or Redefine Lattice dialog and convert to the primitive representation.
3. Convert the symmetry of the crystal to P1, to prevent core holes being placed on symmetrically equivalent atoms.
4. Select *Modify | Electronic Configuration* from the menu bar to display the Core Hole tab of the Electronic Configuration dialog.
5. Set up the core hole(s) in the structure as desired (see Changing Core Hole values for further guidance). Close the Electronic Configuration dialog.
6. Open the Find Symmetry dialog and select the *Options* tab. Check the *CoreShellWithHole* checkbox in the list of properties. On the *Find* tab click the *Find Symmetry* button then the *Impose Symmetry* button.
7. Choose *Modules | CASTEP | Calculation* from the menu bar to open the CASTEP Calculation dialog.
8. On the [Electronic](#) tab check the *Use Core Hole* checkbox.
9. Select *On the fly* from the *Pseudopotentials* dropdown list.
10. Click the *Run* button.

Note: To prevent interactions between periodic images of core hole sites sufficiently large supercells might be necessary.

Note: CASTEP calculations with core holes assume by default that an electron is removed from the system, so it is treated as having a charge of 1 (or one more than specified in the *Charge* field on the [Setup](#) tab of the CASTEP Calculation dialog). In some circumstances, for example when studying impurities, it might be more appropriate to consider the system as charge neutral. In order to achieve this you should specify the *Charge* of -1 on the [Setup](#) tab, in this way the CASTEP input file will have a zero charge. It is also possible to edit the `seedname.param` file to specify a fractional charge. The strength of the core hole can be adjusted by editing the `seedname.cel` file and modifying the pseudopotential definition string (for example, change `{1s1}` to `{1s0.5}` to use a core hole with the charge of 0.5).

Setting up a work function calculation

The work function is the minimum energy (usually measured in electron Volts) required to remove an electron from a solid to a point immediately outside the solid surface (or the energy needed to move an electron from the Fermi energy level into a vacuum). This energy depends on the orientation of the crystal, different crystallographic surfaces have different work function values. The typical range of values of work function for all crystalline elements is from 2 to 6 eV, and the orientational dependence of the work function is of the order of 1 eV.

A practical way of evaluating work function is to compare the values of the Fermi energy and that of the electrostatic potential in a vacuum away from the surface. CASTEP calculations for crystal surfaces are carried out on slabs with a region of vacuum. Effectively, an infinite array of 2D-periodic slabs of material is separated by wide vacuum spacings. CASTEP produces the Fermi energy for such systems, and the spatial distribution of the electrostatic potential. Materials Studio averages the electrostatic potential in the planes parallel to the surface. This approach allows the value of electrostatic potential in vacuum, and hence the work function, to be determined.

The work function can have a large dependence on the crystal structure and surface orientation. It is recommended that the structure is carefully prepared before calculation of the work function, as

described in the steps below. The recommended sequence of steps includes the geometry optimization of the bulk structure, preparation of the surface followed optionally by optimization of atomic coordinates in the surface and bulk layers. It is possible to perform work function calculations without this optimization, so that the effects of surface relaxation on the work function can be investigated. It is reasonable to keep the structure of the middle of the slab as close to the perfect bulk structure as possible, for example by imposing fixed atom constraints on some inner atoms of the slab.

It is important to have a fair representation of the bulk material, by including at least 8-10 Å of material in the slab calculation. It is equally important to provide enough vacuum between layers of materials so that the electrostatic interactions between two sides of a slab are negligible and electrostatic potential reaches its asymptotic value; there should be at least 30 Å of vacuum in the cell.

To set up a work function calculation

1. Either import a structure of the bulk material from a pre-existing file or construct a new structure using the sketching and crystal building tools in the Materials Visualizer.
2. [Geometry optimize](#) the bulk structure using CASTEP.
3. Cleave the required crystallographic surface using the Cleave Surface dialog so that the thickness provides a meaningful representation of the bulk.
4. Build a slab using the Build Vacuum Slab Crystal dialog, you should ensure that the distance between the surface and the end of the vacuum is great enough that there can be no potential interactions between the surface and the next layer.
5. Choose *Modules | CASTEP | Calculation* from the menu bar.
6. Select the [Setup](#) tab.
7. Choose the [Geometry Optimization](#) task.
8. Fix fractional atomic positions of some atoms in the middle of the slab using the Edit Constraints dialog, accessible from the *Modify* menu.
9. Select either the [LDA](#) or [GGA Functional](#) from the dropdown list (see the [theory](#) section for more information on functionals).
10. Click the *Run* button.
11. Follow the steps in the [Displaying the averaged potential chart for work function calculations](#) topic.

Note: CASTEP calculations using non-local exchange functionals do not produce well defined local potentials so [Potentials](#) analysis is not available for these functionals. You have to use either LDA or GGA functionals in work function calculations.

The result of this procedure is a chart of the electrostatic potential as a function of position along the surface normal, with Fermi energy and the vacuum energy level marked as two horizontal lines. The work function value is reported in the chart caption.

Setting up a reaction kinetics calculation

Information generated by CASTEP as part of the transition state search task enables you to predict the reaction rate coefficient of a chemical reaction. The algorithm is based on transition state theory and involves evaluation of the partition functions of reactant(s), product(s), and transition state. Calculation of a partition function involves obtaining the vibration spectra, this in turn is calculated from the Hessian matrix.

The reaction rate calculation requires three main ingredients:

1. Transition state search, performed after optimizing geometry of reactants and products
2. Calculation of the Hessians for all the reaction species
3. Calculation of the partition functions and reaction rates for forward and reverse reactions

Transition state searching in CASTEP can be performed using either the LST or QST formalism. To optimize the reactant and product structures as part of the TS Search run, check the *Optimize reactants and products* checkbox on the [CASTEP Transition State Search](#) dialog. It is important to set constraints correctly in the initial documents - this has effect both on the cost of the subsequent calculations, and on the accuracy of the results obtained.

To calculate the Hessians for all the reaction species you should check the *Calculate partition functions* checkbox on the [CASTEP Transition State Search](#) dialog. This setting causes vibrational frequencies to be evaluated for reactant, product, and transition state structures. A partial Hessian will be used if there are constrained atoms in the system. Since the calculations rely on finite displacements, the cost can be reduced significantly by fixing coordinates of substrate atoms that are not involved in the surface reaction itself.

The result of the transition state search is an 3D Atomistic Collection Document containing reactant, product, and transition state structures. You can select the "TS" physical system and use the Vibrational Analysis tool to verify the nature of the imaginary mode associated with the reaction.

Note: The reaction rate coefficient can be calculated only if the transition state has exactly one imaginary frequency with its eigenvector along the reaction path.

The 3D Atomistic Collection Document generated will contain all the necessary information to perform the [reaction rate calculation](#) itself.

To set up a reaction kinetics calculation

1. Prepare two documents containing reactant and product structures. Set any necessary fixed atom constraints (fixed atoms should be present in both documents and should have the same coordinates).
2. Follow the steps required to set up [transition state search calculation](#).
3. Check the *Optimize reactants and products* checkbox on the [CASTEP Transition State Search](#) dialog, unless you have optimized both structures prior to constructing reaction preview document.
It is recommended to select **Ultra-fine** for the convergence tolerance for geometry optimization by changing the task to [Geometry Optimization](#), opening [CASTEP Geometry Optimization](#) dialog, editing convergence settings, and then changing the task again to **TS Search**. Such an accurate setting may be necessary to eliminate spurious imaginary modes in the vibrational analysis.
4. Check the *Calculate partition functions* checkbox on the [CASTEP Transition State Search](#) dialog.
5. It is recommended to impose more strict convergence criteria than the default values; lack of convergence can result in spurious imaginary modes of the transition state itself.

Setting up a calculation on an isolated molecule

CASTEP can be used to calculate the electronic structure and to optimize the geometry of isolated molecules as well as of solids. In order to study molecules using CASTEP, it is necessary to treat them as periodic systems by assuming that they are in a box. This can be achieved by creating a supercell containing the molecule of interest. There is no limitation on the shape of the supercell, but the simplest approach is to use a rectangular (or even cubic) supercell with a sufficiently large separation between molecules to eliminate spurious interactions between periodic images.

Since both the properties being investigated and the nature of the molecule itself have an influence on the degree of molecular separation required, it is not possible to give a definitive distance that should be established between molecules in a supercell. As a general rule, a box with dimensions that are 4-5 times the size of the molecule should be sufficient. However, it is still important that you check that the size of your supercell is adequate by investigating the convergence of the properties you are interested in against the molecular separation.

Tip: Carrying out a stress analysis is a good way of checking that the molecular separation in a supercell is sufficient to preclude any interactions between periodic images, since the stress value provides a guide as to the size of the cell. Alternatively, you could check the band dispersion: the less dispersion in the valence band, the better the molecular separation in the supercell.

CASTEP is an efficient tool for optimizing the geometry of molecules and also enables you to calculate a range of molecular properties, including:

- [Densities of states](#)
- [NMR shielding tensors and electric field gradients](#)
- [Vibrational properties](#)
- [Polarizabilities and IR absorption intensities](#)
- [Bond and band populations](#)

Note: It is recommended that only the Γ -point is used for electronic calculations on molecular systems. In addition, the all bands/EDFT electronic minimizer is known to be more efficient for studies of isolated molecules in supercell geometry than the density mixing minimizer. Therefore, it is recommended that you change the *Electronic minimizer* setting to [All Bands/EDFT](#) on the [SCF](#) tab of the CASTEP Electronic Options dialog when performing such calculations.

Tip: Calculations for "molecule in a box" systems that do not require geometry optimization can be sped up if the molecular symmetry is utilized. Use the Find Symmetry tool to find and apply the symmetry of the molecule to the supercell.

To create a molecule in a box

1. Either import a structure from a pre-existing file or construct a new molecule using the sketching tools in the Materials Visualizer.
2. Construct a crystal using the crystal building tools in the Materials Visualizer.
3. If your system does not require geometry optimization, find and impose the symmetry of the system using the Find Symmetry tool in the Materials Visualizer.

Requesting electronic, structural, and vibrational properties

CASTEP can calculate a number of electronic, structural, and vibrational properties, either as part of an [Energy](#), [Geometry Optimization](#), or [Dynamics](#) calculation, or during a separate [Properties](#) run.

Note: In the descriptions below, it is assumed that properties are being requested as part of another CASTEP calculation. It is also possible to request properties separately after a CASTEP calculation has been carried out. This is done using the [Properties](#) option, available under *Tasks* on the [Setup](#) tab. The procedures used to determine properties in this way are identical to those described below but additionally, the output files from a suitable SCF run must be available in the appropriate local Project directory.

Multiple properties can be requested when the CASTEP job is setup. The properties are calculated when the *Run* button (or [Run Files](#) button) is clicked.

Tip: The *Population analysis* checkbox on the [Properties](#) tab of the CASTEP Calculation dialog is checked by default.

Electronic properties data are produced in CASTEP by running separate non-self-consistent calculations. This means that *Band structure*, *Density of states*, *Optical properties*, and *Vibrational properties* calculations will all generate their own set of output files. *Population analysis* and *Stress* properties are calculated as part of the main run. This output can be found in the appropriate .castep file. The

Electric field response is generated either as part of a *Vibrational properties* calculation, in which case the output can be found in the appropriate .CASTEP file, or as a separate calculation.

Requesting band structure

Calculating band structure properties produces electronic energies along high symmetry directions in the Brillouin zone. The standard path for each lattice type is taken from [Bradley and Cracknell \(1972\)](#). The path can be modified using the [CASTEP Band Structure Options](#) dialog. The density of points along the path, which affects the appearance of the resulting chart, can be controlled by the selection for the *k-point set* dropdown list or the approximate k-point separation can be manually specified in the *Separation* text box, in \AA^{-1} , on the [Properties](#) tab of the CASTEP Calculation dialog. Conduction band states can be included by specifying a nonzero value in the *Empty bands* text box on the same tab.

Note: You are not required to use the same exchange-correlation functional in the band structure calculation as in the main calculation. This allows you to select a nonlocal screened-exchange functional to study the electronic structure after performing, for example geometry optimization with a variable cell using the GGA functional.

Note: CASTEP does not support the use of nonlocal functionals (screened exchange, exact exchange, and so on) for ultrasoft pseudopotentials, that is, nonlocal functionals can only be requested if all the pseudopotentials for the calculation are specified as norm-conserving.

To calculate band structure

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Properties](#) tab.
3. Check the *Band structure* option on the Properties list.
4. If necessary, modify the *Number of empty bands* to include more or less states in the conduction band.
5. Optionally, adjust the density of k-points along the high symmetry directions by using *k-point set* dropdown list.
6. Click the *More...* button to open the [CASTEP Band Structure Options](#) dialog.
7. Click the *Path...* button to open the Brillouin Zone Path dialog. This dialog allows you to inspect and modify the Brillouin zone path used for the band structure calculation.
8. On the CASTEP Band Structure Options dialog check the *Use separate XC functional for band structure calculation* checkbox to use a nonlocal functional for the electronic structure calculation.
9. Select the alternative *Functional* you wish to use from the dropdown list.

Requesting core level spectroscopy

Calculating core level spectra produces electronic energies on the Monkhorst-Pack mesh of k-points and the matrix elements for electronic interband transitions. The [CASTEP Analysis](#) dialog can be used to generate observable core level spectra based on this information. Detailed analysis of the impact of calculation parameters (k-point set, number of empty bands, and so on) on the accuracy of the spectra generated can be found in the [core level spectroscopy](#) theory topic.

To calculate core level spectra

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Select the [Properties](#) tab.
3. Check the *Core level spectroscopy* option on the properties list.
4. If necessary, modify the number *Energy range* above the Fermi level for which you wish to calculate the spectrum.
5. Optionally, adjust the density of Monkhorst-Pack k-points used for the optical properties calculation by using *k-point set* dropdown list.
6. Click the *More...* button to open the [CASTEP Core Level Spectroscopy Options](#) dialog.
7. Select the *Core level spectroscopy k-points* option you want to use and the *Band energy tolerance*.

Note: CASTEP calculations with core holes assume by default that an electron is removed from the system, so it is treated as having a charge of 1 (or one more than specified in the *Charge* field on the [Setup](#) tab of the CASTEP Calculation dialog). In some circumstances, for example when studying impurities, it might be more appropriate to consider the system as charge neutral. In order to achieve this you should specify the *Charge* of -1 on the [Setup](#) tab, in this way the CASTEP input file will have a zero charge. It is also possible to edit the `seedname.param` file to specify a fractional charge. The strength of the core hole can be adjusted by editing the `seedname.cel` file and modifying the pseudopotential definition string (for example, change `{1s1}` to `{1s0.5}` to use a core hole with the charge of 0.5).

Requesting density of states

Calculating densities of states produces electronic energies on the Monkhorst-Pack mesh of k-points. CASTEP can always produce a density of states plot, based simply on the results of the main self-consistent run. The purpose of a density of states property run is typically to:

- use a finer k-point mesh than in the self-consistent run or
- include more states in the conduction band

Such calculations are intended to provide a better quality density of states over a larger energy range.

This type of run can be also used to request a partial density of states. The quality of the k-points set is controlled by the *k-point set* dropdown list on the [Properties](#) tab on the Calculation dialog. Conduction band states can be included by specifying a nonzero value in the *Empty bands* text box on the same tab.

Note: You are not required to use the same exchange-correlation functional in the density of states calculation as in the main calculation. This allows you to select a nonlocal screened-exchange functional to study the electronic structure after performing, for example geometry optimization with a variable cell using the GGA functional.

Note: CASTEP does not support the use of nonlocal functionals (screened exchange, exact exchange, and so on) for ultrasoft pseudopotentials, that is, nonlocal functionals can only be requested if all the pseudopotentials for the calculation are specified as norm-conserving.

Note: To obtain representative density of states it is recommended to use a k-point set which is either the same or finer quality than the one used in the SCF calculations.

To calculate density of states

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Properties](#) tab.
3. Check the *Density of states* option on the properties list.
4. If necessary, modify the *Number of empty bands* to include more or less states in the conduction band.
5. Optionally, adjust the density of Monkhorst-Pack k-points used for the density of states calculation by using *k-point set* dropdown list.
6. If you would like to generate partial or local densities of states, check *Calculate PDOS*.
7. Click the *More...* button to open the [CASTEP Density of States Options](#) dialog. This dialog gives you complete control over setting up the Monkhorst-Pack grid.
8. Check *Use separate XC functional for DOS calculation* on the [CASTEP Density of States Options](#) dialog if you want to use, for example, a nonlocal functional for the electronic structure calculation.
9. Select the alternative *Functional* you wish to use from the dropdown list on the same dialog.

Requesting electron density difference analysis

Materials Studio provides the option of generating the electron density difference in two different ways:

- Electron density difference with respect to a linear combination of the atomic densities.
- Electron density difference with respect to a linear combination of the densities of sets of atoms contained in the model.

The former option produces a density difference field which shows the changes in the electron distribution that are due to formation of all the bonds in the system. This object is appropriate for bulk solids to illustrate the charge redistribution due to chemical bonding.

The latter option generates a density difference field which effectively corresponds only to the formation of bonds between atoms in different sets and to charge redistribution within the sets that is due to the presence of other sets. This property is useful to describe such processes as bonding of molecule(s) to external and internal (for example zeolites) surfaces, or creation of large molecules from smaller fragments.

Note: Materials Studio supports the calculation of the density difference with respect to the densities of sets of atoms only for tasks that do not involve changes in atomic geometry. For [Geometry Optimization](#) and [Dynamics](#) values of the *Task* property, you can request this type of density difference after the run is complete by using the [Properties](#) task.

To perform an electron density difference analysis

1. Choose *Modules | CASTEP | Calculation* from the menu bar to open the [CASTEP Calculation](#) dialog.
2. Select the [Properties](#) tab.
3. Check the *Electron density difference* checkbox on the properties list.
4. Use the radio buttons to select the appropriate type of density difference to be created.
5. When density difference with respect to sets of atoms is requested, it is necessary to create at least one set of atoms in the model. There is a naming convention for sets that are taken into account: they should have "DensityDifference" as part of the set name. In order to create the sets:
 - a. Choose *Edit | Edit Sets* from the menu bar.
 - b. Make sure that the correct 3D structure document is active.
 - c. Select the atoms that will constitute the first set.
 - d. Click the *New...* button to create a new set.
 - e. Give the set a name, for example DensityDifference1.
 - f. Repeat the above steps to create further sets if required.

Note: Multiple sets should be mutually exclusive.

Tip: When only one set with the correct name is present in the structure, Materials Studio assumes that the rest of the atoms should be treated as a second set. Thus, in the case of a molecule-surface interaction, it is sufficient to create a single set that comprises all the atoms in the molecule.

Requesting electron localization function

Electron localization function (ELF) provides a useful qualitative description of chemical bonding. CASTEP can calculate ELF at the end of a run and return the results for volumetric analysis.

To request an ELF calculation

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the [Properties](#) tab.
3. Check the *Electron localization function* checkbox in the list of properties.

Requesting electronic excitations (TD-DFT)

CASTEP allows you to calculate electronic excitation energies and the corresponding oscillator strengths (transition probabilities) using time-dependent density functional theory (TD-DFT). These excitation energies correspond to the locations of absorption peaks in the optical spectrum of a material and represent an improvement over Kohn-Sham excitation energies in terms of accuracy. The calculations are carried out using the Tamm-Dankoff approximation ([Hirata and Head-Gordon 1999](#)). Knowledge of the excitation energies and corresponding transition probabilities allows one to calculate full set of optical properties.

To calculate TD-DFT optical properties

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Select the [Properties](#) tab.
3. Check the *Electronic excitations (TD-DFT)* option in the properties list.
4. Check the *Calculate energies* checkbox to obtain excitation energies.
5. Check the *Calculate optical properties* checkbox to calculate the transition probabilities which can be used for [analysis](#).
6. If necessary, modify the number of excitations which should be calculated.

The excitation data will be reported in the <seedname>_TDDFT.castep output file.

In certain applications the lifetime of an excited state can be sufficiently long to justify the need for geometry optimization of this state; this requires calculation of forces within TD-DFT formalism which is provided by CASTEP.

To optimize geometry for a particular excitation

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Select the [Properties](#) tab.
3. Check the *Electronic excitations (TD-DFT)* option in the properties list.
4. Check the *Optimize geometry* checkbox.
5. Modify the excitation number which should have its geometry optimized.

The optimized structure for the specified excitation will be saved in the <seedname>_TDDFT_GO.xsd output file.

Limitations of electronic excitation calculations in CASTEP

The current version of CASTEP has a number of limitations related to the TD-DFT calculation of electronic excitations:

- The structure must be an insulator (the *Metal* checkbox on the [Setup](#) tab of the CASTEP Calculation dialog must be unchecked)
- Norm-conserving pseudopotentials must be used (see the [Setting up pseudopotentials](#) topic)
- Fixed orbital occupancies are required (see the [Setting up SCF parameters](#) topic)
- Only a [Gamma point](#) calculation is allowed, which should be sufficiently accurate for a "molecule in a box" geometry
- LDA+U calculations are not supported

Requesting Fermi surface data

Fermi surfaces are generated from information from CASTEP calculations which is stored in the [.bands](#) output file. In order to ensure that the Fermi surface generated is accurate it is recommended that you use as many k-points as is computationally viable. Fermi surfaces can be considered as the equivalent to isosurfaces in reciprocal space.

To generate Fermi surfaces for any CASTEP calculation

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Electronic](#) tab on the CASTEP Calculation dialog and click the *More...* button to open the CASTEP Electronic Options dialog.
3. Select the [k-points](#) tab and click the *Separation* radio button.
4. Specify a value of **0.01** 1/Å or less for the k-point separation. This ensures that enough k-points are used over the entire calculation for generating the Fermi surface data.

To generate Fermi surfaces for a CASTEP calculation with DOS properties

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Properties](#) tab.
3. Check the *Density of states* option on the properties list and set the appropriate [DOS options](#).
4. Click the *More...* button to open the [CASTEP Density of States Options](#) dialog.
5. Click the *Separation* radio button and specify a value of **0.01** 1/Å or less. This ensures that enough k-points are used for generating the Fermi surface data without requiring such fine settings for the rest of the calculation.

Requesting NMR properties

NMR calculations can generate the shielding tensor and/or electric field gradients for all of the atoms in the selected system. NMR properties are very sensitive to atomic positions, which makes NMR such a useful experimental tool for structure analysis. This means that it is highly recommended to perform a geometry optimization run before the NMR calculation. If the structure of a crystal or molecule under investigation is obtained from an experimental study, it is advisable to optimize positions of hydrogen atoms first of all. If the forces on heavy atoms as reported by CASTEP are high (in excess of 1 eV/Å), complete structure optimization is recommended.

A detailed review of the CASTEP NMR formalism and numerous examples of practical applications are discussed in Bonhomme et al. (2012).

Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Chemical shielding tensor

The chemical shielding tensor, $\sigma(\mathbf{r})$, is defined as the ratio between an external applied magnetic field, \mathbf{B} , and the non-uniform induced magnetic field, $\mathbf{B}_{in}(\mathbf{r})$:

$$\mathbf{B}_{in}^{(1)}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}$$

The isotropic shielding, σ_{iso} , is given by one third of the trace of $\sigma(\mathbf{r})$. From the symmetric component of the shielding tensor, the chemical shielding anisotropy, σ_{aniso} and the asymmetry parameter, η , can be defined in terms of the principal components of the shielding tensor:

$$\sigma_{aniso} = \frac{\sigma_{zz} - (\sigma_{xx} + \sigma_{yy})}{2}$$

and:

$$\eta = \frac{\sigma_{xx} + \sigma_{yy}}{\sigma_{aniso} + \sigma_{xx}}$$

where:

$$|\sigma_{yy} - \sigma_{iso}| \leq |\sigma_{xx} - \sigma_{iso}| \leq |\sigma_{zz} - \sigma_{iso}|$$

For values of σ_{aniso} close to zero the asymmetry parameter will be ill-defined.

Electric field gradient

The interaction of a quadrupolar nuclei with an external magnetic field can be characterized by the quadrupolar coupling constant, C_Q , and the asymmetry parameter, η_Q . If the principal components of the traceless electric field gradient tensor are labeled, V_{xx} , V_{yy} , and V_{zz} such that:

$$|V_{zz}| \leq |V_{yy}| \leq |V_{xx}|$$

then:

$$C_Q = \frac{eQV_{zz}}{h}$$

where Q is the nuclear electric quadrupole moment, and:

$$\eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

For very small values of V_{zz} the asymmetry parameter will be ill-defined.

The value of the quadrupolar moment depends on the actual isotope; CASTEP makes a suggestion based on the most typical isotope used in solid state NMR experiments. The value of Q affects only the quadrupolar coupling constant, C_Q , calculated and printed out by CASTEP. If you find that the wrong value of Q was used you can rescale the generated C_Q constant using a different Q value.

Note: The list of default values is based on the compilation by [Pyykkö \(2008\)](#). CASTEP versions prior to the 5.0 release used an older compilation by [Harris \(1996\)](#), so some results for quadrupolar coupling constants may have changed in later versions.

J-couplings

NMR J-coupling or nuclear spin-spin coupling is an indirect interaction of the nuclear magnetic moments mediated by the bonding electrons. It is manifested as the fine structure in NMR spectra, providing a direct measure of bond strength and a map of the connectivities of the system.

Induced magnetization density and current density are expected to be short-ranged. This forms the basis of using J-coupling as a tool for probing the strength of interatomic bonds. However, in a periodic calculation the perturbing nucleus can be viewed as similar to a defect in a defect calculation. Hence, sometimes it might be necessary to construct a supercell which is large enough to inhibit the interaction between the periodic defects or perturbations. Convergence with respect to the cell size should represent an important test in establishing accuracy of J-coupling calculations in either periodic systems or in molecule in a box calculations.

Note: J-coupling can be calculated only for non-magnetic systems. J-coupling calculations are supported only for systems with P1 symmetry. If your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.

To calculate NMR properties

1. Choose *Modules | CASTEP | Calculation* from the menu bar.
2. Choose the [Electronic](#) tab on the CASTEP Calculation dialog and select [On the fly](#) from the *Pseudopotentials* dropdown list.
3. On the [Properties](#) tab, check the *NMR* option on the list of properties.
4. Select the properties you wish to determine:
 - *Shielding*
 - *EFG*
 - *J-coupling*
 - *G-tensor*
5. Choose the method you wish to use to determine the NMR properties from the *System type* dropdown list ([Crystal](#), [Molecule](#), or [Auto](#)). The [Molecule](#) option refers to the supercell description of isolated molecules.
6. If *J-coupling* is selected, then there are some requirements:
 - At least one atom in the system must be selected, J-couplings will be calculated between the selected atom(s) and all other atoms in the system
 - On-the-fly-generated pseudopotentials must be used
 - The *Relativistic treatment* of the on-the-fly-generated pseudopotentials (on the [Electronic](#) tab of the CASTEP Calculation dialog) must be set to either [Schroedinger](#) for non-relativistic treatment or [ZORA](#) for scalar-relativistic effects to be taken into account.

Note: NMR parameters will be calculated only for the elements for which the on-the-fly-generated pseudopotentials are chosen.

Tip: It is not recommended to use PW91 exchange-correlation functional when requesting NMR properties. PW91 functional may result in sharp real-space features of on-the-fly-generated pseudopotentials; PBE, RPBE, WC, BLYP, or PBESOL are better options when a GGA functional is required.

EPR G-tensor

Electron Spin Resonance (EPR - also known as Electron Paramagnetic Resonance) is a powerful experimental probe of the structure of defects in solids. EPR spectra of spin $\frac{1}{2}$ centers are made up of two contributions:

- the hyperfine parameters
- the g-tensor

The g-tensor arises from the interaction of the electronic spin with external magnetic field. This term plays a somewhat similar role to the shielding in NMR; induced electronic currents in the sample modify the g tensor from its vacuum value.

EPR spectrum can be modeled using the following effective Hamiltonian, bilinear in the total electron spin S , and the applied uniform magnetic field or nuclear spins, B and I_I , respectively:

$$H_{eff} = \frac{\alpha}{2} S \cdot g \cdot B + \sum_I S \cdot A_I \cdot I_I$$

where:

atomic units are used

α is the fine structure constant

the summation I runs over the nuclei

The tensors A_I are the hyperfine parameters, and the tensor g is the EPR g-tensor.

Requesting optical properties (DFT)

CASTEP currently implements two approaches for optical properties calculations; one is based on standard DFT Kohn-Sham orbitals and the other uses more accurate but much more time-consuming time-dependent DFT (TD-DFT) theory. In this section we consider only DFT Optical properties. Setting up TD-DFT optical properties calculations are described in the section [Requesting electronic excitations \(TD-DFT\)](#).

Calculating optical properties produces electronic energies on the Monkhorst-Pack mesh of k-points and the matrix elements for electronic interband transitions. The [CASTEP Analysis](#) dialog can be used to generate observable optical properties based on this information. Detailed analysis of the impact of calculation parameters (k-point set, number of empty bands, and so on) on the accuracy of the optical properties generated can be found in the [Optical properties](#) theory topic.

Note: You are not required to use the same exchange-correlation functional in the optical properties calculation as in the main calculation. This allows you to select a nonlocal screened-exchange functional to study the optical properties after performing, for example, geometry optimization with a variable cell using the GGA functional.

To calculate optical properties

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Properties](#) tab.
3. Check the *Optical properties* option on the properties list.
4. If necessary, modify the *Number of empty bands* to include more or less states in the conduction band.

Note: The number of empty bands used should be greater when calculating optical properties than for band structure or density of states calculations (see the [Optical properties](#) theory topic for more details).

5. Optionally, adjust the density of Monkhorst-Pack k-points used for the optical properties calculation by using *k-point set* dropdown list.
6. Click the *More...* button to open the [CASTEP Optical Properties Options](#) dialog. This dialog gives you complete control over setting up the grid.
7. Check *Use separate XC functional for optics calculation* on the [CASTEP Optical Properties Options](#) dialog if you want to use, for example, a nonlocal functional for the optical properties calculation.
8. Select the alternative *Functional* you wish to use from the dropdown list on the same dialog.

TD-DFT Optical properties

Requesting orbital analysis

Although wavefunctions are generated by every CASTEP run, they are not returned to the client by default, as the file containing the wavefunctions is very large. To perform orbital analysis it is necessary to explicitly request that these files be returned to the client.

Note: Orbitals are required to calculate the STM profile.

To perform an orbitals analysis

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Properties](#) tab.
3. Check the *Orbitals* option on the properties list.

Requesting vibrational properties

CASTEP allows you to set up calculations that provide vibrational frequencies and eigenvectors at a selected set of q-vectors in the Brillouin zone. Two approaches to calculating these data are provided:

- Linear response formalism
- Finite displacement method

There are two predefined modes of calculation: the phonon dispersion spectrum along high symmetry directions and the phonon density of states spectrum, which is a prerequisite for the calculation of thermodynamic properties.

Note: Phonon calculations take into account existing fixed atom constraints, regardless of the overall *Task* setting. Such fixed atoms are excluded from the calculation of vibrational properties, which corresponds to the "partial Hessian" approach. Constrained lattice dynamics approach is applied for both linear response and finite displacement approach.

Tip: You must check the *Fix fractional position* checkbox on the *Atom* tab of the Edit Constraints dialog, accessible from the *Modify* menu.

Phonon frequencies from linear response calculations

The linear response scheme treats atomic displacements as perturbations. In addition, an electric field response is evaluated to calculate a non-analytical correction to longitudinal optical (LO) phonon frequencies at the Γ -point. Longitudinal and transverse modes at the Γ -point are identical (no LO-TO splitting), unless this correction is applied.

The linear response scheme allows the calculation of phonon spectra in any commensurate or incommensurate q-vector of the reciprocal space, thus providing full flexibility in the choice of q-vectors to be used for calculations. Nevertheless, linear response calculations at a general q-vector are very time consuming and are often not necessary as a real space dynamical matrix that defines vibrational properties is often a short range property. This real space dynamical matrix can be calculated using a coarse Monkhorst-Pack mesh and then used to obtain the phonon spectrum at any given q-vector in the Brillouin zone. Thus, there two major modes of linear response calculations: direct and using interpolation.

Limitations of the linear response implementation in CASTEP

The current version of CASTEP has a number of limitations related to phonon calculations. The only settings that are supported for linear response calculations or for finite displacement calculations that require LO-TO splitting correction are:

- Norm-conserving pseudopotentials (see the [Setting up pseudopotentials](#) topic)
- Non-spin-polarized calculations (see the [Setting system parameters](#) topic)

If any of these restrictions is violated by the current settings, an error message is displayed with an explanation of the problem. The offending setting must be changed in order to proceed with the phonon calculation.

Note: Gradient-corrected exchange-correlation functionals are supported in linear response calculations, although the results may be less accurate than those obtained with LDA and the computational cost is noticeably higher.

Phonon frequencies from finite displacements calculations

CASTEP provides an alternative method of calculating phonon frequencies that is based on the finite displacements method ([Montanari and Harrison, 2002](#)). This technique is based on numerical differentiation of forces on atoms that are calculated for a number of unit cells with atomic displacements. CASTEP determines the optimum number of such displacements automatically, based on the crystal symmetry. Displacements with a very small magnitude give results that are similar to the linear response frequencies. An advantage of the finite displacements method is that it is also possible to investigate phonon anharmonicity by increasing the amplitude of the displacements. A further important advantage is that none of the linear response limitations mentioned above are relevant for finite displacements calculations. This method can be used to obtain vibrational frequencies for:

- Metallic systems
- Spin-polarized systems
- Any system treated with efficient ultrasoft potentials

The formalism is based on evaluation of the dynamical matrix at a (coarse) commensurate grid of q-points at the cost of creating a supercell, and then dynamical matrix is re-interpolated onto a requested set of q-points. There are two available approaches to dynamical matrix calculation:

- Create a large supercell with the size defined by a real space cutoff parameter; the supercell size then dictates a coarse grid.
- Create a set of non-diagonal supercells ([Lloyd-Williams and Monserrat, 2015](#)) which are commensurate with a q-point set of a coarse grid; in this case the coarse grid is defined by the grid spacing for interpolation.

Limitations of the finite displacements implementation in CASTEP

There is a limitation with the current implementation of the finite displacements method in CASTEP related to the treatment of the non-analytical term that is responsible for the LO-TO splitting in insulators. This term is currently calculated using linear response with an electric field as a perturbation; thus, all the computational restrictions mentioned in the previous section apply to finite displacements calculations if the LO-TO splitting is requested.

Note: A LO-TO calculation imposes all the restrictions that apply when the linear response technique is used. You might want to proceed with finite displacement calculations without LO-TO splitting if these restrictions affect your study. In this case, only TO modes will be reliably produced when there is LO-TO degeneracy in the results.

Requesting phonon dispersion

Calculating the phonon dispersion produces phonon frequencies and eigenvectors along high symmetry directions in the Brillouin zone. The standard path for each lattice type is taken from Bradley and Cracknell ([1972](#)). The path can be modified using the Brillouin Zone Path dialog. The density of points along the path, which affects the appearance of the resulting chart, is controlled by the *Quality* setting in the *Dispersion* section on the [CASTEP Phonon Properties Setup dialog](#).

To calculate phonon dispersion

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the [Properties](#) tab.
3. Check the *Phonons* checkbox in the list of properties, then select the *Dispersion* radio button which appears below the list.
4. If required, check the *Calculate LO-TO splitting* checkbox.
5. Select the technique to be used to calculate the phonon frequencies from the *Method* dropdown list.
6. Click the *More...* button to display the CASTEP Phonon Properties Options dialog.
7. For linear response calculations, specify the convergence criterion for the force constants in the *Convergence tolerance* text box. If you do not want to carry out a direct calculation, check the *Use interpolation* checkbox and specify the q-point separation in the *q-vector grid spacing for interpolation* text box.

For finite displacement calculations, specify the cutoff radius to be used to construct the appropriate supercell in the *Supercell defined by cutoff radius* text box.

8. Optionally, adjust the density of q-vectors along the high symmetry directions used for the phonon dispersion calculation using the *Quality* control in the *Dispersion* section.
9. If you wish to inspect or modify the Brillouin zone path used for the phonon dispersion calculation, click the *Path...* button to display the Brillouin Zone Path dialog and alter the path segments accordingly.
10. Optionally, accelerate the calculation by using partial Hessian approach - apply fixed atom constraints to the atoms that are not essential to the calculation (for example substrate atoms in a molecule on surface calculations).

Requesting phonon density of states

Calculating the phonon density of states produces phonon frequencies and eigenvectors on the regular Monkhorst-Pack mesh of q-vectors. This information is required to produce either the total or projected (partial) phonon density of states and, thus, to calculate thermodynamic properties. The quality of the q-vector set is controlled by the *Quality* setting in the *Density of states* section on the CASTEP Phonon Properties Options dialog.

Note: When you request phonon density of states CASTEP will also calculate atomic displacement parameters, allowing [assignment of temperature factors](#) during analysis.

To calculate the density of states

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the *Properties* tab.
3. Check the *Phonons* checkbox in the list of properties, then select the *Density of states* radio button which appears below the list.
4. If required, check the *Calculate LO-TO splitting* checkbox.
5. Select the technique to be used to calculate the phonon frequencies from the *Method* dropdown list.
6. Click the *More...* button to display the CASTEP Phonon Properties Options dialog.
7. For linear response calculations, specify the convergence criterion for the electronic eigenvalues in the *Convergence tolerance* text box. If you do not want to carry out a direct calculation, check the *Use interpolation* checkbox and specify the q-point separation in the *q-vector grid spacing for interpolation* text box.

For finite displacement calculations, specify the cutoff radius to be used to construct the appropriate supercell in the *Supercell defined by cutoff radius* text box.

8. Optionally, adjust the density of Monkhorst-Pack q-vectors used for the phonon density of states calculation using the *Quality* control in the *Density of states* section.
9. If you wish to inspect or modify the setup of the Monkhorst-Pack grid, click the *More...* button to display the [Phonon Density of States Options dialog](#) and alter the settings accordingly.
10. Optionally, accelerate the calculation by using partial Hessian approach - apply fixed atom constraints to the atoms that are not essential to the calculation (for example, substrate atoms in a molecule on surface calculations).

Tip: If you choose quality gamma frequencies then eigenvectors will be only calculated at the Γ -point, which determines most of the experimental data on IR or Raman spectra. This can accelerate finite displacement calculations tremendously as no supercell is constructed for this case. However, the accuracy of thermodynamic properties obtained with this single q-vector is very poor as no acoustic degrees of freedom can be taken into account.

Calculating vibrational frequencies of an isolated molecule

CASTEP can be used to calculate vibrational frequencies of isolated molecules as well as the phonon dispersion of solids. It is recommended that only the Γ -point is used for electronic calculations and that the Γ -point is requested when performing either phonon dispersion or phonon density of states calculations. In addition, the all bands/EDFT electronic minimizer is known to be more efficient for studies of isolated molecules in supercell geometry than the density mixing minimizer. Therefore, it is recommended that you change the *Electronic minimizer* setting to *All Bands/EDFT* on the [SCF](#) tab of the CASTEP Electronic Options dialog when performing such calculations.

Tip: Calculations for "molecule in a box" systems that do not require geometry optimization can be sped up if the molecular symmetry is utilized. Use the Find Symmetry tool to find and apply the symmetry of the molecule to the supercell.

Note: Do not calculate LO-TO splitting for a "molecule in a box" system. There is no physical meaning to this term when studying molecular, rather than crystalline, vibrations.

Guidelines for the successful calculation of vibrational properties using CASTEP

1. Parameters for geometry optimization

The results of a phonon calculation will be inaccurate unless the geometry of the input structure is well converged. Geometry optimization to a true ground state requires that the forces are well converged.

In general, using a *Quality* setting of **Ultra-fine** for the geometry optimization on the **Setup** tab of the CASTEP Calculation dialog should be sufficient for the purposes of obtaining accurate forces, but the safest procedure is to investigate the convergence of the forces as a function of calculation parameters - primarily the k-point sampling. It is recommended that you carry out a series of single-point energy calculations using increasingly dense k-point meshes. Monitor the convergence of the forces until they converge to within the force tolerance criterion.

2. Geometry optimization of the input structure

Once you have generated reasonably well-converged forces, you can carry out the geometry optimization. Use the same force convergence tolerance as for the force convergence test. A well-converged geometry optimization is of little value if the forces are inaccurate because of convergence errors.

You may wish to perform a fixed-cell or variable-cell geometry optimization, depending on your goals for the calculation. The lattice-dynamical problem is well defined in either case, but, of course, the pressure or stress will be different. You should also monitor the convergence of the stress before carrying out a variable-cell optimization (though the behavior is usually similar to the convergence of forces).

3. Use of consistent electronic settings

To be a valid lattice dynamics calculation, the phonon run must use the same specification as the geometry optimization. If you want to change anything of significance, such as the cutoff, XC functional or k-point sampling, you must carry out a fresh geometry optimization using these new settings before starting the lattice dynamics run.

4. Checking the convergence of the results

Unfortunately, following the above guidelines does not guarantee that your final phonon frequencies will be converged to any given tolerance. The only way to determine that this is the case is to actually check the convergence behavior of the final properties. This requires a subtle judgment of whether you are measuring a 'primary' change due to the convergence of force constants or a 'secondary' one consequent on the slightly different geometry.

As noted in the literature, and from experience, phonon frequencies are more sensitive to k-point convergence than geometries, assuming tolerance criteria of a few cm^{-1} and a few hundredths of an angstrom. Acoustic phonons near the Γ -point are the most sensitive, as they depend on near-cancellation between large force constant terms in the dynamical matrix. Dielectric properties and Born charges tend to be more sensitive than phonons, on a fractional proportion tolerance.

The ultimate convergence test would require geometry optimization performed for a denser k-point grid, followed by a new phonon calculation - this is the only way to determine whether the k-point sampling has an effect on the accuracy of the calculated vibrational frequencies.

Note: Phonon spectra in metallic compounds are very sensitive to the details of the Fermi surface. To obtain reasonable spectra using linear response method for metals, the k-point sampling must be extremely dense: much denser than the [Fine](#) mesh. It is recommended to consider setting the *Separation* parameter on the [k-points tab](#) of the CASTEP Electronic Options dialog to less than **0.02**. A clear sign of insufficient quality of k-point sampling is the presence of imaginary acoustic modes near the Γ -point.

Requesting polarizability, IR and Raman spectra

Within the electric field [linear response formalism](#), CASTEP enables you to calculate optical ($\omega = \infty$) and dc ($\omega = 0$) dielectric permittivity or optical ($\omega = \infty$) and static ($\omega = 0$) molecular polarizability. These properties are calculated when the TASK keyword in the input parameters ([.param](#)) file is set to either [Efield](#) or [Phonon+Efield](#). In the latter case, infrared intensities (response to an electric field in the infrared range) are calculated as well if there is a Γ -point among the phonon k-points.

The calculated results are somewhat sensitive to the value of the scissors correction. This correction amounts to the difference between the calculated and experimental band gap. It is possible to estimate this correction when the experimental data are available by performing the band structure run with CASTEP and comparing the calculated band gap with the experimental value.

To calculate polarizability, IR and Raman spectra

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the [Properties](#) tab.
3. Check the *Polarizability, IR and Raman spectra* checkbox in the list of properties.
4. Choose the correct description of the system from the *System type* dropdown list ([Crystal](#), [Molecule](#), or [Linear molecule](#)). The last two options refer to the supercell description of isolated molecules.
5. Specify whether to *Calculate Raman intensities* using the checkbox.
6. Click the *More...* button to open the [CASTEP IR and Raman Options](#) dialog.
7. Optionally, alter the accuracy of the calculation by entering a new value in the *Convergence tolerance* field.
8. If the value of the scissors operator is known, enter it in the *Scissors operator* text box and close the dialog.

Calculating the polarizability, IR and Raman spectra of an isolated molecule

CASTEP can be used to calculate the electric field response of isolated molecules as well as of solids. It is recommended that only the Γ -point is used for electronic calculations on molecular systems. In addition, the all Bands/EDFT electronic minimizer is known to be more efficient for studies of isolated molecules in supercell geometry than the density mixing minimizer. Therefore, it is recommended that you change the *Electronic minimizer* setting to [All Bands/EDFT](#) on the [SCF](#) tab of the CASTEP Electronic Options dialog when performing such calculations.

Tip: Calculations for "molecule in a box" systems that do not require geometry optimization can be sped up if the molecular symmetry is utilized. Use the Find Symmetry tool to find and apply the symmetry of the molecule to the supercell.

Note: It is important to select the correct description of the system from the *System type* dropdown list when calculating the electric field response for a molecular system. The wrong system description can significantly affect the molecular polarizability values obtained.

Limitations of the electric field response implementation in CASTEP

The current version of CASTEP has a number of limitations related to electric field response calculations; they are essentially the same as those for phonon calculations. The only settings that are supported for electric field response calculations are the following:

- Norm-conserving pseudopotentials (see the [Setting up pseudopotentials](#) topic)
- Non-spin-polarized calculations (see the [Setting system parameters](#) topic)
- Fixed orbital occupancies (see the [Setting up SCF parameters](#) topic)

Note: It is not sufficient to use fixed orbital occupancies (that is, by checking the *Fix occupancy* checkbox on the [SCF](#) tab of the CASTEP Electronic Options dialog) if the system under investigation should be nonmetallic according to DFT results from a non-spin-polarized calculation. Attempting to study a metallic system using fixed orbital occupancies will result in poor convergence of the electric field response calculation; the symptoms of which will very large numbers for IR and Raman intensities and for polarizability in the output file. If this is the case, check whether your system is metallic by running either [density of states](#) or [band structure](#) calculations.

If any of these restrictions is violated by the current settings, an error message will be displayed with an explanation of the problem. The offending setting must be changed in order to proceed with the calculation.

Note: Gradient-corrected exchange-correlation functionals are supported in linear response calculations, although the results may be less accurate than those obtained with LDA and the computational cost is noticeably higher.

Requesting population analysis

Performing population analysis produces Mulliken charges, Mulliken magnetic moments, Mulliken partial charges for each angular momentum component, Mulliken bond populations (charge and spin), and Hirshfeld charges. You can use the *Distance cutoff for bond populations* option on the [Properties](#) tab to limit the amount of output from the bond population analysis. You can also use the *Calculate band populations* option to calculate the band contributions to the Mulliken charges, so that the results can be used to generate a PDOS chart.

If a system has a P1 symmetry orbital-resolved Mulliken populations are returned for each atom, specifying the amount of charge in, for example, the *px*, *dxy* (and so on) orbitals.

Tip: The *Population analysis* checkbox on the [Properties](#) tab of the CASTEP Calculation dialog is checked by default.

Note: It is not possible to specify the number of atomic orbitals to be used in the population analysis explicitly in the CASTEP interface. If the spilling parameter reported in the `.castep` output file is too large (more than 5%), it may be that the default CASTEP parameters were insufficient for this calculation. In such circumstances you should edit the `.cell` file and change the SPECIES_LCAO_STATES parameters for atomic species, then run the input files again. The SPECIES_LCAO_STATES parameter for a species should be set such that it results in a complete set of angular momentum states. For example, to use a single *s* and single *p* state SPECIES_LCAO_STATES must be 2.

To perform population analysis

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Select the [Properties](#) tab.
3. Ensure that the *Population analysis* option on the properties list is checked.
4. Optionally, modify the *Distance cutoff for bond populations* field to include more or less atomic pairs in the calculation.
5. If you wish to generate partial and local densities of states for the valence band, check the *Calculate band populations* option.

Requesting stress analysis

Calculating stress involves performing a stress tensor calculation, even when the cell parameters are fixed. The stress is a useful measure of the accuracy of the structural description: for example, after performing geometry optimization with a fixed cell, you can get an idea of how accurate the cell parameters are from the magnitude of the remaining stress. Similarly, when studying an isolated molecule in a supercell, the value of the stress provides a guide as to the size of the cell required to remove unphysical interactions between periodic images.

Note: It is important to use finite basis set correction when calculating the stress tensor (see [Setting up the basis set](#) for details). Choosing either *Smart* or *Always* as the *Apply finite basis set correction* setting on the [Basis tab](#) of the CASTEP Electronic Options dialog will achieve this.

To perform a stress analysis

1. Choose *Modules | CASTEP | Calculation* from the menu bar to display the CASTEP Calculation dialog.
2. Select the [Properties](#) tab.
3. Check the *Stress* checkbox in the list of properties.
4. Select the [Electronic](#) tab.
5. Click the *More...* button to display the CASTEP Electronic Options dialog.
6. Select the *Basis* tab.
7. Select either *Smart* or *Always* from the *Apply finite basis set correction* dropdown list.

Manipulating files

CASTEP is a file-based application which means that all input information is provided in various ASCII text files and the output is delivered in a mixture of text and binary files. This section describes some file handling issues which may arise, especially when the CASTEP server is run in a standalone mode and not through a gateway.

Input files

CASTEP allows you to save input files, for subsequent manual editing instead of running the job directly.

To save input files

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Click the *Files...* button to open *CASTEP Job Files* dialog.
3. Click the *Save Files* button.

Note: The *Save Files* button is enabled only if a suitable 3D model document is active.

Only one input file, [.param](#), is displayed in the Project Explorer. This file contains the parameters specified using the CASTEP interface. However, it also contains a few parameters that allow you to access

functionality which is not supported through the interface. The other input files are hidden, since they are unlikely to be edited manually.

Input files can be run on a server after they have been edited:

To run CASTEP using an existing set of input files

1. Choose *Modules | CASTEP | Calculation* from the Materials Studio menu bar.
2. Click the *Files...* button to open *CASTEP Job Files* dialog.
3. Click the *Run Files* button.

Note: The *Run Files* button is enabled only if a suitable [.param](#) file is active.

If your server does not support the gateway protocol, you may have to run CASTEP in standalone mode using the `RunCASTEP.sh` or `RunCASTEP.bat` files provided with the installation.

In such circumstances it is necessary to copy all the input files from the Materials Studio Project folder to the appropriate directory on the server machine. The scripts required for standalone execution are provided with accompanying `RunCASTEP.Readme` files that explain, in detail, how to use them. Alternatively, you can obtain help by typing one of the following:

```
RunCASTEP.sh -h
```

```
RunCASTEP.sh
```

Note: The Materials Studio Project folder does not contain the pseudopotential files required to run a job. When transferring input files to the server, you must therefore determine which pseudopotential files are required by examining the [.cell](#) file. Then you must locate those potential files in Materials Studio installation, typically in a sub-directory called `share\Resources\Quantum\Castep` and copy the required files to the same directory on the server as the rest of the input files.

Output files

Only one output file, `.castep`, is displayed in the Project Explorer. However, there are many more files created during a CASTEP run. These are hidden by Materials Studio. All of these output files are placed in the correct Materials Studio Project folder automatically, when the job is run using the Gateway. However, if CASTEP is run in standalone mode, the output files must be copied manually from the server to the appropriate Project folder.

Some output files can be quite large. If these files are not likely to be required to restart the job, then it is recommended that you delete or archive them periodically.

Restarting a CASTEP calculation

It is not possible to restart a completed CASTEP job automatically using the interface. However, there are circumstances in which you may wish to do this, for example, if you are running a geometry optimization which does not converge in the given number of steps, or a you wish to continue your calculation with manually modified runtime parameters. To restart such jobs you should edit `.param` file and add the `CONTINUATION` keyword to the file.

Note: Any additional changes to this file may make it impossible to restart the CASTEP job successfully.

Tip: It is possible to remove everything from `.param` and leave only the `CONTINUATION` line. This will ensure that all of the settings remain exactly the same as those from the previous run.

Note: In order to restart a job, the output files from the previous run must be present in the Project folder. This check and the subsequent transfer of the files to the server happens automatically whenever CASTEP is used to run an existing file set or to calculate additional properties.

Analyzing CASTEP results

CASTEP results can be analyzed when a job has been completed and all of the output files have been downloaded successfully to the appropriate results folder.

Select the results to be analyzed by opening the structure document in the results folder or the results (.castep) file from the CASTEP calculation. This allows you to analyze all related CASTEP results.

Note: The structure is updated automatically on successful download of output files from a completed CASTEP job that was run using a gateway (the structure is not automatically updated if the CASTEP job was run in standalone mode).

The atoms in the updated structure document have an extra property, [ServerAtomName](#), associated with them. This shows the atom sequence numbers as used in the CASTEP output files and can be seen by labeling atoms in the structure with the [ServerAtomName](#) property. (This property will be seen only in structures generated from CASTEP and other similar applications).

All other analysis functions require you to perform certain actions using the [CASTEP Analysis dialog](#).

Note: Only structure updates take place automatically after a CASTEP job is completed and the results files have been downloaded successfully (this only applies to jobs that are run on a server through the gateway, not jobs that are run in a standalone mode). All other analysis functions are performed manually, using the options on the [CASTEP Analysis dialog](#).

Displaying trajectory and chart data

Depending on the type of calculation performed, a CASTEP run may produce a trajectory document and one or more chart documents. These documents have a special association with each other because each of the points on the graphs correspond to a frame in the trajectory.

CASTEP produces a trajectory (.xtd) file whenever you run a geometry optimization, molecular dynamics or elastic constants calculation, or a transition state search. In all cases, a history of the optimization is returned in a file called `<name> Trajectory.xtd`, where `<name>` is the name used for the job description on the [Job Control](#) tab of the CASTEP Calculation dialog.

When you run a geometry optimization, two chart documents are generated:

- `<name> Energies.xcd`: Contains a plot of total energy vs. frame for all steps of the calculation
- `<name> Convergence.xcd`: Contains three (possibly four) plots that describe the degree of convergence of the optimization as a function of frame:
 - Change in energy vs. frame
 - Maximum Cartesian force vs. frame
 - Maximum Cartesian step size vs. frame
 - Maximum stress tensor component vs. frame (for cell optimization runs)

Because these values span several orders of magnitude, the data are plotted on a \log_{10} scale.

Similar charts are produced for each structure in an elastic constants calculation.

When you run a transition state search, a single chart containing a graph of energy vs. reaction coordinate for each step of the calculation, `<name> TSSearch.xcd`, is generated. This includes an

individual graph for each LST or QST 'uphill' cycle as well as a graph for each conjugate gradient minimization. The [CASTEP Transition State Search task](#) topic contains more details.

When you run a molecular dynamics simulation, either two or three chart documents are generated:

- *<name>* Constant .xcd: Contains a plot of the constant of motion vs. simulation time
- *<name>* Temperature .xcd: Contains a plot of temperature vs. simulation time
- *<name>* Pressure .xcd: Contains a plot of pressure vs. simulation time (only produced by the [NPH](#) or [NPT](#) ensemble)

Trajectory files can be animated using the controls on the Animation toolbar.

If you have access to the Forcite module, you may find some of its dynamics, statistical, and structural analysis features useful for analyzing trajectories. Refer to the [Using Forcite Analysis](#) topic for details.

Creating a trajectory and chart

When you run CASTEP using the Materials Studio interface, the creation and display of these trajectories and charts is automatic. If you selected *Automatically view output* on the [CASTEP Job Control Options dialog](#), the graphs will be displayed automatically on completion of the run. If you selected *Update graphs* on the CASTEP Job Control Options dialog, these graphs will be displayed and updated with intermediate results throughout the course of the calculation.

To create charts from output files generated by a standalone calculation

1. Download the files from the compute server to your PC using the procedure described in [Running CASTEP in standalone mode](#). Be sure to retrieve the .check, .castep, and .geom, .md, or .ts files.
2. Select *Modules | CASTEP | Analysis* from the menu bar.
3. Select [Energy evolution](#) from the list on the [CASTEP Analysis dialog](#).
4. Make sure that the .castep file is the currently active document.
5. Click the *View* button.

If you used the Materials Studio interface to set up and launch your job, you can regenerate the chart documents by following a similar procedure.

To regenerate charts

1. Open either the .xsd or .castep file and make it the currently active document.
2. Select *Modules | CASTEP | Analysis* from the menu bar.
3. Select [Energy evolution](#) from the list on the CASTEP Analysis dialog.
4. Click the *View* button.


Animating the trajectory

You can use the controls on the Animation toolbar to animate the trajectory, stepping through each of the frames of the document. If the chart is open during the animation, the point corresponding to the active frame will be highlighted.

Chart Viewer point selection

Alternatively, you can use Chart Viewer point selection to display the trajectory frames of the points you select from the chart document.

To display a trajectory frame for a point on a chart document

1. Choose the *Selection* tool  on the Chart Viewer toolbar to enter selection mode.
2. Making sure you have the corresponding trajectory document open, select a data point on the chart document.
3. The corresponding trajectory frame is displayed.
4. Drag the mouse over other data points on the chart document to display their corresponding trajectory frames.
5. If CASTEP generated multiple chart documents, the related data points will be highlighted on all of them.

Tip: To make it easier to see the chart and trajectory documents, close all the other documents and then maximize the sizes of these two documents by selecting *Window | Tile Vertically* from the menu bar.

Visualizing volumetric data

You can visualize the spatial distribution of [electronic charge](#), [electron density difference](#), [electron localization function](#), and [electrostatic potential](#) calculated by CASTEP. In addition, charge densities of particular [orbitals](#) and the approximate [STM profile](#) for surfaces in a slab supercell geometry can be visualized. The relevant data from the CASTEP results files are used to add a field to the model. This field can be visualized in a variety of ways (direct field visualization, isosurfaces, slices, and so on).

- [Electronic charge](#)
- [Electron density difference](#)
- [Electron localization function](#)
- [SCF local potential](#)
- [Orbitals](#)
- [STM profile](#)
- [Field visualization](#)

Electronic charge

Materials Studio uses the information stored in the CASTEP binary output file to create a field that corresponds to the electronic charge. When you analyze a spin-polarized calculation, you can create additional separate fields for the density of spin-up (alpha) or spin-down (beta) electrons, as well as a field for the spin density (the difference between the density of alpha and beta electrons). The latter field allows you to visualize the spatial distribution of the magnetic moment in a spin-polarized system.

Note: Maxima in the electronic density field correspond to interatomic bonds or to the position of atoms that have semicore states which are explicitly treated as valence. When there are no semicore states in the system (this can be verified by analyzing the atomic charges displayed on the [Potentials](#) tab of the [CASTEP Electronic Options dialog](#)), the density will display minima at the positions of atomic nuclei. This is to be expected in the pseudopotential formalism.

To create a density field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [Electron density](#) from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. For spin-polarized calculations, select the type of field required from the *Density field* dropdown list.
5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the density field is imported.
6. Click the *Import* button.

You also have the option of creating a plain text file which contains the values of charge (and spin, when appropriate) density on a regular grid along three lattice vectors. The file has the extension `.charg_frm` and is hidden by default. Select *Tools | Folder Options...* in Windows Explorer to open the Folder Options dialog, then select the *View* tab and click the *Show hidden files and folders* radio button to reveal the hidden file. The format of the file is self-explanatory:

a	b	c	Charge
1	1	1	1.8133362740
2	1	1	1.5071161497
3	1	1	1.1111633102
4	1	1	0.9584556846

or, for a spin-polarized calculation:

a	b	c	Charge	Spin
	1	1	1.8130116660	0.0006370238
	2	1	1.5068114569	0.0004814296
	3	1	1.1108593919	0.0002249406
	4	1	0.9580778273	0.0001768619

Note: The charge and spin density in the `.charg_frm` file are in the same units as those used by CASTEP during calculations. The values are normalized to the number of electrons per cell. The density fields displayed in the 3D model are, however, normalized to the number of electrons per \AA^3 .

To create a plain text density file

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [Electron density](#) from the list of properties.
3. Click the *Save density to file* button.

Electron density difference

Materials Studio provides the option of generating the electron density difference in two different ways:

- Electron density difference with respect to a linear combination of the atomic densities
- Electron density difference with respect to a linear combination of the densities of sets of atoms contained in the model

The former option produces a density difference field which shows the changes in the electron distribution that are due to formation of all the bonds in the system. This object is appropriate for bulk solids to illustrate the charge redistribution due to chemical bonding.

The latter option generates a density difference field which effectively corresponds only to the formation of bonds between atoms in different sets and to charge redistribution within the sets that is due to the presence of other sets. This property is useful to describe such processes as bonding of molecule(s) to

external and internal (for example, zeolites) surfaces or creation of large molecules from smaller fragments.

To create a density difference field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [Electron density difference](#) from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Use the *Use atomic densities* checkbox to request the density difference with respect to a linear combination of the atomic densities. The density difference with respect to the sets of atoms will be produced when this checkbox is unchecked.
5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.
6. Click the *Import* button.
7. A field is created in the model; its name is either "CASTEP density difference from atoms" or "CASTEP density difference from sets", depending on whether the *Use atomic densities* checkbox is checked.

Note: Analysis based on atomic densities requires the presence of a binary file with the extension `.chdiff`; analysis based on sets of atoms requires that for each set of input files, `seed_Subset*.*`, there are binary files with the extension `.check` present. The *Import* button is disabled if the files required for the current setting of the *Use atomic densities* checkbox are not present in the results folder.

Electron localization function

Materials Studio uses the information stored in the CASTEP binary output file to create a field that corresponds to the localization of electrons.

To create an electron localization function field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [Electron localization function](#) from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the density field is imported.
5. Click the *Import* button.
6. A field is created in the model, named "CASTEP electron localization function".

SCF local potential

Materials Studio uses the information stored in the binary `.cst_esp` file to create a field that corresponds to the local part of the Kohn-Sham potential. In fact, the data in the file correspond to minus a Kohn-Sham potential. Thus, this field is closely related to the electrostatic potential used in quantum chemistry programs, where it represents the electrostatic energy of a proton at a given point. The units of the potential are eV/electron.

The local SCF potential analyzed in Materials Studio includes all the DFT contributions, except for the nonlocal part of the pseudopotential: the Hartree term, the local pseudopotential term, and the exchange-correlation term. This potential can be used to analyze important solid-state properties such as band offsets and work function (the latter is a specific case of the band offset calculation where one of the materials is a vacuum). An excellent description of the formalism for band offset calculations based on CASTEP results is given by [Al Allak and Clark \(2001\)](#).

To create a local potential field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [Potentials](#) from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Select the type of field required from the *Potential field* dropdown list.

Note: Materials Studio currently supports only the local SCF potential field type.

5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.
6. Click the *Import* button.

Orbitals

Materials Studio uses the information stored by CASTEP in a binary `.check` file to create a field that corresponds to any of the orbitals in the system. In this context, the orbital is the square of the absolute value of the wavefunction for a given electronic band, summed over all k-points. A band is defined by the position of its eigenvalue in the ordered list of electronic energies at each k-point. For example, orbital (or band) number 3 is obtained by summation over all k-points of the wavefunctions with the third lowest energy. The sum of the "orbital densities" obtained in this way gives the total electron density of the crystal.

Note: Because of the size of the `.check` file orbital analysis is only available if [orbitals](#) are explicitly requested.

The *Filter* dropdown list, which becomes available on the CASTEP Analysis dialog when [Orbitals](#) is selected from the list of properties, allows you to control which orbitals are displayed in the table:

- *Alpha* displays data for alpha-spin orbitals (spin up) only
- *Beta* displays data for beta-spin orbitals (spin down) only

Note: For non-spin-polarized calculations, this option is not available.

The orbital analysis table provides you with a list of eigenvalues and information about each orbital. The list of eigenvalues starts with the lowest energy orbital. The accompanying information includes:

- *N* - number of the orbital, with **1** corresponding to the lowest energy orbital.
- *s* - spin: + for alpha, - for beta.

Note: In a non-spin-polarized calculation, all orbitals are labeled +.

- *From* - lowest value of the energy of the Nth band at any k-point (in eV)
- *To* - highest value of the energy of the Nth band at any k-point (in eV)

You can artificially change the band gap value for insulators or semiconductors by using the scissors operator. This parameter effectively describes the difference between the theoretical and experimental band gap values. When the experimental value is known, you can perform a band structure calculation to find the theoretical band gap. Then, simply set the scissors operator to the difference between the two values. The eigenvalues of the conduction band states displayed in the scrollable list will be shifted upward by the value of the scissors operator.

To create an orbital field

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [Orbitals](#) from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. From the scrollable list, select the row(s) corresponding to the orbital(s) you wish to display.

Tip: Multiple selections are allowed. To select more than one orbital, hold down the SHIFT key and click on the first and last orbitals in the block you want to select, or hold down the CTRL key and click to select orbitals individually.

5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.
6. Click the *Import* button.

Note: The units for the isovalues are $e/\text{\AA}^3$ and correspond to the wavefunction density, ψ^2 .

STM profile

CASTEP models the scanning transmission microscope (STM) profile by representing it as an isosurface of the electron density generated only by states at a certain energy away from the Fermi level. The distance from the Fermi level corresponds to the applied bias in actual STM experiments. Positive bias corresponds to the imaging of empty (conduction) states, while negative bias produces images of occupied (valence) states. This approach neglects the actual geometry of the STM tip and makes use of the Tersoff-Hamman approximation for tunneling transport ([Tersoff and Hamman, 1985](#)).

STM profile visualization makes sense only for models that represent surfaces in the slab supercell geometry. In addition, information about charge density at a distance from the surface is likely to be inaccurate as a result of the DFT failing to reproduce the asymptotics of the wavefunction decay into a vacuum.

Note: Because of the size of the `.check` file STM analysis is available only if [orbitals are explicitly requested](#).

Note: Visualization of the images created by conduction band states requires that the calculation was performed with an increased number of empty bands. The recommended procedure is to use electronic density of states (DOS) calculations and specify a sufficiently high number of empty states.

To create an STM profile

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [STM profile](#) from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Specify the *STM bias* value.
5. Optionally, check the *View isosurface on import* checkbox to automatically create an isosurface when the potential field is imported.
6. Use field visualization tools to create an isosurface that represents the STM profile.
7. Click the *Import* button.

Field visualization

Materials Studio provides a number of tools for field visualization. They are accessed from the Volume Visualization toolbar and *Field*, *Isosurface*, and *Slice* tabs on the Display Style dialog.

The *Volume Visualization* toolbar provides access to the Volumetric Selection dialog, which enables you to specify the field to be visualized and set visibility attributes for fields, slices, and isosurfaces. This toolbar also contains controls for creating new isosurfaces and slices, including the shortcuts for orienting the slice based on either the cell axes or the coordinates of selected atoms. The Color Maps dialog, which can also be accessed from the *Volume Visualization* toolbar, provides control over the coloring of volumetric objects (it also provides useful shortcuts for determining the minimum and maximum values of the field).

The Field tab of the Display Style dialog allows you to visualize the field directly using either the *Dots* or *Volume* display styles.

The Isosurface tab of the Display Style dialog allows you to alter the visualization style of a selected isosurface, change its isovalue, or use another field for color mapping.

The Slice tab of the Display Style dialog allows you to alter the visualization style of a selected slice.

Note: The volumetric visualization tabs on the Display Style dialog are displayed only if an object of the relevant type is present in the active document. If a field, isosurface, or slice is selected, for example by using the Volumetric Selection dialog, the volumetric visualization tabs that are not relevant to the selection will be removed from the Display Style dialog.

Tip: Field visualization in Materials Studio fully supports periodic display. You can use the *Field* tab on the Display Style dialog to change the range of a field to display more or less than one unit cell of a structure.

Note: The default settings for field visualization result in the fields being displayed over one unit cell of a structure. Use the *In-Cell* display mode for the lattice (accessible from the Lattice tab of the Display Style dialog) to make sure that the field is positioned around the displayed atoms.

Displaying band structure charts

Band structure charts show how electronic energies depend on k-vector, along high symmetry directions in the Brillouin zone. These charts provide a useful tool for qualitative analysis of the electronic structure of a material, for example, it is easy to identify the narrow bands of *d* and *f* states as opposed to the free electron like bands that correspond to *s* and *p* electrons. It is also instructive to look for directions with relatively flat, dispersionless bands, as these directions are likely to contribute strongly to optical absorption. Thus, allowing explanation of the anisotropy of optical properties. The energy band gap is also easily deduced from the band structure plots as it normally corresponds to the energy difference between two states at high symmetry points.

An example of the CASTEP output for band structure is shown in [Figure 1](#). Electronic states with different spins are presented using different colors and the Fermi level is shown with the dashed line. All energies are relative to the Fermi level (or to the top of the valence band in the case of insulators or semiconductors). The labels along the X axis of the band structure graph correspond to the standard definitions of high symmetry points for the given lattice type ([Bradley and Cracknell, 1972](#)). The Γ -point is denoted by a *G*.

The density of states included in this plot was created using [Interpolation](#) as an *Integration method* and [Alpha and Beta](#) as the *DOS display*.

Note: If you have calculated DOS for a spin polarized system with a non-zero initial spin and the total spin is not optimized two charts will automatically be displayed, `<seedname> Band Structure Alpha.xcd` and `<seedname> Band Structure Beta.xcd`.

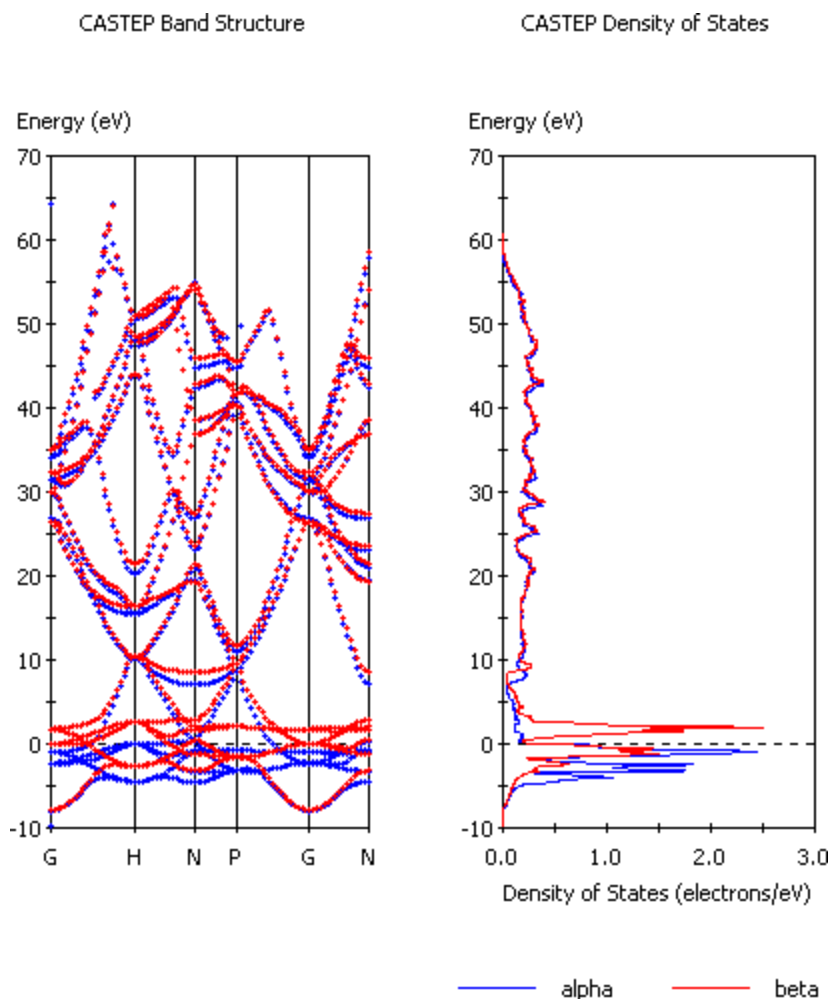


Figure 1. Band structure with DOS for Fe (spin-polarized GGA calculation).

To create a band structure chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select **Band structure** from the list of properties.
3. Use *Results file selector* to pick the appropriate results file (it should have a BandStr suffix).
4. Select a required display style (**Points** or **Lines**) from the *Graph style* dropdown list.
5. Optionally, check *Show DOS* and set the relevant DOS options.
6. Click the *View* button.
7. A new chart document, *seedname* Band Structure.xcd, is created in the results folder.

Displaying core level spectra

The CASTEP Analysis dialog can be used to generate observable core level spectra based on electronic energies on the Monkhorst-Pack mesh of k-points obtained during a calculation. Detailed analysis of the impact of calculation parameters (k-point set, number of empty bands, and so on) on the accuracy of the spectra generated can be found in the core level spectroscopy theory topic.

Note: Core level spectra can only be calculated for single atoms. One atom should be selected in the active 3D Atomistic document before carrying out a core level spectroscopy analysis.

To create a core level spectrum

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis](#) dialog.
2. Select [Core level spectroscopy](#) from the list of properties.
3. In the 3D Atomistic document containing the 3D periodic structure, select the atom for which you wish to simulate a core level spectrum. Click the *Atom Selection* button on the CASTEP Analysis dialog to open the Atom Selection dialog.
4. Use the [Results file selector](#) to pick the results file or make the *seedname_EELS.castep* file the active document.
5. Select the electron configuration of the *Spectrum*.
6. Specify the *Type* of spectrum you want to calculate, options are [Absorption](#) and [Emission](#).
7. Click the *More...* button to open the [CASTEP EELS Analysis Options](#) dialog.
8. Set the *Instrumental smearing* value.
9. Specify whether to take *Lifetime effects* into account by checking or unchecking the checkbox, if checked set the *Core level broadening* value.
10. Specify whether to take *Include spin-orbit splitting* into account by checking or unchecking the checkbox, if checked set the *Spin-orbit splitting* value and close the CASTEP EELS Analysis Options dialog.
11. Select the incident radiation polarization from the *Calculation* dropdown list. If you specify [Polarized](#) radiation choose the direction of the *Polarization* of the incident radiation in fractional (lattice) coordinates.
12. Make the 3D periodic structure the active document and click the *View* button.
13. A new chart document, *seedname_EELS.xcd*, is created in the results folder and becomes the active document.

Note: If you carry out several core level spectroscopy analyses, each new spectrum will be displayed in a new chart document.

Displaying density of states charts

Density of states (DOS) and partial density of states (PDOS) charts give a quick qualitative picture of the electronic structure of a material and sometimes they can be related directly to experimental spectroscopic results.

Note: If you have calculated DOS for a spin polarized system and the total spin is not optimized two charts will automatically be displayed, *<seedname> DOS Alpha.xcd* and *<seedname> DOS Beta.xcd*.

Full density of states

Materials Studio can produce DOS plots from any *.bands* CASTEP output file. These files are hidden in the Project Explorer but a *.bands* file is generated with every *.castep* file. All the files that can be used in the analysis of the current calculation will be presented in the [results file selector](#). However, it is recommended that you create DOS plots based on the results of a band structure calculation that only uses k-points in high-symmetry directions.

Tip: When evaluating DOS, use only the results of eigenvalues calculations on the Monkhorst-Pack grid. If you have more than one such set of results, for example, DOS and Optics, select the one with the highest density of k-points, that is, the highest Monkhorst-Pack mesh parameters.

To create a DOS chart

1. Choose *Modules* | *CASTEP* | *Analysis* from the Materials Studio menu bar.
2. Select [Density of states](#) from the list of properties.
3. Use [Results file selector](#) to pick the right results file.
4. Select [Full](#) to display the total DOS.
5. For spin-polarized calculations, select the required DOS component from the *DOS display* dropdown list.
6. Specify the *Function* to use, either [DOS](#) or [Integrated DOS](#).
7. Optionally, click the *More...* button to open the [CASTEP DOS Analysis Options](#) dialog. Set the *Integration method* and other options, [Interpolation](#) gives more accurate results than the [Smearing](#) method, although it is slightly slower.
8. Click the *View* button.
9. A new chart document, *seedname* DOS .xcd, is created in the results folder.

Partial density of states

Materials Studio produces PDOS plots for certain angular momenta on selected atoms. The [Sum](#) curve represents the local density of states (LDOS) when one atom is selected. If more than one atom is selected, the contributions in each angular momentum channel from all selected atoms are added together. When no atoms are selected the behavior is the same as if all atoms were selected.

Note: PDOS analysis formalism is not valid for high energy states in the conduction band: PDOS representation will usually decay to zero at about 20 eV above the Fermi level. This is related to the fact that expansion of essentially free electron states in terms of a limited number of atomic-like basis functions is impossible to carry out with any degree of accuracy. Only the valence band and lower part of the conduction band are meaningful in the PDOS plot.

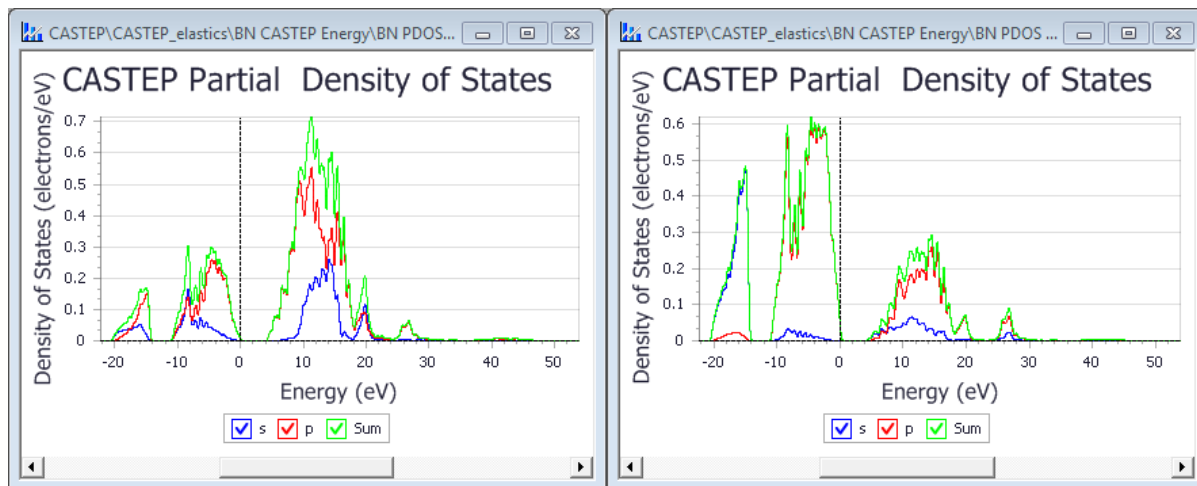


Figure 1. PDOS for BN. The left window is for boron, the right for nitrogen.

To create a PDOS chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select [Density of states](#) from the list of properties.
3. Use [Results file selector](#) to pick the right results file.
4. Select [Partial](#) to display the partial DOS.
5. Check the required angular momentum components for the PDOS.
6. Select the atom or atoms in the model, for which the PDOS is to be created.
7. For spin-polarized calculations, select the required DOS component from the *DOS display* dropdown list.
8. Optionally, set additional [CASTEP DOS analysis options](#). The *Interpolation Integration method* gives more accurate results than the *Smearing* method, although it is slightly slower.
9. Click the *View* button.
10. A new chart document, *seedname* PDOS .xcd, is created in the results folder.

Tip: You should rename this file to indicate the atoms on which it is based. In the example above (see [Figure 1](#)) suitable names for the two files created might be BN N PDOS .xcd and BN B PDOS .xcd (the default names are BN PDOS .xcd and BN PDOS (2) .xcd).

Calculating elastic constants

CASTEP results for the [Elastic Constants](#) task are returned as a set of .castep output files. Each of them represents a geometry optimization run with a fixed cell, for a given strain pattern and strain amplitude. The naming convention for these files is:

seedname_cij__m__n

Where *m* is the current strain pattern and *n* is the current strain amplitude for the given pattern.

CASTEP can then be used to analyze the calculated stress tensors for each of these runs and generate a file with information about elastic properties. The information in this file includes a summary of the input strains and calculated stresses; results of linear fitting for each strain pattern, including quality of the fit; the correspondence between calculated stresses and elastic constants for a given symmetry; a table of elastic constants, C_{ij} , and elastic compliances, S_{ij} ; and finally, the derived properties such as bulk modulus and its inverse, compressibility, Young modulus and Poisson ratios for three directions and the Lamé constants that are needed for modeling the material as an isotropic medium.

To calculate elastic constants

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select [Elastic constants](#) from the list of properties.
3. Use the [Results file selector](#) to pick the appropriate results file.
4. Click the *Calculate* button.
5. A new text document, *seedname* Elastic Constants .txt, is created in the results folder.

Description of the elastic constants file

Below, the example of a hexagonal crystal, Cd, is used to explain the contents of the *Elastic Constants .txt* output file produced by CASTEP.

Two strain patterns are required for this lattice type. For each strain pattern there is a summary of calculated stresses as extracted from the respective .castep files:

```
Summary of the calculated stresses
*****
```

Strain pattern: 1
 =====

Current amplitude: 1
 Transformed stress tensor (GPa) :
 0.103397 -0.000000 -0.000000
 -0.000000 0.103397 -0.000000
 -0.000000 -0.000000 0.141636

Current amplitude: 2
 Transformed stress tensor (GPa) :
 0.012212 -0.000000 -0.000000
 -0.000000 0.012212 -0.000000
 -0.000000 -0.000000 0.027695

Information about the connection between components of the stress, strain, and elastic constants tensors is provided. At this stage each elastic constant is represented by a single compact index rather than by a pair of *ij* indices. The correspondence between the compact notation and the conventional indexing is provided later in the file:

Stress corresponds to elastic coefficients (compact notation):
 8 8 3 0 0 0

as induced by the strain components:
 3 3 3 0 0 0

A linear fit of the stress-strain relationship for each component of the stress is given in the following format:

Stress index	Cij index	value of stress	value of strain
1	8	0.103397	-0.003000
1	8	0.012212	-0.001000
1	8	-0.076634	0.001000
1	8	-0.163088	0.003000
C (gradient)	:	44.415050	
Error on C	:	0.374023	
Correlation coeff:		0.999929	
Stress intercept :		-0.031028	

The gradient provides the value of the elastic constant (or a linear combination of elastic constants), the quality of the fit, indicated by the correlation coefficient, provides the statistical uncertainty of that value. The stress intercept value is not used in further analysis, it is simply an indication of how far the converged ground state was from the initial structure.

The results for all the strain patterns are then summarized:

=====
 Summary of elastic constants
 =====

id i j cij (GPa)

1	1	1	127.56650 +/-	1.588
3	3	3	56.99120 +/-	0.051
4	4	4	25.73690 +/-	0.165
7	1	2	48.06835 +/-	0.329
8	1	3	44.44692 +/-	0.180

The errors are only provided when more than two values for the strain amplitude were used, since there is no statistical uncertainty associated with fitting a straight line to only two points.

Elastic constants are then presented in a conventional 6x6 tensor form, followed by a similar 6x6 representation of the compliances:

=====
Elastic Stiffness Constants Cij (GPa)
=====

127.56650	48.06835	44.44692	0.00000	0.00000
0.00000	48.06835	127.56650	44.44692	0.00000
0.00000	44.44692	44.44692	56.99120	0.00000
0.00000	0.00000	0.00000	25.73690	0.00000
0.00000	0.00000	0.00000	0.00000	25.73690
0.00000	0.00000	0.00000	0.00000	0.00000
39.74908				

=====
Elastic Compliance Constants Sij (1/GPa)
=====

0.0109928	-0.0015861	-0.0073362	0.0000000	0.0000000
0.0000000	-0.0015861	0.0109928	-0.0073362	0.0000000
0.0000000	-0.0073362	-0.0073362	0.0289894	0.0000000
0.0000000	0.0000000	0.0000000	0.0388547	0.0000000
0.0000000	0.0000000	0.0000000	0.0000000	0.0388547
0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
0.0251578				

The final part of the file contains the derived properties:

Bulk modulus = 54.17693 +/- 0.080 (GPa)

Compressibility = 0.01846 (1/GPa)

Elastic Debye temperature = 209.41266 K
 Averaged sound velocity = 1939.37187 (m/s)

Axis	Young Modulus (GPa)	Poisson Ratios	
X	90.96865	E _{xy} = 0.1443	E _{xz} = 0.6674
Y	90.96865	E _{yx} = 0.1443	E _{yz} = 0.6674
Z	34.49534	E _{zx} = 0.2531	E _{zy} = 0.2531

The elastic Debye temperature is evaluated according to the recipe by Anderson (1963), where the averaged sound velocity is evaluated numerically as an integral over all propagation directions. The Debye temperature is proportional to the averaged sound velocity, v_m :

$$\theta = \frac{h}{k} \left[\frac{3q}{4\pi} \frac{N\rho}{M} \right]^{1/3} v_m$$

Where:

- h is the Planck constant
- k is the Boltzmann constant
- N is Avogadro's number
- ρ is the density
- M is the molecular weight of the solid
- q is the number of atoms in the molecule.

Note: Elastic Debye temperature and averaged sound velocity are not reported if the calculated elastic constants do not produce physically meaningful sound velocities in some directions (for example, if certain C_{ij} values or their combinations are negative when they should be positive). This can happen for low quality calculations or for calculations that were not preceded by a geometry optimization (including optimization of the lattice parameters).

The last section of the file contains average properties that describe the elastic response of a polycrystal, for example:

```

=====
Elastic constants for polycrystalline material (GPa)
=====
Bulk modulus                :      Voigt      Reuss      Hill
Shear modulus (Lame Mu)    :      65.11651  54.17693  59.64672
Lame lambda                 :      29.92204  25.97242  27.94723
Young modulus               :      45.16848  36.86199  41.01523
Poisson ratio               :      77.84279  67.18163  72.51599
Hardness (Tian 2012)       :      0.30076   0.29332   0.29737
                             :      4.21526   4.00144   4.10621

Universal anisotropy index:      0.96227
  
```

This output contains the bulk modulus, shear modulus, Young modulus, and Poisson ratio averaged according to Voigt, Reuss, and Hill schemes (Nye 1957).

In addition an universal anisotropy index suggested by Ranganathan and Ostoja-Starzewski (2008) is evaluated.

Vickers hardness in GPa is evaluated based on the Tian (2012) empirical formula that expresses hardness in terms of the polycrystalline bulk, B , and shear, G , moduli (using Pugh's modulus ratio, $k=G/B$):

$$H_V = 0.92k^{1.137} G^{0.708}$$

The correlation between the results from this macroscopic model and experimentally measured hardness values is quite good when hardness is larger than 5 GPa, but empirical formula overestimates hardness of softer materials.

Note: The empirical expression for Vickers hardness cannot be applied if the calculated shear modulus is negative (this can happen, for example, when the calculation settings are not sufficiently accurate). In such a case the summary report will not include the hardness.

Visualizing Fermi surfaces

Fermi surfaces are generated from information from CASTEP calculations which is stored in the [.bands](#) output file. Fermi surfaces can be considered as the energy isosurfaces in reciprocal space.

Tip: To ensure that the generated Fermi surface(s) are reliable you must use as many k-points as computational resources will allow when [setting up](#) the calculation.

To create a Fermi surface

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis dialog](#).
2. Select [Fermi surface](#) from the list of properties.
3. Ensure that the 3D Atomistic document to be analyzed is the active document.
4. Select the *Band* for which to display the Fermi surface.
5. Click the *Import* button.

To change the Fermi level used for the Fermi surface

1. Create a Fermi surface according to the steps above.
2. Open the Display Style dialog and select the Isosurface tab.
3. In the *Generation* section change the *Isovalue*. The Fermi surface will be updated appropriately.

Visualizing vibrational spectra

When a CASTEP calculation returns a Hessian (dynamical matrix) at the Γ -point, then vibrational frequencies for the bonds in the system being studied can be calculated and visualized using the Vibrational Analysis tool.

Note: After a CASTEP job that included calculation of the electric field response (that is, the *Polarizability, IR and Raman spectra* checkbox was checked on the *Properties* tab of the CASTEP Calculation dialog) is complete and the results files have been downloaded successfully, Materials Studio will automatically import the Hessian matrix, provided that the CASTEP job was not a [Properties](#) run.

A dynamical matrix is returned if the TASK keyword in the input parameters (`.param`) file is set to either [Efield](#) or [Phonon+Efield](#) and there is a Γ -point among the phonon k-vectors. You can achieve this either by checking the *Polarizability, IR and Raman spectra* checkbox on the [Properties](#) tab of the CASTEP Calculation dialog or, alternatively, if you wish to calculate the phonon dispersion or phonon density of states, by checking the *Phonons* checkbox in the list on the *Properties* tab, checking the *Dispersion* or *Density of states* checkboxes, as appropriate, that appear below the list, and ensuring that there is a Γ -point in the q-vector set.

IR spectra

In order to carry out a vibrational analysis, you will need to import a Hessian matrix from the output of a CASTEP run.

To import a Hessian and display an IR spectrum

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the [CASTEP Analysis dialog](#).
2. Select [IR spectrum](#) from the list of options at the top of the dialog.
3. Ensure that the 3D Atomistic document to be updated is the active document.
4. Click the *Import Hessian from CASTEP output* button.

If you requested that the [electric field response](#) be calculated as part of the CASTEP job by checking the *Polarizability, IR and Raman spectra* checkbox on the *Properties* tab of the CASTEP Calculation dialog, you will be able to display vibrational mode frequencies and absorption intensities for the structure being studied in the form of a list of values or graphically as a vibrational spectrum using the Vibrational Analysis tool.

Raman spectra

To display a Raman spectrum

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the [CASTEP Analysis dialog](#).
2. Select [Raman spectrum](#) from the list of options at the top of the dialog.
3. Use [Results file selector](#) to pick the right results file.
4. Ensure that the 3D Atomistic document containing the structure is the active document.
5. Select the *Function* of the mode to be calculated.
6. If the *Function* is set to [Intensity](#) set the *Temperature*.
7. Set the *Smearing* value to be used.
8. Select the *Units* for the X axis.
9. Specify whether to reverse the wavenumber and intensity axes.
10. Click the *View* button.
11. A new chart document, *seedname Raman .xcd*, is created in the results folder.

Displaying NMR results

A CASTEP NMR calculation computes the chemical shielding tensor and the electric field gradients for all of the atoms in the system.

Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Note: NMR properties are dynamic (that is, they are not present on atoms until they are assigned during analysis).

To display the shielding tensor

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select [NMR](#) from the list of properties.
3. Make sure that the desired 3D Atomistic document is the active document.
4. Click the *Assign isotropic chemical shielding to structure* button to import the data into the model.
5. Right-click in the 3D Viewer and select *Label* from the shortcut menu. Set the *Object type* to [Atom](#), select [NMRShielding](#) from the *Properties* list, and click the *Apply* button to display the shielding tensors.

To display the electric field gradients

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select **NMR** from the list of properties.
3. Make sure that the desired 3D Atomistic document is the active document.
4. Click the *Assign electric field gradients to structure* button to import the data into the model.
5. Right-click in the 3D Viewer and select *Label* from the shortcut menu. Set the *Object type* to **Atom**, select **EFGQuadrupolarCoupling** or **EFGAsymmetry**, as appropriate, from the *Properties* list, and click the *Apply* button to display the electric field gradients.

To display the J-coupling constants

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select **NMR** from the list of properties.
3. Use [Results file selector](#) to pick the right results file; in this case it should be a *seedname_NMRJC.castep* file.
4. Click the *Show J-coupling constants* button to generate and open a study table reporting the calculated J-coupling constants. The study table document will be named *seedname_NMRJC_JCoupling.std*.

The study table contains two sheets, one with the summary of the results (atom pairs, corresponding interatomic distances, and isotropic and anisotropic components of the J-coupling tensor) and one with the detailed breakdown of contributions to the isotropic coupling (Fermi contact term, spin-dipole term, paramagnetic, and diamagnetic contributions).

5. Right-click in the 3D Viewer and select *Label* from the shortcut menu. Set the *Object type* to **Atom**, select **ServerAtomName** from the *Properties* list, and click the *Apply* button to display the atom names that are shown in the first two columns of the Summary sheet of the study table.

Displaying optical properties

Analysis of optical properties involves two main steps.

Dielectric function calculation

When a CASTEP calculation returns the matrix elements for electronic interband transitions ([Eq. CASTEP 56](#)) in the (hidden) file *.cst_ome*, it is necessary to calculate the dielectric function using [Eq. CASTEP 55](#). This calculation results in the creation of a grid document that contains two sheets. The first is the summary of the calculation that includes the value of the scissors operator, the geometry of the calculation and the smearing applied. The second sheet contains a table of the real and imaginary parts of the dielectric function versus the photon energy (eV).

It is important to set the parameters for this type of calculation correctly in order to be able to compare the results obtained with experimental optical constants.

Scissors operator: This parameter effectively describes the difference between the theoretical and experimental band gap values. When the experimental value is known, you can perform a band structure calculation to find the theoretical band gap. Then simply set the scissors operator to the difference between the two values.

Tip: When there is no experimental band gap value but there are data on the dielectric function, you can repeat the calculations with varying scissors operator values and select the one that gives a theoretical absorption edge which matches the experimental value.

In the absence of any experimental data, use a fixed proportion of the theoretical band gap as the scissors operator, for example 25%. This approach allows you to study trends in optical properties across a family of similar compounds.

Calculation: This parameter and the related *Polarization* or *Incidence* settings, specify the experimental geometry. These are irrelevant for optically isotropic crystals but they are necessary to study anisotropy of optical properties in crystals with lower symmetry. A good example of the theoretical study of optical anisotropy of crystalline polymers was given by Ambros-Drachl et al. (1995). A more detailed discussion of the meaning of these settings is given in the [Optical properties](#) theory topic.

Smearing: This parameter specifies the width of the Gaussian broadening that is used to produce the dielectric function. It is similar to the broadening that is used in density of states calculations.

To create a dielectric function grid

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select [Optical properties](#) from the list of properties.
3. Use [Results file selector](#) to pick the right results file.
4. Select the geometry of the calculation from the *Calculation* dropdown list.
 - If [Polarized](#) geometry is selected, specify the *Polarization* direction in the text boxes.
 - If [Unpolarized](#) geometry is selected, specify the *Incidence* direction in the text boxes.
 - If [Polycrystalline](#) geometry is selected, no additional parameters need to be specified.
5. Specify a *Smearing* value in the text box (0.5 eV is a good default setting).
6. Click the *Calculate* button.
7. A new grid document, *seedname Optical Properties.xgd*, is created in the results folder and becomes the active document.

Display optical constants

The following [optical constants](#) can be evaluated based on the calculated dielectric function:

- Reflectivity
- Absorption
- Refractive index, *n* and *k*
- Complex optical conductivity
- Energy loss function

Any of these constants and the complex dielectric function itself, can be plotted using Materials Studio. The only additional information that might be required are the Drude correction parameters.

The empirical [Drude contribution](#) to the spectra is due to intraband excitations that are not included in the spectra calculated by CASTEP. The Drude contribution, which may be non-zero only for metals and semi-metals, is determined by the *DC Conductivity* and *Drude Damping* parameters. Appropriate values for these quantities cover a wide range and are usually taken from experiment. A typical value of the *Drude Damping* parameter for metals is 0.05 eV. Typical values for the *DC Conductivity* in metals are around 250 eV. But it must be 0 for insulators. Another common unit for the *DC conductivity* is 1/(Ohm*cm). The conversion factor between this unit and eV is $1/(\text{Ohm}\cdot\text{cm}) = 5.924 \times 10^{-4}$ eV.

To create a chart with optical properties

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select **Optical properties** from the list of properties.
3. Ensure that the grid document, *seedname* Optical Properties.xgd, is active.
4. Specify the property to be plotted using the *Function* dropdown list.

Tip: If the system is a molecule in the box the only relevant property to display is the **Absorption** calculated for **Polycrystalline** geometry.

5. Specify the energy units for the plot using *Units* dropdown list.
6. Set the Drude correction parameters for metallic systems. Click the *More...* button to access the **Optics Analysis Options dialog**.

Tip: Ensure that the Drude term is ignored for the nonmetallic systems, that is, check that the *DC Conductivity* is **0** on the CASTEP Optical Properties Options dialog.

7. Click the *View* button.
8. A new chart document, *seedname* Optical Properties.xcd, is created in the results folder. The summary from the first sheet of the grid document is used as the graph title to assist in identification of the graphs.

Note: The *View* button is enabled only if a suitable grid document is active.

Tip: If the only experimental information available is the value of the static dielectric constant, it is still possible to assess the value of the scissors operator. Calculate the refractive index repeatedly, using different scissors operator values and select the one that gives the best fit between the calculated $n(0)$ value and the square root of the experimental static dielectric constant.

Displaying phonon dispersion and density of states

Phonon dispersion curves show how phonon energy depends on the q-vector, along high symmetry directions in the Brillouin zone. This information can be obtained experimentally from neutron scattering experiments on single crystals. Such experimental data are available for only a small number of materials and thus, theoretical dispersion curves are useful for both establishing the validity of a modeling approach and to demonstrate the predictive power of *ab initio* calculations.

In certain circumstances it is possible to measure the density of states (DOS) rather than the phonon dispersion. Furthermore, the electron-phonon interaction function, which is directly related to the phonon DOS can be measured directly in the tunneling experiments (see, for example, [Yanson, 1988](#)). It is therefore important to be able to calculate phonon DOS from first principles, in order to compare the results with experimentally observed spectra.

Materials Studio can produce phonon dispersion and DOS charts from any **.phonon** CASTEP output file. These files are hidden in the Project Explorer but a **.phonon** file is generated with every **.castep** file that has a PhonDisp or PhonDOS suffix. All the files that can be used in the analysis of the current calculation will be presented in the [results file selector](#). However, it is not recommended that you create phonon DOS plots based on the results of a phonon dispersion calculation that only uses q-vectors in high-symmetry directions.

Tip: When evaluating phonon DOS, use only the results of the phonon calculations on the Monkhorst-Pack grid.

To create a phonon dispersion chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select [Phonon dispersion](#) from the list of properties.
3. Use *Results file selector* to pick the appropriate results file (it should have a PhonDisp suffix).
4. Select the required frequency units for the chart from the *Units* dropdown list.
5. Select a required display style ([Points](#) or [Line](#)) from the *Graph style* dropdown list.
6. Optionally, check *Show DOS* and set the relevant DOS options.
7. Click the *View* button.
8. A new chart document, *seedname Phonon Dispersion.xcd*, is created in the results folder.

To create a phonon DOS chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select [Phonon density of states](#) from the list of properties.
3. Use *Results file selector* to pick the right results file (it should have a PhonDOS suffix).
4. Select a required DOS type ([Full](#) or [Partial](#)) from the *DOS display* dropdown list.
5. Optionally, set additional [CASTEP Phonon DOS analysis options](#). The [Interpolation Integration method](#) gives more accurate results than the [Smearing](#) method, although it is slightly slower.
6. Click the *View* button.
7. A new chart document, *seedname DOS.xcd*, is created in the results folder when [Full](#) density of states is selected. A document *seedname PDOS.xcd*, is created in the results folder when [Partial](#) density of states is selected.

Displaying population analysis results

A CASTEP calculation can compute atomic charges, spins, and bond orders using Mulliken analysis, and atomic charges using Hirshfeld analysis.

Note: CASTEP bond orders may be incorrect for small unit cells, when an atom is bonded to a number of periodic images of itself. For example, bond orders for the primitive cell of silicon are reported as 3.0, while the same calculation for the conventional cell gives 0.75. The factor of four appears because CASTEP sums up the bond orders for the four bonds that link the Si atom at the origin with the periodic images of itself in the primitive cell. A manual analysis of the multiplicities is required in such cases, specifically: determine the number of bonds to periodic images of the same atom and divide the bond order by that number. In cases where the bonds are not symmetry equivalent, you can only obtain an average bond order.

Displaying computed charges, spins, and bond orders

Mulliken charge analysis is one of the most common types of charge analysis. The spin density matrix and atomic overlap matrix are used to partition charges among the atoms. An alternative method of charge partitioning is based on deformation density and produces so-called Hirshfeld charges.

To import and display computed atomic charges, spins, and bond orders, you need to have the structure file (*.xsd*) and CASTEP output file (*.castep*) in a folder within the current project.

To display atomic charges or spins

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the [CASTEP Analysis dialog](#).
2. Select [Population analysis](#) from the list of properties at the top of the dialog.
3. Make sure that the structure file from the CASTEP calculation is the active document.
4. Select the type of charges ([Mulliken](#) or [Hirshfeld](#)) that you wish to apply from the dropdown list.
5. Click the *Assign charges to structure* or *Assign Mulliken spins to structure* button, as appropriate, to import the charge or spin data into the structure.
6. Right-click in the 3D Viewer and select *Label* from the shortcut menu to display the Label dialog.
7. Set the *Object type* to [Atom](#), select [Charge](#) or [Spin](#), as appropriate, from the *Properties* list, and click the *Apply* button to display the charges or spins.

To display bond orders

1. Choose *Modules | CASTEP | Analysis* from the menu bar to display the CASTEP Analysis dialog.
2. Select [Population analysis](#) from the list of properties at the top of the dialog.
3. Make sure that the structure file from the CASTEP calculation is the active document.
4. Click the *Assign Mulliken bond orders to structure* button to import the bond order data into the structure.
5. Right-click in the 3D Viewer and select *Label* from the shortcut menu to display the Label dialog.
6. Set the *Object type* to [Bond](#), select [BondOrder](#) from the *Properties* list, and click the *Apply* button to display the bond orders.

Calculating reaction kinetics

Reaction kinetics are described in terms of reaction rate coefficients. The rate coefficients are evaluated in the transition state theory framework using information about the energies, geometries, and vibrational frequencies of reactants, products, and transition state. In order to achieve better agreement with experiment it might be advantageous to increase the reaction threshold value from the DFT calculated one and to scale calculated harmonic frequencies to account for DFT deficiency and for anharmonic effects.

The threshold correction can be applied either on a basis of more accurate ab initio calculations or based on the comparison of calculated and experimental rate coefficients. It appears that a value in the region of 6-7 kcal/mol describes DFT error adequately.

The recommended correction factors for DFT frequencies can be found at the NIST website for a variety of exchange-correlation functionals: <http://cccbdb.nist.gov/vibscalejust.asp>.

To calculate reaction kinetics

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select [Reaction kinetics](#) from the list of properties.
3. Ensure that the desired 3D Atomistic collection document (*seedname.xod*) is the currently active document.
4. Specify the temperature range of interest.
5. Check the *Apply tunneling correction* checkbox if the reaction involves motion of light elements.
6. Optionally specify a *Threshold correction* and a *Vibrational frequencies scaling* factor.
7. Click the *Calculate* button.
8. A new study table document, *seedname.std*, is created in the results folder.

Displaying the averaged potential chart for work function calculations

The CASTEP Analysis dialog can be used to generate plots of the change in electrostatic potential through a slab, which is related to the energy required to remove an electron from the bulk into the vacuum (the work function). The plots are created by averaging the electrostatic potential in the planes perpendicular to the slab normal.

Note: Work function can only be calculated for structures constructed in a slab geometry so that they contain atomic planes separated by a vacuum layer.

Note: If nonlocal exchange was used for the calculation local potentials are poorly defined and are not available for analysis.

The averaged electrostatic potential is reported along the fractional coordinate of the unit cell in the direction of the vacuum. The Fermi level is reported on the work function chart.

To create an averaged potential chart

1. Choose *Modules | CASTEP | Analysis* from the menu bar to open the [CASTEP Analysis](#) dialog.
2. Select **Potentials** from the list of properties.
3. Make the 3D Atomistic document containing the 3D periodic slab the active document.
4. Use the *Results file selector* to pick the results file.
5. Select the *Potential field* from the dropdown list.
6. Optionally check the *View isosurface on import* checkbox.
7. Click the *Import* button.
8. A new chart document, *seedname Potential Profile.xcd*, is created in the results folder and becomes the active document. The selected potential field is imported into the 3D Atomistic document and may be displayed as an isosurface.

Updating structure

Updating cell parameters and atomic coordinates after Geometry Optimization or a Dynamics run should be the first step in the Analysis process.

Note: Structure updates happen automatically after a CASTEP job is completed and the results files have been downloaded successfully. The description below is, therefore, only relevant for jobs which were run in standalone mode and where the results files were transferred manually, or results files in which the final structure produced by CASTEP has been manually modified and you wish to revert to the unmodified form.

You can update the structure if the chemical composition (the number of atomic species and the number of atoms of each kind) has not been changed since Materials Studio saved the structure in the results folder. After the update, the cell parameters and atom coordinates are set to the values returned by the CASTEP run in the (hidden) binary `.check` file.

To update the structure

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select **Structure** from the list of properties.
3. Ensure that the 3D model document to be updated is active.
4. Click the *Update* button.

Note: An error message is generated if the output `.check` file is incomplete, or if the chemical composition of the model has been changed.
The *Update* button is enabled only if the output `.check` file is present and the active document is the 3D model to be updated.

Creating a trajectory file

Note: A trajectory file, *seedname*.xtd, is automatically created when a CASTEP job is completed and the results files have been downloaded successfully. The description below is, therefore, only relevant for jobs which were run in standalone mode and where the results files were transferred manually.

The CASTEP server returns a number of ASCII text files to the client PC that can be used to create a trajectory file for either a geometry optimization or a dynamics calculation. This trajectory is saved in a hidden *seedname* Trajectory.trj file in the results folder.

This file contains complete information on the structure evolution, including changes in the energy, temperature, stress, velocities and forces. Materials Studio does not currently provide tools for analyzing this information. Although, it is possible to animate the trajectory.

Note: To perform statistical analysis of the results or to visualize atomic vectors (forces and velocities) you can use Forcite Analysis.

To create a trajectory

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select *Structure* from the list of properties.
3. Ensure that the current document is either the 3D model in the results folder or the `.castep` file of the corresponding calculation.
4. Click the *Create* button.

Displaying thermodynamic properties

Phonon calculations in CASTEP can be used to evaluate the temperature dependence of the energy, entropy, free energy and lattice heat capacity of a crystal in a quasiharmonic approximation. These results can be used to compare with experimental data (for example on heat capacity measurements), to predict phase stability of different structural modifications, and so on (see [Baroni et al., 2001](#)). Warren et al. demonstrated applicability of CASTEP to theoretical studies of phase transitions ([Warren and Ackland, 1996](#) and [Warren et al., 1998](#)).

An example of the CASTEP output for thermodynamic properties is shown in [Figure 1](#). All energy-related properties are plotted on one graph, and the calculated value of the zero-point energy is included. The heat capacity is plotted separately on the right.

Note: The entropy is presented as an $S \cdot T$ product to allow comparison with the energy.

CASTEP Thermodynamic Properties

Zero point energy=1.3792910 eV

CASTEP Thermodynamic Properties

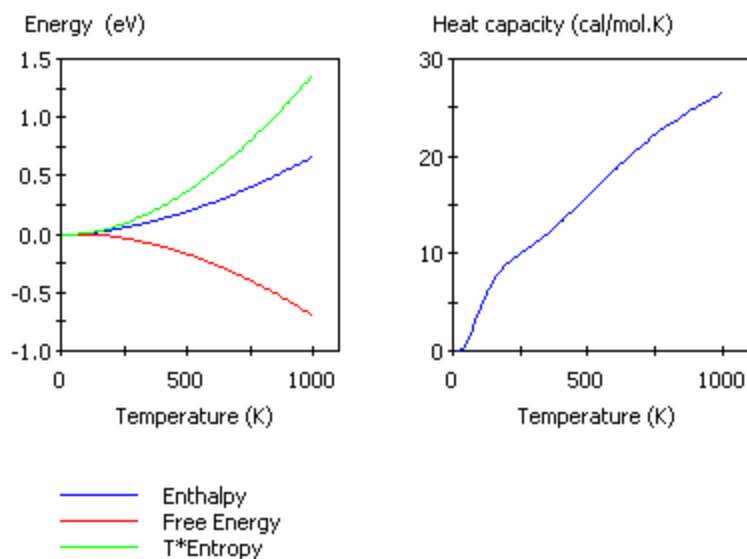


Figure 1. Thermodynamic properties of MgH₂

Note: Thermodynamic properties calculated using the quasiharmonic approximation can be inaccurate for temperatures comparable to the Debye temperature.

To create a thermodynamic properties chart

1. Choose *Modules | CASTEP | Analysis* from the Materials Studio menu bar.
2. Select [Thermodynamic properties](#) from the list of properties.
3. Use the *Results file selector* to pick the appropriate results file (it should have a PhonDOS suffix).
4. Optionally, check *Plot Debye temperature*.
5. Select the desired temperature range.
6. Click the *View* button.
7. A new chart document, *seedname Thermodynamic Properties.xcd*, is created in the results folder.
8. If *Plot Debye temperature* is checked, an additional chart document, *seedname Debye Temperature*, is created in the results folder.
9. Optionally, click the *Assign temperature factors to structure* button to add temperature factor information to the structure.

CASTEP jobs

The topics in this section cover [controlling](#) and running [remote](#) CASTEP jobs, details of a [sample](#) remote run, running jobs in [standalone](#) mode, and potential reasons why CASTEP might [fail](#).

Using CASTEP job control

Materials Studio runs CASTEP jobs as background processes on a server. The following tools are provided to setup and control the jobs:

- Use the [Job Control](#) tab on the [CASTEP Calculation](#) dialog to select the gateway location and job parameters for future jobs.
- Use the Server Console application to add new servers and to monitor multiple jobs.
- Use the Job Explorer to monitor multiple jobs.

For further information on using job control see the main job control and live updates help topics. Live updates can be requested on the [CASTEP Job Control Options](#) dialog.

Running CASTEP jobs in parallel

CASTEP jobs can run in parallel on a server that supports MPI. The CASTEP interface uses the gateway framework of Materials Studio to extract the relevant information for each gateway server. You can select the number of cores to use, up to the maximum number available, as indicated by the text to the right of the *Run in parallel on* control.

Note: It is recommended to use the number of cores which is commensurate with the number of k-points in the calculation. You can determine the number of k-points by using the *Display points...* button on the [k-points tab](#) of the *CASTEP Electronic Options* dialog.

CASTEP jobs can run in parallel using hybrid OpenMP/MPI parallelization. CASTEP uses the Materials Studio gateway framework to extract the relevant information for each gateway server. You can select the number of cores to use, up to the maximum number available, as indicated by the *Run in parallel on* option on the [Job Control](#) tab of the CASTEP Calculation dialog. Furthermore, on Linux gateways you can specify the desired number of threads to be used for each MPI process. The number of threads must be commensurate with the number of cores requested and should not exceed the number of cores on each execution host.

This functionality can substantially decrease the amount of memory required for a job (although it could somewhat decrease speed).

Remote CASTEP jobs

CASTEP uses a client-server architecture that allows you use your PC to control calculations of the total energy and electronic properties of a system or geometry optimizations and dynamics simulations of structures running on a remote computer.

This separation of the client user interface from the server system, which runs the calculations, allows you to use a high performance supercomputer from your Windows desktop PC. It also allows you to make use of spare CPU cycles on other desktop PCs.

Execution of server code can be somewhat reconfigured. In particular, for Linux clusters it can be useful to set *MaxCoresPerProcessor* to the actual number of cores per *chip* for homogeneous clusters. For example, if a cluster node contains two 6-core chips, the value can be set to 6. This modification can speed up parallel jobs for some architectures.

CASTEP jobs are controlled by input files that are generated by Materials Studio when you start a job. CASTEP writes the results of the calculations to various output files, which are downloaded from the server to the appropriate Materials Studio project when the job is completed.

CASTEP remote jobs run according to the standard sequence of processes described in A sample remote job run with the differences explained in the [Sample CASTEP run](#) help topic.

A sample CASTEP run

Whether you perform a single-point energy calculation, minimize a structure, run a molecular dynamics simulation, calculate elastic constants, or perform a transition-state search, the sequence of steps that is executed to run a remote CASTEP job is always the same. When you click the *Run* button on the CASTEP Calculation dialog, the steps described in A sample remote job run happen with the following differences:

For [Energy](#) calculations, if

- *Update structure* is checked: there is no effect, as no structural changes are associated with this task.
- *Update graphs* is checked: Materials Studio creates a chart document called `[seedname] Energies.xcd`, showing the total energy versus SCF iteration, and another chart document called `[seedname] Convergence.xcd`, showing, on the logarithmic scale, the convergence of the total energy versus SCF iteration.
- *Update textual results* is checked: Materials Studio downloads a text file called `Status.txt` that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), the SCF iteration number, the total energy, and the total energy convergence (that is, the change from the previous iteration).

For [Geometry Optimization](#) calculations, if

- *Update structure* is checked: Materials Studio downloads a snapshot of the structure and modifies a copy of the original structure accordingly.
- *Update graphs* is checked: Materials Studio creates a chart document called `[seedname] Energies.xcd`, showing the total energy versus optimization step, and another chart document called `[seedname] Convergence.xcd`, showing, on the logarithmic scale, the total energy change, the maximum displacement, the maximum force, and the maximum stress versus optimization step.
- *Update textual results* is checked: Materials Studio downloads a text file called `Status.txt` that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), the SCF iteration number, the total energy, the total energy convergence (that is, the change from the previous iteration), the maximum displacement, the maximum force, and the maximum stress for the last completed optimization step.

For [Dynamics](#) calculations, if

- *Update structure* is checked: Materials Studio downloads a snapshot of the structure and modifies a copy of the original structure accordingly.
- *Update graphs* is checked: Materials Studio creates a chart document called `[seedname] Constant .xcd`, showing the constant of motion versus simulation time, and another chart document called `[seedname] Temperature .xcd`, showing the temperature versus simulation time. In addition, the chart document `[seedname] Pressure .xcd` is created if the calculation is run using the [NPH](#) or [NPT](#) ensembles.
- *Update textual results* is checked: Materials Studio downloads a text file called `Status .txt` that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), the number of completed dynamics steps, the temperature, and the constant of motion for the last completed optimization step.

For [Elastic Constants](#) calculations, if

- *Update structure* is checked: there is no effect, as no structural changes are associated with the original structure. CASTEP performs an [Energy](#) calculation for the initial structure.
- *Update graphs* is checked: Materials Studio creates a chart document called `[seedname] Energies .xcd`, showing the total energy versus optimization step, and another chart document called `[seedname] Convergence .xcd`, showing, on a logarithmic scale, the total energy change, the maximum displacement, and the maximum force versus optimization step. These charts refer to the structure currently being processed, as indicated by the index of the strain pattern and of the strain magnitude for that pattern.
- *Update textual results* is checked: Materials Studio downloads a text file called `Status .txt` that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), a description of the structure currently being processed (as indicated by the index of the strain pattern and of the strain magnitude for that pattern), the number of completed optimization steps, the total energy, and the total energy convergence (that is, the change from the previous iteration), the maximum displacement, and the maximum force for the last completed optimization step.

For [TS Search](#) calculations, if

- *Update structure* is checked: Materials Studio downloads a snapshot of the structure and modifies a copy of the original structure accordingly.
- *Update graphs* is checked: Materials Studio creates a chart document called `[seedname] TSSearch .xcd`, showing the total energy versus reaction coordinate. For each phase of the transition-state search, a separate graph is displayed within the chart document.
- *Update textual results* is selected: Materials Studio downloads a text file called `Status .txt` that contains a summary of the calculation performed (task, DFT functional, energy cutoff for plane wave basis set, electronic minimization method, system charge and spin, and so on), a description of the phase of the transition-state search currently being processed, the reaction path coordinate, the total energy, the total energy convergence (that is, the change from the previous iteration), the maximum displacement, and the maximum force for the last completed search step.

For [Properties](#) runs or for any other task where electronic structure properties (band structure, density of states, or optical properties) are requested, textual updates are modified as follows.

When the CASTEP run enters the properties stage, the task description in the `Status .txt` file is changed to either [Eigenvalues](#) (for band structure or density of states) or [Eigenvalues + Optical Properties](#) (for optical properties). This file now contains a summary of the calculation, the number of completed non-self-consistent iterations of the eigenvalues calculation, the maximum convergence of

electronic energies, and the maximum change in electronic energies on the last completed iteration for any band or k-point.

Once the job has finished, Materials Studio will transfer the output files back to your PC, where you can [view and edit](#) them, [analyze the results](#), or use them for further calculations. Additional output files may be generated or modified depending on the type of calculation you performed.

- For [Energy](#) runs, Materials Studio downloads all the CASTEP output files.
- For [Geometry Optimization](#) runs, Materials Studio downloads all the CASTEP output files, updates the structure it has copied into the results folder to show the final geometry, and creates a trajectory file, `[seedname].xtd`, that contains the history of the optimization process. The trajectory file can be animated using the tools on the Animation toolbar.
- For [Dynamics](#) runs, Materials Studio downloads all the CASTEP output files, updates the structure it has copied into the results folder to show the configuration at the beginning of the dynamics run, and creates a trajectory file, `[seedname].xtd`, that describes the molecular dynamics calculation. The trajectory file can be animated using the tools on the *Animation* toolbar.
- For [Elastic Constants](#) runs, Materials Studio downloads all the CASTEP output files for all strain patterns and strain amplitudes.
- For [TS Search](#) runs, Materials Studio downloads all the CASTEP output files, updates the structure it has copied into the results folder to show the resulting configuration, and creates a trajectory file, `[seedname].xtd`, that contains the history of the optimization process. The trajectory file can be animated using the tools on the *Animation* toolbar.

If a remote CASTEP job fails

Materials Studio checks most of the data and settings required to perform a CASTEP job prior to launch. If it cannot start the job, error messages are generated detailing the reasons.

However, sometimes jobs may fail for reasons which cannot be checked prior to launch. In such cases, more detailed information about the error may only be available in the `[seedname].castep` file produced by the job or in the project log file. Other files stored in the job directory on the server, for example, `Castepexe.log`, may also contain further clues. To view the server-side files, you can use the Remote View facility of the Job Explorer.

Below is a list of the most common reasons for CASTEP jobs to fail. It may help you to identify and fix any problems you have with your remote CASTEP jobs. For generic reasons for remote job failures please consult the [If a remote job fails](#) help topic.

Tip: Select *View | Project Log* from the menu bar to see if any error or warning messages have been reported.

Common reasons for a CASTEP job to fail to start

Server-side problems

- Parallel CASTEP job fails with [Error writing ...](#) message under Linux.

Depending upon the options selected, CASTEP may use significant amounts of disk space to store scratch files. Scratch files are created by each node during the execution of a parallel CASTEP job. CASTEP uses the value of the environment variable `GATEWAY_TMP` as the location to be used to save these files; this variable is set by `share/bin/ms_vars.sbd` and can be changed using the gateway's web interface. You should ensure that the location that will be used on each node points to a file system with at least 1 GB of free space. Note that the `./tmp` setting for `GATEWAY_TMP` corresponds to using the common file space on the head node, in the actual job directory, to store the temporary files. This setting can have a detrimental effect on the performance of Linux clusters.

An additional problem may occur if the `GATEWAY_TMP` is set to the location on a shared disk resource which is NFS mounted from the nodes. This mount should be done in a synchronous mode using hard mounts.

Tip: It is important to identify the reason for the failure of a CASTEP job before taking any action. In most cases, the error message produced will give a good indication of the reason for the failure. If the error message indicates that the job failed, but does not provide specific reasons, check the `[seedname].castep` file produced by the job or check the project log.

Running CASTEP in standalone mode

The most convenient way of running CASTEP is through the Materials Studio interface, which performs all the preparatory tasks required to run a CASTEP job. However, in some circumstances, it may be necessary to run CASTEP in standalone mode with a set of input files prepared elsewhere. For example, you may wish to run a calculation on a server that has not been configured as a gateway, that is, a computer that does not communicate with your Materials Studio client (perhaps because a firewall prevents automatic file transfer and job launch).

For more general information on using standalone mode, see the [Running jobs in standalone mode](#) help topic.

Generate the input files

CASTEP requires various input files that contain details of the calculation. More information about these files can be found in the [CASTEP file formats](#) topic. You can create these files using a text editor, such as WordPad on Windows or vi on Linux. However, because the information contained in the input files is quite complex, you should use Materials Studio to generate them for you. You can create the required files using the [CASTEP Job Files dialog](#), see the [Running jobs in standalone mode](#) help topic for further information.

Tip: Only the `.param` input file is displayed in the Project Explorer. The other input files are saved as hidden files. You should ensure that your Windows folder settings allow you to view hidden files so that you are able to see all of the files you need to copy to the server in order to run CASTEP. It may also help to turn off the Windows option of hiding file extensions for known file types.

Transfer the input files to the server

If you generated the input files manually using a text editor on the server machine, then no file transfer is required. However, if you generated the files on your PC using Materials Studio, you must transfer them to the server before you can start the calculation.

If you are unable to access the hard drive on the server, you should use the File Transfer tool to transfer files from the client to the server.

Execute the job

To assist you in running CASTEP in standalone mode, a batch/shell file called `RunCASTEP` is supplied. It can be found in the directory in which the CASTEP executables are located, usually `etc/CASTEP/bin/` in the main Materials Studio directory. `RunCASTEP` scripts are used to start CASTEP jobs in standalone mode. `RunCASTEP.sh` is provided for Linux servers, while `RunCASTEP.bat` is provided for Windows servers.

Usage:

```
RunCASTEP.sh [-h] [-np number of cores] [-nt number of threads] [-q queue name] seedname (Linux)
```

or

```
RunCASTEP [-h] [-np number of cores] [-q queue name] seedname (Windows)
```

Argument	Description
<code>-h</code>	Displays the help text.
<code>-np</code>	Specifies the number of cores on which to run CASTEP. When this option is not specified a single core is used.
<i>number of cores</i>	The number of cores to use.
<code>-nt</code>	Specifies desired number of threads. When this option is not specified a single thread for each process is used.
<i>number of threads</i>	The number of threads to use.
<code>-q</code>	Submits the job to the specified queue.
<i>queue name</i>	The name of the queue on which to run the job.
<i>seedname</i>	The seed used to identify the set of CASTEP input and output files. The input files should be present in the directory in which the CASTEP script is started.

If you wish to calculate properties, you should execute the script with all the seednames as parameters for the `RunCastep.sh`:

```
RunCASTEP.sh -np 4 seedname seedname_BandStr seedname_DOS seedname_Optics
```

Note: By default large `seedname.check` files are removed after the execution to save space. In most cases the `seedname.castep_bin` files are enough to restart the calculation. However, if check files are needed they can be requested by adding the following command:

```
-extraoptions KeepCheckFiles:Yes
```

For example:

```
RunCASTEP.sh -extraoptions KeepCheckFiles:Yes seedname
```


Download the output files from the server

When the CASTEP calculation is complete, you must transfer the output files back to your PC for analysis in Materials Studio. See [Running jobs in standalone mode](#) for further information.

To transfer the output files back to your PC

1. Transfer the output files to the client PC using either copy and paste or the File Transfer tool.
2. A complete list of the output files that are generated and descriptions of their contents can be found in the [CASTEP file formats](#) topic. All of the files, *seedname.**, *seedname_BandStr.**, *seedname_DOS.**, *seedname_Optics.**, *seedname_PhonDOS.**, *seedname_PhonDisp.**, and *seedname_Subset*.**, should be downloaded from the server.

Tip: After you have transferred the output files, you may wish to modify their attributes such that all of them except the *.castep* file are hidden files. This avoids cluttering up the display in the Project Explorer.

Tip: If you have transferred files into a Materials Studio project folder, but you cannot see them in the Project Explorer, try using the *Refresh* button  to update the Project Explorer.

Open the output files in Materials Studio

Provided that you have transferred the correct files from the server to your PC and stored them in a folder in a Materials Studio project, you should be able to make use of the CASTEP analysis options described in the topic [Analyzing CASTEP results](#). Specifically, you can open the 3D Atomistic document containing the starting structure and update it, create a trajectory document and animate it, visualize volumetric properties, calculate DOS and optical spectra, and plot band structure.

CASTEP file formats

The CASTEP server program is a file-based application. It requires input files and produces a number of output files. The precise number and type of output files produced depends on the details of the CASTEP job being performed.

The table below summarizes information on the format and purpose of all the major file types, and provides links to further information.

File type	Input or Output	Brief description
.param	Input	General input file (text)
.cell *	Input	Structure input file (text)
.castep	Output	Report on the calculation (text)
.check , .castep_bin *	Output	Charge density, wavefunctions, structure, and so on (binary)
.bands *	Output	Eigenvalues (text)
.cst_esp *	Output	Electrostatic potentials (binary)
.geom *	Output	Geometry optimization trajectory data (text)
.md *	Output	Molecular dynamics trajectory data (text)
.ts *	Output	Transition state search trajectory data (text)
.phonon *	Output	Phonon data (text)

File type	Input or Output	Brief description
.pdos_weights*	Output	Weights required to calculate PDOS (binary)
.cst_ome*	Output	Matrix elements required to calculate optical properties (binary)
.elf*	Output	Electron localization function, ELF (binary)
.bib	Output	Bibliography file in BibTeX format (text)
.otfg*	N/A	Information required for generating pseudopotential files on the fly stored on the client (text)
.tddft	Output	Results of a CASTEP calculation of excitations in the time-dependent DFT approach

* These files are hidden by default, so they will not appear in the Materials Studio Project Explorer; these files are only visible in Windows Explorer if Windows on your machine is configured to show hidden files.

CASTEP file formats - PARAM

The `.param` file contains all of the control parameters required to run a CASTEP job, including the type of calculation, the charge, the spin state, and convergence tolerances. The file consists of lines containing keywords and associated values.

A `.param` file is generated by Materials Studio when you launch a calculation or when you click the *Save Files* button on the [CASTEP Job Files](#) dialog. Job options selected using the interface appear as keywords in the resulting `.param` file.

Under certain circumstances, you may wish to manually add keywords to a `.param` file. The procedure is described in the topic [Running CASTEP in standalone mode](#).

The following rules govern keywords in the `.param` file:

- Keywords may appear in any order.
- The keywords and values are case- and punctuation-insensitive.
- Only one keyword and its options may appear on a line.
- Keywords that do not appear in the `.param` file are set to their default values.
- Units may be specified for physical quantities.

Note: Recognized units and their identifiers are listed in the UNIT keyword topics. If no units are specified, the default units will be assumed.

- Comment lines (those beginning with `#`, `;`, `!` or `COMMENT`) and blank lines are ignored.

Keywords and their values are fully described in the topic [CASTEP keywords](#).

CASTEP file formats - CELL

The `.cell` file contains geometry information, including cell parameters, atomic coordinates, and k-point coordinates and weights. The file consists of lines containing keywords and data blocks, and associated values.

A `.cell` file is generated by Materials Studio when you launch a calculation or when you click the *Save Files* button on the [CASTEP Job Files dialog](#).

Under certain circumstances, you may wish to manually add keywords to a `.cell` file. The procedure is described in the topic [Running CASTEP in standalone mode](#).

The following rules govern keywords and data blocks in the `.cell` file:

- Keywords and data blocks may appear in any order.
- The keywords, data blocks, and values are case- and punctuation-insensitive.
- Only one keyword and its options may appear on a line.
- Data blocks are preceded by `%BLOCK <keyword>`, followed by a series of data lines, and terminated by `%ENDBLOCK <keyword>`.
- Keywords and data blocks that do not appear in the `.cell` file are set to their default values.
- Units may be specified for physical quantities.

Note: Recognized units and their identifiers are listed in the UNIT keyword topics. If no units are specified, the default units will be assumed.

- Comment lines (those beginning with `#`, `;`, `!` or `COMMENT`) and blank lines are ignored.

Keywords and their values are fully described in the topic [CASTEP keywords](#).

CASTEP file formats - CASTEP

The `.castep` file contains the numerical output of a CASTEP job in ASCII format. The header describes the settings used, followed by the calculation results.

CASTEP file formats - binary checkpoint files

The `.check` and `.castep_bin` files contain the numerical output of a CASTEP job in binary format. The difference between the two files is that the `.check` file stores electronic wavefunctions in addition to all other information (calculation parameters, structure, electron density, electronic, and vibrational properties) and can become very large for large systems.

At least one of these files is required by the Materials Studio client to analyze CASTEP results. The CASTEP module in Materials Studio allows you to choose which of the two binary files to download after job execution.

Note: Visualization of orbitals or of STM images requires information about electronic wavefunctions, hence the `.check` file is always downloaded if any of these properties were requested.

CASTEP file formats - BANDS

The `.bands` file contains electronic eigenvalues for all k-points in a CASTEP job. The data in this file are used for band structure plotting and optics, DOS, and PDOS calculations.

The file has the following format:

The eigenvalues are given in atomic units. The k-points are specified using fractional coordinates, which are followed by the corresponding k-point weight.

CASTEP file formats - CST_ESP

The `.cst_esp` file contains the electrostatic potentials output from a CASTEP job.

CASTEP file formats - task-specific files

CASTEP produces additional output files only when certain tasks are selected:

- `.geom` - Geometry optimization
- `.md` - Molecular dynamics
- `.ts` - Transition state search

These files contain trajectory information and have the following format:

```
      -1.82539879E+002      -1.82539879E+002  
<-- E
```

Values are always specified in atomic units and one of the following letter codes will be present:

- E - total energy and enthalpy
- T - temperature
- R - atomic coordinates (Cartesian)
- h - cell matrix
- hv - derivatives (velocities) of the cell matrix
- F - forces
- V - velocities
- S - stress tensor
- P - pressure

CASTEP file formats - PHONON

The `.phonon` file contains phonon frequencies and eigenvectors for all q-vectors in a CASTEP phonon calculation. The data in this file are used for phonon dispersion plotting, phonon DOS, and projected (partial) phonon DOS calculations. Phonon frequencies are always given in wavenumbers (cm^{-1}).

CASTEP file formats - TDDFT

The `.tddft` file contains detailed information about the results of a CASTEP calculation of excitations in the time-dependent DFT approach.

The header contains information about the structure, this block is followed by the representation of excited states as a superposition of Kohn-Sham one-electron bands. The overlap between occupied and unoccupied states gives a useful indication of the degree of charge transfer in every given excitation (if the value is significantly lower than 1.0, the TD-DFT description might be inaccurate since it does not take charge transfer into account).

The final section contains spectroscopic data; excitations energy, singlet or triplet character, level of convergence, and transition dipoles (the position operator between the ground-state wavefunction and the first order response wavefunction for the N^{th} excited state from TDDFT, $\langle \mathbf{u}^0 | \mathbf{r} | \mathbf{u}^N \rangle$). The transition dipole is projected onto the Cartesian axes. The character can be marked as "spurious" to reflect the fact that there are mathematically valid solutions to the linear-response TDDFT eigenvalue problem that are not physical ([Heßelmann and Görling, 2009](#)). These are solutions that provide a pure Kohn-Sham orbital transition, with no contribution from the exchange-correlation action. In terms of observables, the matrix elements will be zero (numerically so for computed quantities), and therefore harmless unless you want to select a specific state, for example for a structure optimization.

CASTEP file formats - PDOS_WEIGHTS

The `.pdos_weights` file contains the weights that are required to generate partial densities of state (PDOS), based on the results of a CASTEP job.

CASTEP file formats - CST_OME

The `.cst_ome` file contains the matrix elements for electronic interband transitions that are required to generate the dielectric function and other optical properties, based on the results of a CASTEP job. This is a binary file which contains the array of matrix elements; $M(\text{band1}, \text{band2}, \text{coord}, k, \text{spin})$. The loop is over the number of bands (band1, band2), x, y, z components (coord), k-points (nk), and spins (ns).

CASTEP file formats - ORBITALS

The `.orbitals` file contains the electronic wavefunctions from a CASTEP job. This file is created only for band structure or optics runs; the wavefunctions for all other types of CASTEP calculations are stored in the `.check` file. The `.orbitals` file is required to carry out analysis of orbitals and of the STM profile based on the output of band structure or optics calculations.

CASTEP file formats - CHDIFF

The `.chdiff` file contains the electron density difference calculated as part of a CASTEP job. The density difference is evaluated by subtracting the sum of the atomic densities from the total electron density of the system.

CASTEP file formats - ELF

The `.elf` file contains the electron localization function output from a CASTEP job.

CASTEP file formats - OTFG

The information required for generating CASTEP pseudopotential files on the fly is stored on the client in the files with the `.otfg` extension. These files are intended for the use on the client only, they are not expected to be transferred to the gateway server. The purpose of these files is to create a correct string in the SPECIES_POT block in `.cell` file.

The `.otfg` files can be edited manually, and new files with this extension can be created and stored in the Resources\Quantum\Castep\Potentials folder on the client. The most likely purpose for the editing would be to change the default core radius in order to create a softer (bigger core radius) or a more accurate and hard (smaller core radius) version of a pseudopotential for a given element. Occasionally, when core holes are used for some elements [different settings](#) are more appropriate.

The latest set of OTFG settings introduced in Materials Studio 8.0 has been developed in order to minimize the error with respect to fully converged all-electron DFT calculations. The error achieved by this set is 0.5 meV/atom which puts CASTEP among the most accurate pseudopotential codes available. A full definition of the test framework and the meaning of the error is given by Lejaeghere et al. (2014) and on the website of the [Delta project](#). The files that correspond to this set have an `_80` suffix. Some of these files have been subsequently improved to eliminate ghost states. The recommended set of OTFG settings includes files with an `_2017R2` (ultrasoft) or an `_2017R2ncp` (norm-conserving) suffix.

See Prof. David Vanderbilt's website on pseudopotential generation for more information:

<http://www.physics.rutgers.edu/~dhv/uspp/>

The format can be described as:

- The order of the blocks and of single lines with keywords in the file is irrelevant.
- The order of the lines inside the BLOCK constructs is irrelevant.
- The separator between the keyword and the value can be any of the **designated separators**: "=", ":", tab, space.
- The case of the keyword is irrelevant.
- The comments are allowed after the value as long as they are separated by at least one designated separator.
- The **compulsory fields** are the ones in red in the description above.
- The string fields have to be enclosed in single quotation marks.
- The energy shifts, CHANNEL_INFO_SHIFT, can be given either as shifts relative to the atomic eigenvalues or as an absolute value (in which case, the value should be preceded by VAL and a designated separator).

- The level shifts, CHANNEL_INFO_LEVELSHIFT, are artificial shifts of atomic eigenvalues relative to their DFT positions. Such shifts can be used to correct DFT error in relative positions of bands in a solid state calculation, see [Profeta et al. \(2004\)](#) for details.
- Information about multiple projectors in the CHANNEL_INFO lines should be separated by "&&", and there should be also at least one of the designated separators on either side of the "&&" construct.
- CHANNEL_INFO_TYPE, CHANNEL_INFO_SHIFT and CHANNEL_INFO_BETA_RC values within a CHANNEL_INFO block are all optional; if either of these entries is omitted CASTEP will use the default values for the respective property. The default setting is to use two ultrasoft projectors, using atomic eigenvalues as reference energies, and using BETA_RADIUS value specified elsewhere in the .otfg file.
- If two or three out of CHANNEL_INFO_TYPE, CHANNEL_INFO_SHIFT and CHANNEL_INFO_BETA_RC fields are present, then each of these fields should contain the same number of values.
- A block enclosed in STARTCOMMENT and ENDCOMMENT tags can be inserted anywhere in the file; its contents are ignored and can be used to keep a record of, for example, convergence testing and validation studies.
- The only value currently allowed on the COMPATIBILITY line is 'compat7'. The generator has been improved in the 8.0 release, so that it produces slightly different (although functionally equivalent) pseudopotential from the same input. The COMPATIBILITY option has been added to all 00.otfg files to ensure compatibility with the earlier releases.

Note: COARSE, MEDIUM and FINE values are used by the CASTEP GUI in order to determine the cutoff energy for the calculations carried out at the specified level of accuracy. If you are generating a new file, you would have to carry out the convergence testing to determine the appropriate values for the new potentials.

In order to ensure that the OTFG for core holes is appropriate some conditional settings have been appended for certain elements, in a section which is only used when core holes are requested. If core holes are not being used in the calculation the CORE_HOLE_INFO keywords are ignored and the preceding settings are used.

Reaction Kinetics Study Table

The results of the reaction rate calculation are collected in a study table which contains the following tabs:

- *Summary* - contains a summary of the results, reporting the main parameters of the calculation, fit coefficients, and root-mean-square error (RMSE) which is calculated for $\ln(k(T))$. If the fit parameters (also shown on the *Graphs* tab) produce too high n , or E_a becomes negative, the corresponding lines in the study table are highlighted in red.
- *Structures* - contains the collection document representing the entire reaction as well as one atomistic document for each of the reactants and products.
- *Graphs* - contains the temperature dependence of the reaction rates coefficients ($k(T)$) for forward and backward reactions together with equilibrium constants. It also contains results of the fit using Arrhenius form (see Kinetics constants theory) with temperature $T_0 = 298.15$ K together with standard Arrhenius form ($n = 0$, the temperature independent pre-exponential coefficient).
- *Partition Function* - contains the calculated partition functions for reactant(s), product(s), and transition state.

Theory in CASTEP

The following topics provide specific details about the theory behind CASTEP.

CASTEP background theory

This section provides information specific to the implementation of DFT in the CASTEP program. A general overview of DFT is provided elsewhere. The general overview provides information on the concepts of charge density, DFT functionals, the SCF procedure, and band structures, which are applicable to any computational implementation of DFT. The application of dispersion corrections to DFT is also described.

In contrast, this section provides background information on aspects of DFT that are specific to CASTEP.

The CASTEP program provides a robust and efficient implementation of DFT which is based on the following concepts:

- [Pseudopotential description](#) of the electron-ion interaction
- [Supercell approach](#) with periodic boundary conditions
- [Plane wave basis set](#)
- Extensive use of [fast Fourier transform \(FFT\)](#) for evaluation of the Hamiltonian terms
- Iterative schemes for the [self-consistent electronic minimization](#)
- Implementation of the most popular DFT expressions for the [exchange-correlation functional](#), including the screened and exact exchange schemes.

Some of these topics are expanded on in this section. More detailed information can be found in the links listed at the end of this topic.

Supercell approach

CASTEP is based on a supercell method, wherein all studies must be performed on a periodic system, even when the periodicity is superficial. Thus, for example, a crystal surface must be represented by a finite-length slab ([Figure 1](#)). Similarly, to study molecules it is necessary to assume that they are in a box and treat them as periodic systems. There is no limitation on the shape of the supercell.

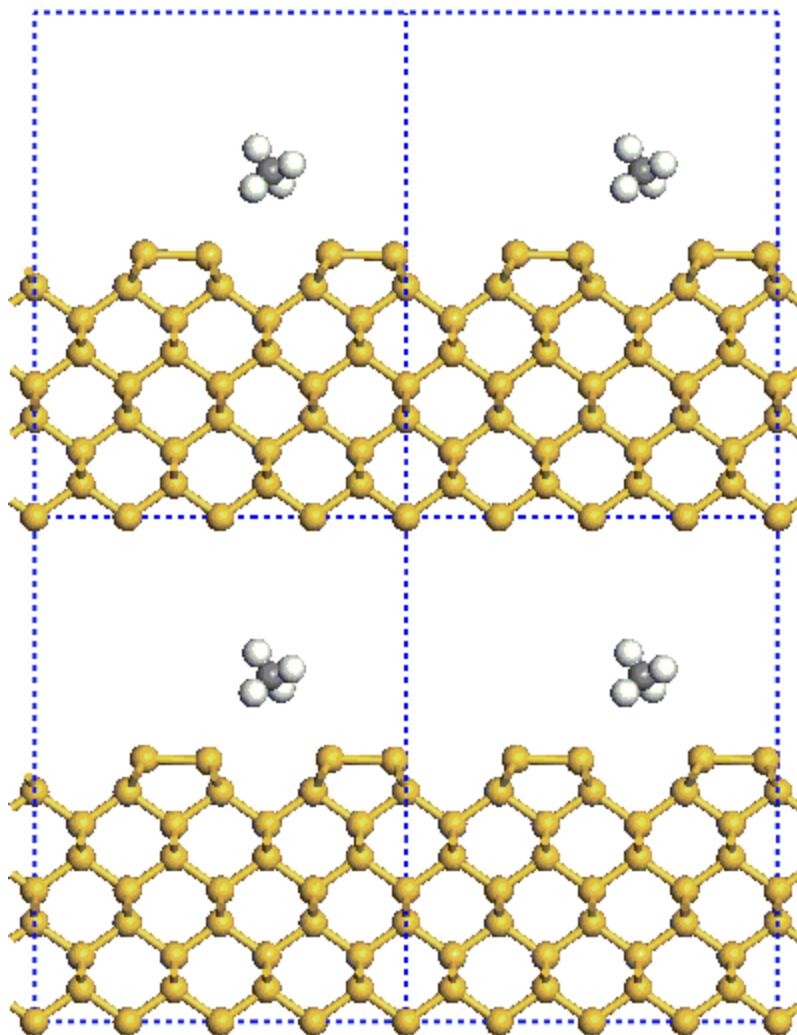


Figure 1. Schematic representation of the supercell calculation of a small molecule adsorption on a surface

The main advantage of imposing periodic boundary conditions relates to Bloch's theorem, which states that in a periodic system each electronic wavefunction can be written as a product of a cell-periodic part and a wavelike part ([Payne et al. 1992](#)):

Eq. CASTEP 1

$$\psi_i(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_i(\mathbf{r})$$

The cell periodic part, ψ , can then be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal:

Eq. CASTEP 2

$$\psi_i(\mathbf{r}) = \sum C_{i,\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{R}}$$

Therefore, each electronic function can be written as a sum of plane waves, $\exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{R}]$. Advantages and technical details of the plane wave basis set are described in a [separate section](#).

Among the major gains is the simplified form of the Kohn-Sham equations:

Eq. CASTEP 3

$$\sum \left[|\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{ion}(\mathbf{G} - \mathbf{G}') + V_H(\mathbf{G} - \mathbf{G}') + V_{xc}(\mathbf{G} - \mathbf{G}') \right] C_{i,\mathbf{k}+\mathbf{G}'} = \varepsilon_i C_{i,\mathbf{k}+\mathbf{G}}$$

In this form, the kinetic energy is diagonal, and the various potentials (electron-ion, Hartree, exchange-correlation) are described in terms of their Fourier transforms.

Another advantage of the plane wave basis set is the ease of calculating derivatives of the total energy with respect to atomic displacements (that is, stresses and forces are computationally cheap in this approach), so that efficient geometry optimization and molecular dynamics schemes can be implemented. It is also straightforward to study and improve convergence of plane-wave basis set calculations, as there is a systematic way of adding more basis functions.

However, there is an additional cost to using the supercell approach for systems that lack periodicity in three dimensions inherently (isolated molecules, defects in solids, surfaces, and so on). In a study of a single defect, for example, the properties of an infinite array of defects ([Figure 2](#)) would always be calculated. Therefore, it is essential to introduce enough separation between artificial images of such nonperiodic objects to ensure that there is no appreciable interaction between them. The situation is similar for surface calculations that are carried out in a slab geometry. The vacuum layer should be sufficiently thick to eliminate artificial interactions between the slabs.

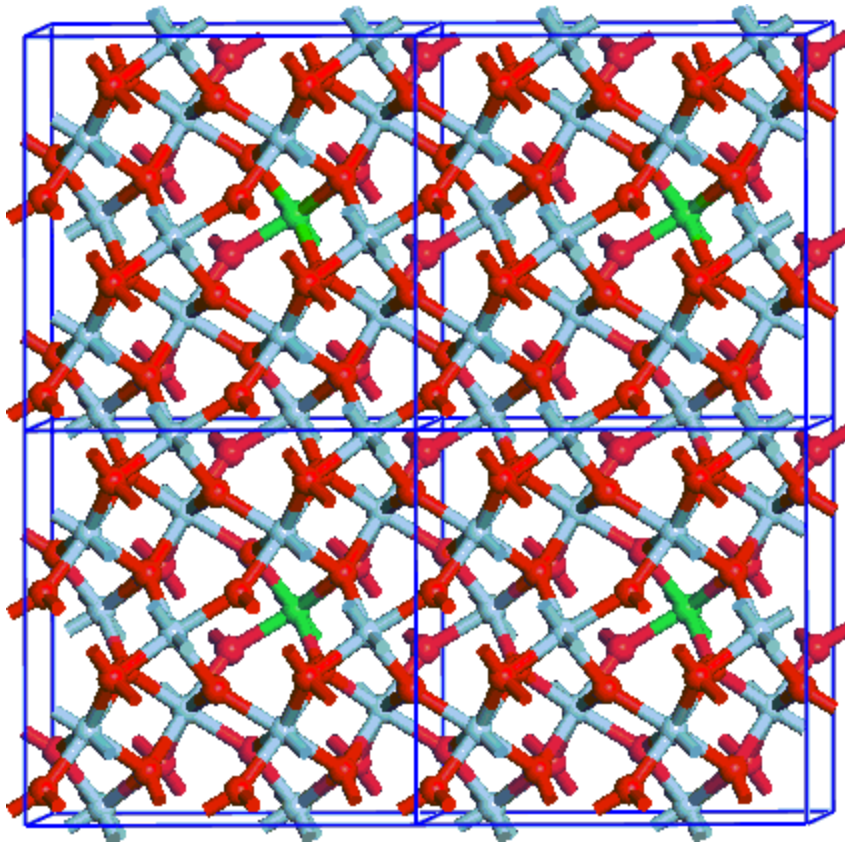


Figure 2. Schematic representation of the supercell calculation of a substitutional impurity in a bulk

Fast Fourier transforms (FFT) in CASTEP

One of the major computational steps in CASTEP is the calculation of the product of the Hamiltonian with a wavefunction, $\mathbf{H}\psi$. It has been shown above that the kinetic energy operator of the Hamiltonian has a diagonal representation in reciprocal space. The same is true of the Hartree operator and of the local pseudopotential operator. Exchange-correlation potential, on the other hand, has a diagonal

representation in real space. This means that there is a need for an efficient way of transforming various entities (wavefunctions, potentials, search directions) from real to reciprocal space and back. FFT provide this, so that the gain due to the evaluating various parts of the Hamiltonian in their "natural" representations is not offset by the cost of the transformation.

Exchange-correlation functionals in CASTEP

CASTEP implements a number of exchange-correlation functionals: [local](#) (LDA), [gradient-corrected](#) (GGA), and fully [nonlocal](#) (based on the exact and screened exchange formalism).

Local exchange-correlation functionals in CASTEP

The exchange-correlation energy is given by Eq. DFT 7. There is only one local functional provided in CASTEP, the Perdew and Zunger ([1981](#)) parameterization of the numerical results of Ceperley and Alder ([1980](#)), CA-PZ.

This particular prescription for the local representation of the exchange-correlation potential is considered to be one of the most accurate descriptions available ([Srivastava and Weaire, 1987](#)).

Gradient corrected exchange-correlation functionals in CASTEP

The so-called nonlocal or gradient-corrected functionals depend on dp/dr as well as on ρ . This provides a considerable increase in the accuracy of predicted energies and structures, but with an additional cost. The nonlocal functionals available in CASTEP include:

Name	Description	Reference
PW91	Perdew-Wang generalized-gradient approximation, PW91	Perdew and Wang
PBE	Perdew-Burke-Ernzerhof functional, PBE	Perdew et al.
RPBE	Revised Perdew-Burke-Ernzerhof functional, RPBE	Hammer et al.
WC	More accurate GGA functional, based on a diffuse radial cutoff for the exchange hole in real space and the analytical gradient expansion of the exchange energy for small gradients	Wu and Cohen
PBEsol	A version of the PBE functional that improves equilibrium properties of densely packed solids and their surfaces	Perdew et al.
BLYP	Becke exchange, Lee-Yang-Parr correlation	Becke; Lee, Yang, Parr

The PBE functional has been designed to give essentially the same results as the PW91 functional but it is more robust in systems with rapidly varying electron density. The RPBE functional has been designed specifically to improve the DFT description of the adsorption energies of molecules on metallic surfaces (for a detailed comparison of these three functionals when applied to surface science problems see [Marlo and Milman, 2000](#)). One of the latest developments, PBEsol functional, is explicitly designed to improve the first-principles gradient expansion for exchange over a wide range of density gradients, and hence to improve the description of equilibrium properties of densely packed solids and their surfaces.

All gradient-corrected functionals in CASTEP are implemented according to the method described by White and Bird ([1994](#)). The application of gradient-corrected exchange-correlation functionals in total-energy calculations using a plane-wave basis set is less straightforward than in localized basis set approaches (used in other programs such as DMol³). The usual form of the exchange-correlation potential includes gradients whose calculation requires the use of a high-quality representation of the density which is computationally expensive in both memory and time. These problems are overcome by defining an exchange-correlation potential for the discrete set of grid points consistent with the discretized form of the exchange-correlation energy that is used in plane-wave total-energy calculations.

This potential is calculated exactly on the minimum fast Fourier transform grid and gives improved convergence and stability as well as computational efficiency.

Nonlocal exchange-correlation functionals in CASTEP

Kohn-Sham schemes based on LDA and GGA functionals have a common feature: they underestimate the band gap substantially. This does not affect the accuracy of the description of the total energy and related properties of crystals and molecules (equilibrium structure, vibrational spectra, elastic constants, and so on). However, an accurate description of the details of the electronic structure is often required to understand the properties of semiconductors and insulators. Then a DFT error of up to 50% in the calculated band gap energy becomes unacceptable.

It is possible to correct for the DFT band gap error by introducing an empirical scissors correction, which is effectively a rigid shift of the conduction band with respect to the valence band. This approach produces satisfactory results for such properties as optical spectra, provided the experimental band gap is accurate. The scissors operator scheme is very difficult to use in predictive studies and in the context of band gap engineering, when there is little or no experimental information about the electronic structure. In addition, the scissors operator approach does not help when an improvement in the description of the electronic structure of metallic systems is required.

There are a wide variety of techniques designed to deal with the band-gap problem in DFT. Most of them are exceedingly complex and time consuming. One of the most practical solutions is the so-called screened exchange, or sX-LDA scheme, developed in the context of the generalized Kohn-Sham procedure ([Seidl et al., 1996](#)). Generalized Kohn-Sham schemes allow one to split the exchange contribution to the total energy into a screened, nonlocal and a local density component.

The following generalized Kohn-Sham schemes are implemented in CASTEP:

- **HF**: exact exchange, no correlation
- **HF-LDA**: exact exchange, LDA correlation
- **sX**: screened exchange, no correlation
- **sX-LDA**: screened exchange, LDA correlation
- **PBE0**: combination of PBE functional with a predefined amount of exact exchange ([Adamo and Barony, 1998](#))
- **B3LYP**: combination of Hartree-Fock exchange with DFT exchange-correlation ([Becke, 1993](#))
- **HSE03**: hybrid functional based on a screened Coulomb potential ([Heyd et al., 2003](#))
- **HSE06**: similar to HSE03, but with optimized screening parameters ([Krukau et al., 2006](#))

Tip: The sX-LDA or HSE06 scheme is recommended for band gap calculations.

The implementation of screened exchange in CASTEP follows closely the recipe suggested by [Seidl et al. \(1996\)](#). The Thomas-Fermi screening function is used (the case of zero screening length, k_{TF} , corresponds to the exact exchange formalism).

CASTEP provides a number of schemes for evaluating the screening length. The most straightforward to use is average density. This is a reasonable approach for bulk solids, but not for systems with large amounts of vacuum in the cell, for example molecules, surfaces, porous materials, and so on.

Alternatively, you can use the k_{TF} value associated with the self-weighted average density of the system. The self-weighted average is given by the integral of the density squared divided by the integral of the density. This removes the problems connected with large regions of vacuum. Otherwise, you can evaluate the self-weighted average of the screened exchange energy density.

Nonlocal functionals have certain limitations compared with LDA and GGA functionals. For example, there is no known analytical expression for the stress tensor components in the exact exchange formalism. Thus, none of the fully nonlocal potentials can be used to optimize the unit cell of a crystal or

to perform NPT/NPH dynamics (only sX-LDA, HSE03, or HSE06 functionals support stress calculations). It is also possible that the optical properties calculated using these functionals may be inaccurate. This problem is related to the introduction of a fully nonlocal component of the Hamiltonian. The addition of a nonlocal potential breaks the usual expressions for transforming the optical matrix element from the position operator to the momentum operator, because the commutator with the Hamiltonian becomes exceedingly complex ([Asahi et al., 1999](#)). However, even with the significant computational overhead of the screened exchange formalism, it provides a state of the art scheme for predictive studies of electronic and optical properties of crystals.

Tip: Nonlocal functionals are currently implemented only for norm-conserving potentials, not for ultrasoft ones.

Note: There is an important difference between standard DFT calculations with local exchange-correlation potentials and the nonlocal exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Spin Orbit Coupling

Spin orbit coupling between the electron's spin and its orbital angular momentum couples the direction of spin with the underlying lattice. This is a relativistic effect that increases in magnitude with the nuclear charge, Z . For materials with heavy elements a scalar relativistic treatment (that is, one that neglects the spin orbit interaction) is insufficient to model the electronic band structure. In magnetic systems, the spin orbit coupling introduces a preferential direction (or set of directions) for the spin density.

The inclusion of spin orbit coupling is required for the prediction of many physical properties; for example, effective masses in semiconductors (modeling light and heavy holes); the anomalous Hall effect; Berry curvature; topological insulators, and magnetoelectrics.

In the plane waves and pseudopotential model, only the pseudized valence electrons are explicitly modeled. These electrons have a velocity, $v \ll c$, and as such the standard (non-relativistic) Kohn-Sham (KS) equations are appropriate. The spin orbit coupling is included using j -dependent pseudopotentials developed based on work by [Dal Corso et al. \(2005\)](#). These pseudopotentials act on KS spinor wavefunctions and an electron density with a vector spin at each grid point.

LDA+U

DFT can only give access to the ground state properties of a system, even if the exact exchange-correlation potential were known. For electronic excitations to be modeled Kohn-Sham equations must be substituted by the Dyson equation, where instead of the unknown exchange-correlation potential the energy dependent self energy operator is used. This operator often can be represented by the local and energy-independent exchange-correlation potential, in which case one recovers the Kohn-Sham equations for one-electron excitations. However, this approach is not appropriate for a large class of compounds, so-called correlated systems. These systems require a mixture of the Hubbard model theory and DFT. The most popular implementation is known as the LDA+U method as introduced by Anisimov and co-workers ([1991](#)).

The CASTEP implementation of LDA+U adopts a simplified, rotationally invariant approach ([Cococcioni and de Gironcoli, 2005](#), [Dudarev et al., 1998](#)). The only external parameter needed for this approach is the effective value of the on-site Coulomb parameter, U , for each affected orbital. This parameter can be calculated theoretically ([Cococcioni and de Gironcoli, 2005](#)). However, experience shows that the best

results are achieved when the U parameter is allowed to vary depending on the property of interest. CASTEP therefore does not calculate the value of U but uses it as an input parameter.

Symmetry in CASTEP

The original ideas of utilizing space group symmetry in plane-wave total energy calculations can be traced back to the *k290* package (Kunc et al., 1985). The importance of this issue for achieving high performance has long been recognized. Often a high symmetry system has a fairly small unit cell. This means that the Brillouin zone is quite large and a high number of k-points are therefore required for efficient Brillouin zone sampling. This number can be greatly reduced if it is recognized that the contributions to the charge density from wavefunctions with k-vectors that are related by symmetry are related. It is then sufficient to use only one k-point from each star of symmetry-related points. Because the cost of a CASTEP calculation increases linearly with the number of k-points, any symmetry-related reduction in the number of k-points gives a direct computational speedup.

Space group symmetry is also used in CASTEP during geometry optimization. Forces on atoms, the stress tensor and consequently atomic displacements and changes in the cell parameters, are always *symmetrized* so that the space group symmetry can never become lower during a CASTEP calculation. However, CASTEP does not perform symmetry analysis. Instead, it uses symmetry information provided by Materials Studio.

Pseudopotentials

The concept of a pseudopotential is a crucial one for plane-wave total energy methods since the alternative full Coulomb potential of the electron-ion interaction decays too slowly to be accurately represented by a small number of Fourier components.

Another way of looking at the problem is to analyze wavefunctions. Consider a solid as a collection of valence electrons and ion cores. The ion cores contain nuclei and tightly bound core electrons. The valence-electron wavefunctions are orthogonal to core-electron wavefunctions. All-electron DFT methods treat core and valence electrons on an equal footing. In the pseudopotential approach ion cores are considered to be *frozen*. This means that properties of molecules or solids are calculated on the assumption that the ion cores are not involved in chemical bonding and do not change as a result of structural modifications.

All-electron wavefunctions of valence electrons exhibit rapid oscillations in the core region in order to satisfy the orthogonality constraint. It is impractical to represent such functions using plane waves as the size of the basis set would be prohibitive. The pseudopotential approximation replaces core electrons and the strong Coulomb potential by a weaker pseudopotential that acts on a set of pseudo wavefunctions. This potential can be represented with only a small number of Fourier coefficients. Pseudo wavefunctions ideally should have no nodes inside the core regions and thus they only require a small basis set. It is now well known that the combination of the power of plane wave technology and the pseudopotential concept is extremely useful for the description of chemical bonding (for a review see [Srivastava and Weaire, 1987](#)).

Traditionally, pseudopotentials are constructed so as to reproduce faithfully the scattering properties of the full ionic potential. The phase shift produced by the ionic core is different for each angular momentum component (s , p , d , and so on) of the valence wavefunction. Thus, the scattering from the pseudopotential must be angular momentum dependent. The most general form for a pseudopotential is:

Eq. CASTEP 4

$$V_L = \sum |lm\rangle V_l \langle lm|$$

where $|lm\rangle$ are the spherical harmonics and V_l is the pseudopotential for angular momentum l . A pseudopotential that uses the same potential in each angular momentum channel is called a local pseudopotential. Local pseudopotentials are computationally much more efficient than a nonlocal ones, however, only a few elements can be described accurately using local pseudopotentials.

An important concept in the pseudopotential applications is the degree of *hardness* of a pseudopotential. A pseudopotential is considered *soft* when it requires a small number of Fourier components for its accurate representation and *hard* otherwise. Early development of accurate [norm-conserving pseudopotentials](#) quickly showed that the potentials for transition metals and for first row elements (O, C, N, and so on) turn out to be extremely hard ([Bachelet et al., 1982](#); [Kerker, 1980](#)). Various schemes have been suggested to improve convergence properties of norm-conserving pseudopotentials ([Troullier and Martins, 1991](#)). Norm-conserving potentials in CASTEP are generated using the kinetic energy optimization scheme developed by Lin et al., ([1993](#)) and Lee ([1996](#)).

A more radical approach was suggested by Vanderbilt ([1990](#)), which involves relaxing the norm conservation requirement in order to generate much softer pseudopotentials. In the [ultrasoft pseudopotential](#) scheme the pseudo-wavefunctions are allowed to be as soft as possible within the core region, so that the cutoff energy can be reduced dramatically. Ultrasoft potentials (USP) have another advantage besides being much softer than the norm-conserving potentials. The generation algorithm guarantees good scattering properties over a pre-specified energy range, which results in much better transferability and accuracy of the pseudopotentials. USP usually also treats shallow core states as valences by including multiple sets of occupied states in each angular momentum channel. This also adds to high accuracy and transferability of the potentials, although at a price of computational efficiency.

Transferability is the main benefit of the pseudopotential technique over all electron DFT implementations. Pseudopotentials are constructed from a fixed electronic configuration of an isolated atom or ion and thus they reproduce the scattering properties of a nucleus in that particular configuration. They can also be used reliably for any other atomic configuration or in various solid-state environments due to the way in which they are generated, which guarantees the correct scattering properties over a wide energy range. An example of the accuracy that can be achieved across a number of structures and chemical environments is given by Milman et al. ([2000](#)).

Nonlocal pseudopotentials, even in their most efficient separable representation ([Kleinman and Bylander, 1982](#)), still consume a large share of the computational time in pseudopotential total-energy calculations. In addition, the cost of applying nonlocal pseudopotentials in reciprocal space increases with the cube of the number of atoms. Therefore, it becomes one of the dominant operations for large systems. The nonlocality of the pseudopotential, however, extends only over the region occupied by the core of the atom. As the core region is relatively small, especially if the system has a lot of vacuum in it (slab calculations, open zeolite systems, and so on), it is more efficient in this case to apply the pseudopotential in [real space](#). The computational cost of this method increases with the square of the number of atoms and so is preferable for big systems. CASTEP uses the scheme developed originally for norm-conserving potentials ([King-Smith et al., 1991](#)) and was subsequently generalized for the case of ultrasoft pseudopotentials.

The separation of electrons into core and valence creates a problem when treating exchange-correlation interactions. Within the core region of the nucleus the densities of the two subsystems overlap which makes it difficult to cleanly *descreen* the pseudopotential during its generation. The only term in the potential energy operator that is nonlinear with respect to the electron density is the exchange-correlation energy. It has been shown by Louie et al. ([1982](#)) that there is a simple explicit scheme for treating the [nonlinear exchange and correlation interaction](#) between the core and the valence charge densities. This approach leads to significant improvements in the transferability of the potential. In particular, the spin-polarized calculations become noticeably more accurate. The nonlinear core correction (NLCC) term is especially important when semicore states are not explicitly treated as

valences. On the other hand, their explicit inclusion into the valence subsystem essentially removes the need for the NLCC treatment.

Norm-conserving pseudopotentials

The main requirement of the pseudopotential approach is that it reproduces the valence charge density associated with chemical bonds. It has been shown (Hamann et al., 1979) that for pseudo and all-electron wavefunctions to be identical beyond the core radius, R_c , it is necessary for the integrals of squared amplitudes of the two functions be the same. This is equivalent to requiring norm-conservation from pseudo wavefunctions, that is, each should carry exactly one electron. This condition ensures that the scattering properties of the pseudopotential are reproduced correctly.

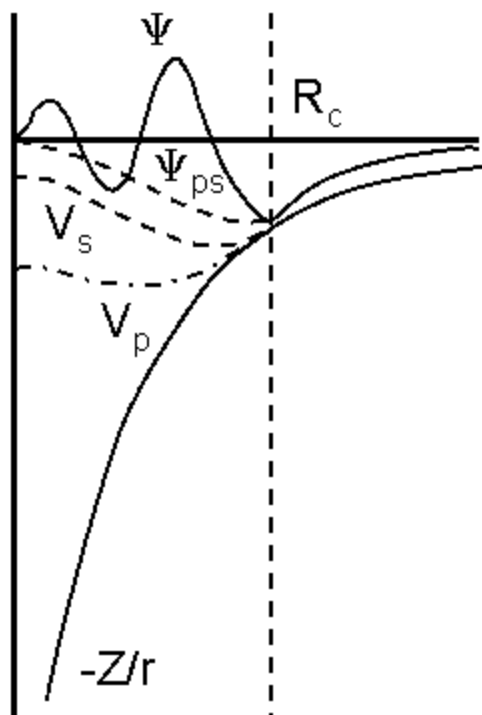


Figure 1. Schematic representation of the all-electron and pseudized wavefunctions and potentials

The typical method for generating pseudopotentials is as follows. All-electron calculations are carried out for an isolated atom in a chosen electronic configuration (not necessarily in the ground state). This provides valence electron eigenvalues and valence electron wavefunctions for the atom (shown as ψ in Figure 1). A parameterized form for the ionic pseudopotential (or the pseudo wavefunction) is chosen. The parameters are then adjusted, so that a pseudoatom calculation with the same exchange-correlation potential as in the all-electron atom gives pseudo wavefunctions, ψ_{ps} (Figure 1), that match the valence wavefunctions outside some cutoff radius, R_c , and pseudo eigenvalues that are equal to the valence eigenvalues. This procedure involves direct inversion of the radial Kohn-Sham equation in the case when the pseudo wavefunction and not the pseudopotential itself are parameterized. If each wavefunction, pseudo and all-electron, is normalized to one, then the norm-conservation constraint is automatically satisfied as a result of matching the wavefunctions outside R_c .

The ionic pseudopotentials are constructed with R_c ranging from one to two times the value of the physical core radius. The smaller the value of R_c , the harder and more transferable the potential. The conflicting effect of R_c creates an obvious trade-off between accuracy and efficiency.

Optimized pseudopotentials

A number of recipes exist for producing pseudopotentials that are optimized with respect to the energy cutoff required in solid-state calculations.

Lin et al. (1993) suggested the following generation scheme based on the earlier work of Rappé et al. (1990):

1. The pseudo wavefunction $\psi_l(\mathbf{r})$ inside a cutoff radius is expressed as:

Eq. CASTEP 5

$$\Psi_l^{ps}(\mathbf{r}) = \sum_{i=1}^4 \alpha_i j_l(q_i r)$$

Where:

$$\frac{j_l'(q_i R_c)}{j_l(q_i R_c)} = \frac{\phi_l'(R_c)}{\phi_l(R_c)}$$

$j_l(q_i r)$ are spherical Bessel functions with $(i-1)$ zeroes between $r=0$ and $r=R_c$. The cutoff radius value is as large as possible, consistent with satisfactory transferability of the potential.

2. The coefficients α_i are determined from minimizing the kinetic energy beyond the cutoff vector q_c :

Eq. CASTEP 6

$$\Delta E_l(\{\alpha_i\}, q_c) = - \int_0^\infty d\mathbf{r} \Psi_l^{ps*}(\mathbf{r}) \nabla^2 \Psi_l^{ps}(\mathbf{r}) - \int_0^{q_c} d\mathbf{q} q^2 |\Psi_l^{ps}(\mathbf{q})|^2$$

where q_c is chosen to be equal to q_4 from Eq. CASTEP 5. Three additional constraints that are satisfied using Lagrange multipliers are the normalization of the pseudo wavefunction and the continuity of the first two derivatives of the pseudo wavefunction at R_c .

3. The standard step of inverting the radial Kohn-Sham equation produces a smooth pseudopotential with optimal convergence properties.

Lee (1996) suggested further enhancements and it is essentially this scheme that was used to generate the bulk of norm-conserving pseudopotentials in the CASTEP database. This generation method eliminates the condition that the second derivative of the pseudo wavefunction must be continuous at a given cutoff radius because it automatically satisfies the second derivative constraint. As a result, the scheme allows one to tune q_c for a given R_c to optimize the accuracy and efficiency of a pseudopotential.

Ultrasoft pseudopotentials

Ultrasoft pseudopotentials (USP) were introduced by Vanderbilt (1990) in order to allow calculations to be performed with the lowest possible cutoff energy for the plane-wave basis set. Since it is understood that there are inherent limits on optimizing the convergence of [norm-conserving pseudopotentials](#), a completely different approach has been designed.

The rationale behind USP is that, in most cases, a high cutoff energy is only required for the plane-wave basis set when there are tightly bound orbitals that have a substantial fraction of their weight inside the core region of the atom. In these situations, the only way to reduce the basis set is to violate the norm-conservation condition by removing the charge associated with these orbitals from the core region. The pseudo wavefunctions are thus allowed to be as soft as possible within the core, yielding a dramatic reduction in the cutoff energy.

Technically, this is accomplished by introducing a generalized orthonormality condition. In order to recover the full electronic charge, the electron density given by the square moduli of the wavefunctions is augmented in the core regions. The electron density can thus be subdivided into a soft part extending through the unit cell and a hard part localized in the core regions.

USP formalism in solid state

The total energy in the USP scheme has the same form as other pseudopotential plane-wave methods, with the nonlocal potential V_{NL} given as:

Eq. CASTEP 7

$$V_{NL} = \sum_{nm,I} D_{nm}^{(0)} |\beta_n^I\rangle \langle \beta_m^I|$$

where the projectors β and coefficients $D^{(0)}$ characterize the pseudopotential and differ for different atomic species. The index I refers to an atomic site. The electron density in the expression for the total energy is given by:

Eq. CASTEP 8

$$n(\mathbf{r}) = \sum_i \left[|\phi_i(\mathbf{r})|^2 + \sum_{nm,I} Q_{nm}^I(\mathbf{r}) \langle \phi_i | \beta_n^I \rangle \langle \beta_m^I | \phi_i \rangle \right]$$

where ϕ are the wavefunctions and $Q(\mathbf{r})$ are the augmentation functions that are strictly localized in the core regions. The ultrasoft potential is fully determined by the local part, $V_{loc}^{ion}(\mathbf{r})$ and by the coefficients $D^{(0)}$, Q , and β . The algorithm that generates these quantities is described [below](#).

The relaxation of the norm-conserving constraint is achieved by introducing a generalized orthonormality condition:

Eq. CASTEP 9

$$\langle \phi_i | S | \phi_j \rangle = \delta_{ij}$$

where S is a Hermitian overlap operator:

Eq. CASTEP 10

$$S = \mathbf{1} + \sum_{nm,I} q_{nm}^i |\beta_n^I\rangle \langle \beta_m^I|$$

where coefficients q are obtained by integrating $Q(\mathbf{r})$. Kohn-Sham equations can be rewritten for the USP case as:

Eq. CASTEP 11

$$H |\phi_i\rangle = \varepsilon_i S |\phi_i\rangle$$

where H can be presented as a sum of kinetic energy and local potential:

Eq. CASTEP 12

$$H = T + V_{eff} + \sum_{nm,I} D_{nm}^I |\beta_n^I\rangle \langle \beta_m^I|$$

where V_{eff} contains $V_{loc}^{ion}(\mathbf{r})$, Hartree and exchange-correlation terms. All the terms arising from the augmented part of the electron density are grouped with the nonlocal part of the pseudopotential ([Eq. CASTEP 7](#)) by defining new coefficients:

Eq. CASTEP 13

$$D_{nm}^I = D_{nm}^{(0)} + \int d\mathbf{r} V_{eff}(\mathbf{r}) Q_{nm}^I(\mathbf{r})$$

The difference compared with the norm-conserving case is the presence of the overlap operator S , the wave-function dependence of the coefficients D and the fact that the number of projector function β is typically twice as large. A number of calculations related to augmentation charges can be carried out in real space because of the localized nature of the function involved, so that the overall impact of these extra steps on efficiency is not large.

Further technical details of the USP implementation, including expressions for the derivatives of the total energy, can be found in Laasonen et al. (1993).

Pseudopotential generation

As in the [norm-conserving case](#), an all-electron calculation is carried out on a free atom, leading to a screened atomic potential, $V_{AE}(r)$. For each angular momentum a set of reference energies, ε_l , is chosen. Typically two reference energies are sufficient. These energies should cover the range over which good scattering properties are required. At each reference energy the solution of the radial Kohn-Sham equation which is regular at the origin is obtained. Next cutoff radii R_{cl} are chosen and for each all-electron wavefunction ψ generated above, a pseudo wavefunction ϕ is constructed. The only constraint is that it should join smoothly to ψ at R_{cl} . A smooth local potential, $V_{loc}(r)$, is generated to match $V_{AE}(r)$ smoothly at a cutoff radius, R_{loc} . An auxiliary radius, R , is defined to be slightly higher than all of the core radii. Finally, the local orbitals are formed (they vanish beyond R):

Eq. CASTEP 14

$$|\chi_n\rangle = (\varepsilon_n - T - V_{loc}) |\phi_n\rangle$$

and their matrix of inner products:

$$B_{nm} = \langle \phi_n | \chi_m \rangle$$

It is now possible to define the quantities needed for the solid state calculation ($V_{loc}^{ion}(\mathbf{r})$, $D^{(0)}$, Q , and β):

Eq. CASTEP 15

$$Q_{nm}(\mathbf{r}) = \Psi_n^*(\mathbf{r}) \Psi_m(\mathbf{r}) - \phi_n^*(\mathbf{r}) \phi_m(\mathbf{r}); q_{nm} = \int d\mathbf{r} Q_{nm}(\mathbf{r})$$

Eq. CASTEP 16

$$|\beta_n\rangle = \sum_m (B^{-1})_{nm} |\chi_m\rangle$$

and $V_{loc}^{ion}(\mathbf{r})$, $D^{(0)}$ are produced using a descreening procedure:

Eq. CASTEP 17

$$V_{loc}^{ion}(\mathbf{r}) = V_{loc}(\mathbf{r}) - V_H(\mathbf{r}) - V_{xc}(\mathbf{r})$$

Eq. CASTEP 18

$$D_{nm}^{(0)} = B_{nm} + \varepsilon_m q_{nm} - \int d\mathbf{r} V_{loc}(\mathbf{r}) n(\mathbf{r})$$

Note: The [non-linear core correction term](#) can be introduced in the descreening procedure, [Eq. CASTEP 17](#), in exactly the same way as in the norm-conserving case.

Note: The formalism described above is based on the non-relativistic Schroedinger approach. With CASTEP you can also use a scalar-relativistic approach either as a [Koelling-Harmon \(1977\)](#) scheme or as its approximation commonly referred to as ZORA, zeroth order regular approximation ([Lenthe et al. 1994](#)).

The following conditions are satisfied in this scheme:

- The pseudo eigenvalues are equal to the all-electron ones, and the corresponding orbitals match exactly outside the core radii.
- The scattering properties are correct at each reference energy. Thus, the transferability can be systematically improved by increasing the number of such energies.
- The valence charge density is precisely equal to the all-electron valence density in the reference configuration.

Nonlinear core correction

The nonlinear core correction (NLCC) was first proposed by Louie et al. ([1982](#)) as a way of obtaining accurate pseudopotential descriptions of magnetic systems. It has been shown, however, that NLCC is equally important for spin non-polarized systems with semicore electrons.

The reason that the NLCC is required is found in the total energy expression in DFT:

Eq. CASTEP 19

$$E_{tot} = T\{\rho\} + E_{ion}\{\rho\} + E_{ee}\{\rho\} + E_{xc}\{\rho\}$$

In the pseudopotential formalism, the charge density is divided into core and valence contributions. The energy of the core is assumed to be constant and is subtracted out. Thus, in [Eq. CASTEP 19](#) above the total charge density is replaced by a (pseudo) valence charge density and E_{ion} is evaluated using pseudopotentials.

As a result all interaction between core and valence electrons is transferred to the pseudopotential. This implies linearization with respect to charge density which can only be an approximation to the kinetic energy and the *explicitly* nonlinear exchange-correlation energy.

This linearization is obviously a good approximation when core and valence densities are well separated in space. However, if there is significant overlap between the two densities, it will be the source of systematic errors and will lead to reduced transferability of the potential.

The solution to the NLCC problem lies in a modifying the pseudopotential generation procedure and the solid-state algorithm. In a typical generation scheme a screened atomic potential V^l is produced for each angular momentum channel subject to certain constraints, for example norm-conservation, matching eigenvalues to all-electron values, and so on.

These screened potentials give rise to atomic pseudowavefunctions that represent valence states only. The valence pseudo charge density is constructed from these wavefunctions and is used to descreen the potential to produce the bare ionic potential:

Eq. CASTEP 20

$$V_{ion}^l(\mathbf{r}) = V^l(\mathbf{r}) - V_{ee}[\rho_\nu(\mathbf{r})] - V_{xc}[\rho_\nu(\mathbf{r})]$$

Since the exchange-correlation potential is a nonlinear function of the charge density, it can be shown that this procedure, especially for spin-polarized systems, creates ionic pseudopotentials that are

dependent on the valence configuration. Louie et al. (1982) suggested substituting Eq. CASTEP 20 with the following expression:

Eq. CASTEP 21

$$V_{iob}^l(\mathbf{r}) = V^l(\mathbf{r}) - V_{ee}[\rho_\nu(\mathbf{r})] - V_{xc}[\rho_\nu(\mathbf{r}) + \rho_c(\mathbf{r})]$$

Here the total exchange-correlation potential is subtracted from the screened atomic potential. In addition, the core charge must now be added to the valence charge whenever the exchange-correlation potential is calculated. This additional atomic information has to be passed on to CASTEP and the core charge is deemed to be the same in all applications. A drawback of this is that the core charge is difficult to represent accurately on the Fourier grid used in pseudopotential calculations. Furthermore, the core density is usually bigger than the valence density, so its presence might mask effects related to valence charge density.

The next step in developing the formalism was to introduce the partial core correction. This approach recognizes the fact that only the area of overlap between the core and valence densities is of interest. Core density close to the nucleus is of no consequence although this is precisely the part of the core density that causes the problems described above. Partial NLCC replaces the full core density with a function that coincides with ρ_c outside a certain radius, and falls off smoothly toward the nucleus.

CASTEP uses a partial core correction with numerical core density in the case of ultrasoft pseudopotentials for certain elements. The database of norm-conserving potentials does not, however, include NLCC information.

Real-space representations of pseudopotentials

The nonlocality of the pseudopotential only extends over the region occupied by the core of the atom. As the core region is relatively small, it should be possible to deal efficiently with the nonlocality of the pseudopotential by working in real space. Only a small number of operations should be required to project the angular momentum components of each wavefunction in the core of each atom.

Furthermore, the number of operations needed to project the angular momentum components of a single wavefunction around a single atom in real space is independent of the size of the system, leading to better scaling with system size than in the reciprocal space projection scheme. The computational cost of the real-space implementation increases with the square of the number of atoms, compared with the cubic relationship that exists for reciprocal space projection methods (Payne et al., 1992).

CASTEP uses the scheme developed originally for norm-conserving potentials (King-Smith et al., 1991) and subsequently generalized for the case of ultrasoft pseudopotentials. The reciprocal-to-real space transformation involves the following steps:

- Select the plane wave cutoff, G_{max} , which is to be used in the solid-state calculation.
- Set $\chi_l(q) = V_l(q)$ for $0 < q < G_{max}$ and $\chi_l(q) = 0$ for $q > \gamma$, where γ is the difference between the ideal Fourier grid size with no wrap-around errors for potential evaluation (at least $4G_{max}$). The Fourier transform of the pseudopotential $V_l(q)$, is defined as:

Eq. CASTEP 22

$$V_l(q) = \int_0^\infty r^2 V_l(r) j_l(qr) dr$$

where $V_l(r)$ is the original nonlocal projector and $j_l(qr)$ is the spherical Bessel function.

- Select a real-space cutoff radius, R_0 . Generally this is about $1.5-2.0 \times R_c$, where R_c is the core radius used in pseudopotential generation.
- Variationally select $\chi_l(q)$ in the intermediate region, $G_{max} < q < \gamma$ by minimizing:

Eq. CASTEP 23

$$I = \int_{R_0}^{\infty} [r\chi_l(r)]^2 dr$$

The object of this step is to achieve the best possible convergence of the modified potential in real space.

- Transform $\chi_l(q)$ back to real space to get $\chi_l(r)$ which is now used in the real-space evaluation of nonlocal potential matrix elements in solid-state calculations.

The modified real-space projectors are no longer identically zero outside R_c , although the minimization in [Eq. CASTEP 23](#) ensures the best possible convergence compatible with the removal of the wrap around error. A quantitative measure of the error introduced by the transformation is given by:

Eq. CASTEP 24

$$W_l(\mathbf{k} + \mathbf{G}) = \int_0^{R_0} r^2 \chi_l(r) j_l(|\mathbf{k} + \mathbf{G}| r) dr$$

This error function should be small (less than 0.001) for all wavevectors, q , and can be inspected in the CASTEP output file.

One should bear in mind that the use of real-space scheme represents an approximation and that more accurate results are obtained with the reciprocal-space version. The accuracy of the real-space transformation is controlled by the value of the cutoff radius, R_0 . The default set of these values in CASTEP is designed to be for accuracy rather than performance. It is advisable to carry out independent tests on small systems before embarking on large-scale calculations with drastically reduced R_0 values.

The real space transformation of the pseudopotential depends on the cutoff energy for plane wave basis set, and thus it is not possible to precalculate real-space projectors in the same way as the reciprocal space potentials (which are provided in CASTEP database).

Plane wave basis set

Bloch's theorem states that the electronic wavefunctions at each k-point can be expanded in terms of a discrete plane-wave basis set. In principle, an infinite number of plane waves is required for such an expansion. However, the coefficients, $C_{\mathbf{k} + \mathbf{G}}$, for the plane waves with small kinetic energies, $|\mathbf{k} + \mathbf{G}|^2$, are more important than those with large kinetic energies. Thus, the plane wave basis set can be truncated to include only plane waves that have kinetic energies that are smaller than some particular cutoff energy as illustrated in [Figure 1](#) (the radius of the sphere is proportional to the square root of the cutoff energy).

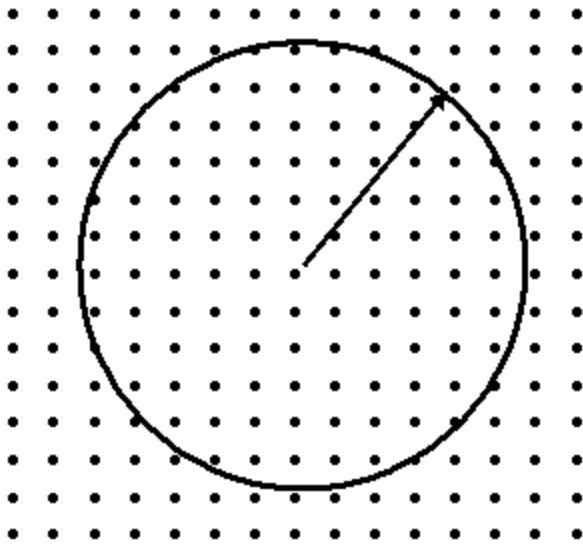


Figure 1. Schematic representation of the cutoff energy concept

Such that:

$$E_{cut} = \frac{1}{2} G_{max}^2$$

The truncation of the basis set at a finite cutoff energy will lead to an error in the computed total energy and its derivatives. It is possible to reduce the magnitude of the error in a systematic way by increasing the value of the cutoff energy. In principle, the cutoff energy should be increased until the calculated total energy converges within the required tolerance. This would be the recommended procedure if, for example, you were conducting a phase stability study where the absolute values of total energies of different structures are compared. However, the energy differences for the *same* structure converge at much lower cutoff energies than the total energy itself. This is due to the cancellation of errors and allows one to use moderate basis sets for reliable geometry optimization or molecular dynamics studies. These arguments are also valid for the convergence testing of Brillouin zone sampling.

Finite basis set correction

One of the difficulties associated with the use of plane-wave basis sets is that the number of basis states changes discontinuously with cutoff energy. In general these discontinuities will occur at different cutoffs for different k-points in the k-point set. In addition, at a fixed cutoff energy, a change in the size or shape of the unit cell will cause discontinuities in the plane wave basis set. This problem can be reduced by using a denser k-point set, so that the weight attached to any particular plane wave basis state is reduced. However, the problem is still present even with quite dense k-point samplings. It can be handled approximately by applying a correction factor that accounts for the difference between the number of a states in a basis set with an infinitely large number of k-points and the number of basis states actually used in the calculation ([Francis and Payne, 1990](#)).

The finite basis set correction is of the utmost importance when cell optimization is performed with a basis set that is not absolutely converged. For example, the norm-conserving silicon pseudopotential is sufficiently soft and provides accurate results with a cutoff energy for plane waves of about 200 eV. However, if one calculates the equation of state using this cutoff (that is, the volume dependence of the total energy and pressure), the volume that corresponds to the minimum in total energy does not coincide with the volume that gives zero pressure. As one repeats such EOS calculations at progressively higher cutoff energies and with better k-point sampling, the difference between the two volume values

becomes smaller and smaller. In addition, the E-V curve calculated at low cutoff energy is jagged but becomes more and more smooth as the cutoff energy is increased. The reason for the jagged appearance of the E-V curve is the discontinuous change in the number of plane waves used at the same cutoff energy but for different lattice constants. The finite basis set correction, when added to the total energy, allows one to perform calculations with a fixed number of basis states and to interpolate the results as if the more physical condition of a fixed energy cutoff were used. A detailed description of the recommended use of this technique can be found in Milman et al. (1994).

The only parameter that must be known in order for this correction term to be evaluated is $dE_{tot}/d \ln E_{cut}$, where E_{tot} is the total energy of the system and E_{cut} is the cutoff energy. CASTEP can calculate this term automatically or you can input this parameter manually.

The value of the $dE_{tot}/d \ln E_{cut}$ gives a good indication of the convergence of the calculation with respect to the energy cutoff and k-point sampling. When its value per atom (that is, the value reported in the CASTEP output file divided by the number of atoms) is smaller than 0.01 eV/atom, the calculation can be considered very well converged. A value of 0.1 eV/atom is sufficient for most calculations.

Self-consistent electronic minimization

CASTEP offers a choice of methods for electronic relaxation. The default method is the most efficient and is based on density mixing (Kresse and Furthmuller, 1996). In this scheme, the sum of electronic eigenvalues is minimized in the fixed potential instead of the self-consistent minimization of the total energy. The new charge density at the end of the minimization is mixed with the initial density and the process is repeated until convergence is reached. A number of options are supported for this scheme: linear mixing, Kerker mixing, Broyden mixing, and Pulay mixing, in order of increasing robustness. The conjugate gradient-based approach is used to minimize the sum of eigenvalues. A slightly more elaborate scheme that involves separate mixing of spin density has been developed for spin-polarized calculations.

CASTEP also supports a more traditional scheme for electronic relaxation, involving minimization of the total energy. The electronic wavefunctions are expanded using a plane-wave basis set and the expansion coefficients are varied so as to minimize the total energy. This minimization is performed by using an all-bands method that allows simultaneous update of all wavefunctions. The scheme uses a preconditioned conjugate gradients technique (Payne et al., 1992).

The main advantage of the density mixing method is its robustness for metallic systems, especially for metallic surfaces. A traditional total energy minimization scheme might become unstable in a metallic system with the cell elongated in one dimension, which is the typical setup for supercell calculations on surfaces. The density mixing scheme converges equally well for insulating and metallic cases, and offers at least a factor of three increase in speed for moderately sized insulator systems.

Note: When using the density mixing method, the SCF energy no longer decreases monotonically to the final converged SCF energy and unconverged energies may have values lower than the final converged energy. This behavior is due to the fact that in the density mixing method, the Harris functional for the energy is used, rather than the Kohn-Sham functional. Unlike the Kohn-Sham functional, the Harris functional does not necessarily have a minimum at the SCF solution.

Preconditioning

All electronic relaxation methods in CASTEP use preconditioning to speed up the rate of convergence (Payne et al., 1992). The idea is to find a matrix which, when multiplied with the residual vector, gives the exact error in the wavefunction. Formally, this matrix can be written down as:

Eq. CASTEP 28

$$\frac{1}{\mathbf{H} - \epsilon_n}$$

where ε_n is the exact eigenvalue for the band being optimized. It is not possible to evaluate this matrix, but by recognizing that the kinetic energy dominates the Hamiltonian for large G-vectors, it is possible to approximate the matrix by a diagonal function which converges to G^{-2} for large G-vectors and is constant for small G-vectors. The actual form of the matrix is ([Payne et al., 1992](#)):

Eq. CASTEP 29

$$\mathbf{K}_{GG'} = \delta_{GG'} \frac{27+18x+12x^2+8x^3}{27+18x+12x^2+8x^3+16x^4}$$

where x is the ratio of $|\mathbf{k} + \mathbf{G}|^2$ to the kinetic energy of the given state.

Application of the preconditioning scheme causes all of the large wave-vector components of a wavefunction to converge at nearly the same rate.

Density mixing schemes

CASTEP supports four schemes for generating new starting charge densities from the results of the previous SCF step ([Kresse and Furthmuller, 1996](#)). The simplest is the linear mixing scheme. This method requires one parameter and the output density is produced as a linear combination of the input and output densities on the last iteration.

Kerker mixing recognizes the fact that small-G components of the charge density should be mixed with smaller weights in order to prevent charge sloshing during SCF optimization. The new density is given by:

Eq. CASTEP 30

$$\rho_{new}(G) = \rho_{in}(G) + A \frac{G^2}{G^2 + G_{max}^2} (\rho_{out}(G) - \rho_{in}(G))$$

The Kerker scheme is, consequently, defined by two parameters, the mixing amplitude, A , and the cutoff wavevector, G_{max} .

The most efficient mixing scheme is Pulay's scheme. In this approach, the input charge density and the residual vectors are stored over a number of SCF optimization steps. A new input density is obtained in each step as a linear combination of charge densities of all previous steps. The new density is determined such that it minimizes the normal of the residual vector subject to the constraint of conserving the number of electrons. Pulay's scheme starts with a Kerker-type step, so it is effectively controlled by three parameters: the mixing amplitude, A , the cutoff wavevector, G_{max} , and the depth of the optimization history.

Broyden mixing is very similar to the Pulay scheme, except that it performs a quasi-Newton relaxation instead of DIIS minimization of the residuals.

Treatment of metallic systems

The main difference between metals and insulators, from the technical point of view, is that the number of occupied bands is not the same at different k-points in the Brillouin zone. The number of occupied bands for insulators is calculated as one half the total number of valence electrons, but this approach is not suitable for metals. Partial occupancies are introduced to eliminate discontinuous changes in total energy that are created when an energy band crosses a Fermi level during SCF minimization.

The overall strategy for treating metallic systems in CASTEP is as follows. The number of bands has to be slightly higher than would be required for an insulator. It may be necessary to add more bands if convergence is slow, especially for spin-polarized systems. An artificial electronic temperature is then introduced by assuming Gaussian-like smearing of each energy level ([de Vita, 1992](#)). Occupation numbers are deduced from the ratio of the area of the Gaussian that falls below the Fermi level to its total area. Thus, a level deep in the valence band has an occupation number of 1, a level directly on the Fermi surface has an occupation number of 0.5, and a level high above the Fermi energy is empty. In

some sense, this is the same as giving the Kohn-Sham particles a finite temperature. Therefore, CASTEP uses the Mermin finite temperature expression for the total energy ([Marzari, 1997](#)):

$$E = E_{KS} - TS$$

where:

T is the temperature (that is, smearing width)

S is the Mermin entropy due to the different ways in which the partially filled bands could have been filled

The CASTEP output is as follows. The line

```
Final energy, E = -861.8315373731 eV
```

gives the Kohn-Sham energy, E_{KS} , which ignores the entropy. However, it is the total Mermin free energy that is minimized by CASTEP and reported in the SCF cycles in the line

```
Final free energy (E-TS) = -861.8315374521 eV
```

If you were actually interested in the electronic states at some reasonable nonzero temperature, you would smear the Fermi level with a thermal (that is, Fermi-Dirac) smearing method and the free energy reported by CASTEP would be the value you require.

Note: Temperature equivalent of energy is given by the conversion factor of 11604.5 K/eV; so the default smearing width of 0.1 eV corresponds to a very high temperature of 1160 K.

However, it is often the $T = 0$ K value that is required and the smearing is necessary to improve the convergence of the numerical algorithm. As the smearing ('temperature') is increased, the TS term increases and the free energy, $E_{KS} - TS$, goes down. At the same time, as the entropy contributes more and more to the free energy, the electronic minimization pays less attention to the E_{KS} term, so the final E_{KS} increases. Because the dependence of the free energy and the Kohn-Sham energy on the smearing width is the same (to first order), averaging the two values gives a much better approximation to the $T = 0$ K result:

```
NB est. 0K energy (E-0.5TS) = -861.8315374126 eV
```

The total energy calculated by CASTEP for metals is thereby corrected for the fact that it now includes the artificial electronic entropy contribution. This correction is possible because a closed analytical form for the dependence of the total energy on the smearing width (or electronic temperature), s , exists. In principle, evaluation of $E_{tot}(s \rightarrow 0)$ is necessary in order to obtain a physically meaningful energy. In the past, values for s as low as 0.01 eV have been used to calculate the converged energy. The total energy correction described above allows the use of a much higher smearing width (up to 1 eV), while still giving results converged with respect to s . The advantage is the added stability of the calculation, since occasional Fermi-level crossings do not create instabilities. However, there is no simple expression for a similar correction for either atomic forces or stress on the unit cell.

The error in the forces introduced by this limitation is generally small and acceptable. Nonetheless, geometry optimizations for metals should be performed with some caution. You should use smaller smearing values than for single-point energy runs. The calculated forces will be more accurate, but there is a risk of instability, since changes in atomic geometry are likely to cause reordering of bands and some Fermi-level crossings. Cell optimization is also more difficult for metallic systems, since the stress tensor could be affected by nonphysical contributions from nearly empty conduction bands.

Disorder in solids

Many crystal structures possess static positional disorder. The crystal may either contain fewer atomic species than there are crystallographically equivalent sites to populate, or there might, for example, be

statistical occupancy of a given crystallographic site by more than one type of atom in different unit cells. This positional disorder is typically manifested in site occupancy factors of less than unity for the average unit cell.

Materials Studio allows you to model positional disorder by specifying atom occupancy and by defining mixture atoms.

Atom occupancy

The vast majority of atoms will have an occupancy of unity. However, in the case of an atom on a partially occupied interstitial position, you can specify an occupancy ranging from 0.0 to 1.0.

Atom occupancies can be modified in the Properties Explorer.

Mixture atoms

Atomic sites in a crystal can also be described in terms of a hybrid atom that consists of two or more element types. The relative concentrations can be set for any number of atoms, but the total concentration must not exceed 100%. The mixture atoms description is the most often used representation of solid solutions, metallic alloys, disordered minerals, and so on.

Disorder and first principles calculations

There are a number of different approaches for dealing with disorder in first principles calculations:

- Virtual crystal approximation (VCA): this offers technically the simplest approach, allowing calculations on disordered systems to be carried out at the same cost as calculations for ordered structures. VCA ignores any possible short range order and assumes that on each potentially disordered site there is a virtual atom which interpolates between the behavior of the actual components. This approach neglects such effects as local distortions around atoms and cannot be expected to reproduce the finer details of the disordered structures very accurately.
- Using large ordered supercells followed by configurational averaging: this is a very expensive approach with limited applicability. For example, it is not possible to treat arbitrary and particularly small concentrations.
- Coherent potential approximation (CPA): this method approximates a configurationally random alloy with an effective medium that is determined self-consistently from the condition of stationary scattering. The CPA technique is used extensively with model Hamiltonians with well-known scattering properties or in the context of multiple scattering methods of band structure calculation (KKR, LMTO). CPA is not well suited to total energy calculations or geometry optimization tasks.
- "Computational alchemy": this method uses the perturbation theory to calculate the response to the difference between the true and VCA potentials. This approach is very demanding computationally, as are all linear response calculations.

The basic ideas of the workable VCA implementation for DFT methods, in particular for the pseudopotential-based techniques, were set out by [Bellaiche and Vanderbilt \(2000\)](#). The main statement for the implementation of VCA with ultrasoft potentials can be expressed as:

Eq. CASTEP 86

$$V_{ext}(\mathbf{r}, \mathbf{r}') = \sum_I \sum_{\alpha} w_{\alpha}^I V_{ps}^{\alpha}(\mathbf{r} - \mathbf{R}_{I\alpha}, \mathbf{r}' - \mathbf{R}_{I\alpha})$$

where the total external potential is generated as the sum of the nonlocal potentials of each atomic species, α , taken with the weights, w , of the component atoms in the mixture atom. This means that all the key components of the ultrasoft potentials, that is, the local part, V_{loc} , and the D and Q matrices, are all weighted according to the site occupancies.

The VCA scheme described above has been applied successfully to study disorder in the perovskites Pb (ZrTi)O₃ ([Bellaiche and Vanderbilt, 2000](#)) and BiScO₃-PbTiO₃ ([Iniguez et al., 2000](#)), and Al-Si disorder in silicates such as hollandite and gehlenite ([Winkler et al., 2002](#)).

Note: [Ramer and Rappé \(2000\)](#) suggested an alternative scheme where the pseudopotentials are generated on the fly for the mixture atoms. Their scheme appears to be less readily generalized for the case of more than two disordered species or where the mixture atom's components have different chemical valences.

Limitations of VCA implementation in CASTEP

The VCA approach is not intended as a universal method for conducting studies of disordered materials. It often produces useful results, but it is important to be aware of its limitations.

Theoretical limitations

VCA is not expected to be better than 50% accurate for excess properties of solid solutions, even for the applications that use simple forcefields. The deviation from the Vegard law, for example, can only be reproduced qualitatively for many systems. In fact, CASTEP calculations for NaCl/KCl mixtures with norm-conserving potentials fail to describe even the shape of the excess volume curve (the difference between the calculated volume at a given concentration and the linear combination of the volumes of the end-members). It should be noted that the excess properties are very sensitive to the accuracy of the data for the end-members and, in general, this is not the preferred application of VCA in CASTEP. On the other hand, properties such as the bulk modulus of the NaCl/KCl solid solution are described very well within the same framework (see [Figure 1](#)).

An important aspect of the VCA implementation has not been discussed by the authors of the formalism ([Bellaiche and Vanderbilt, 2000](#)). One should always test the pseudopotentials for the presence of ghost states. They often manifest themselves in the solid state calculations as a strong change in the total energy as a function of the energy cutoff of the plane wave basis set. It seems that the ultrasoft potentials are prone to generating ghost states in the VCA framework, while none of the individual potentials has a ghost state. The NaCl/KCl system could not be studied with the ultrasoft potentials for this very reason - the finite basis set correction calculated for solid solutions was orders of magnitude higher than for the end-members. This is a clear indication of a ghost state in the calculation. There is no easy way of testing the VCA approach for ghost states, so one should always examine the value of the derivative of the total energy as displayed in the output file during the finite basis set correction calculation. It should be of the same order as the derivatives for the end-member structures.

Technical limitations

Atom occupancy cannot be used with the current CASTEP implementation of the virtual crystal approximation (VCA). Partial atom occupancy can be considered as a special case of a mixture atom, where one part of the mixture is an atom of "nothing". This case is not supported for a number of technical and fundamental reasons.

Current implementation of the molecular dynamics algorithms in CASTEP is not yet compatible with the VCA formalism. None of the MD schemes (NVE, NPT, and so on) works for disordered crystals in the current version.

Linear response calculations (phonons, polarizability) are not supported for disordered crystals.

Test results

The VCA implementation in CASTEP is capable of correctly describing a number of mixture atoms, as shown by the results below.

Bulk modulus of NaCl/KCl solid solution

The bulk modulus of the halite-sylvite mixture (NaCl/KCl) has been calculated as a function of concentration by calculating the P - V equation of state for different Na concentration and fitting them with the third-order Birch-Murnaghan analytical expression. The results agree with the experimental data (Figure 1) to better accuracy than is typically achieved for the ordered crystals. The norm-conserving pseudopotentials were used in this study (all other tests described below were carried out with ultrasoft pseudopotentials).

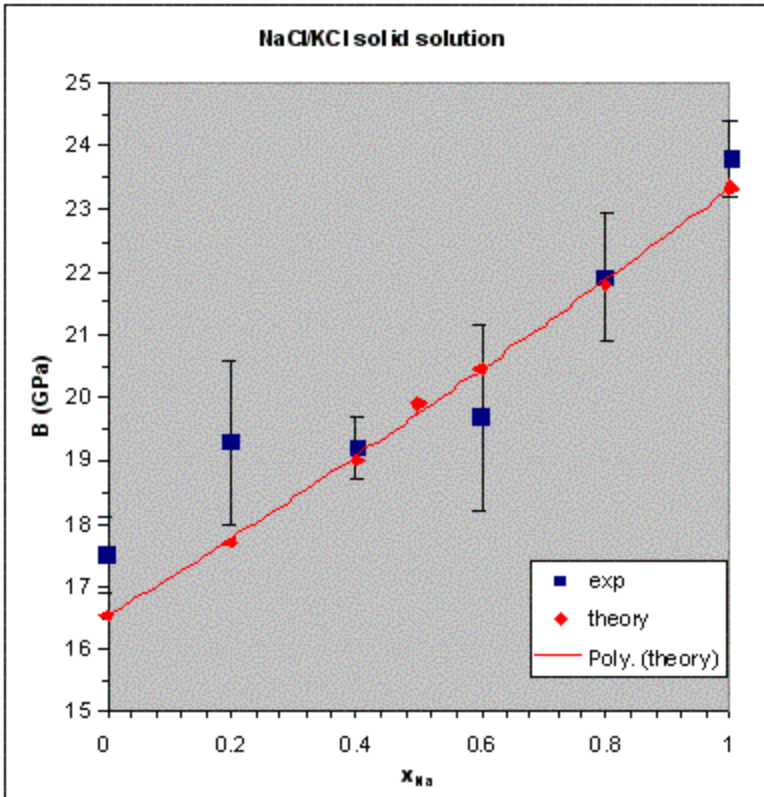


Figure 1. Dependence of the bulk modulus of the NaCl/KCl solid solution on concentration. Experimental data are from [Walker et al. \(2004\)](#). The solid line shows a polynomial fit to the calculated results.

The structure of bicchulite

The structure of the cubic mineral bicchulite, $Ca_2[Al_2SiO_6](OH)_2$, was calculated and compared to the experimental results ([Sahl, 1980](#)). Each Si/Al site is completely disordered in this structure, so the weights are 2/3 and 1/3 for Al and Si atoms, respectively. The lattice parameter is calculated as 8.675 Å, or 1.7% lower than the experimental value. The interatomic distances calculated for the structure are (Si,Al)-O = 1.6968 Å (-1.1%) and Ca-O = 2.3009 Å (-0.4%) and 2.3794 Å (-3.2%). This level of accuracy in the structural description is acceptable for a DFT calculation.

The structure and stability of $Pb(Zr,Ti)O_3$ perovskites

The structures and energies of three different modifications of the 1:1 PZTO ceramics were calculated and the results compared with the experimental data and the earlier VCA results ([Ramer and Rappé, 2000](#)). The modifications studied include tetragonal $P4mm$ and rhombohedral $R3m$ and $R3c$ phases. The results are summarized in the tables below.

Table 1. Structure of the $P4mm$ tetragonal phase of PZTO. Experimental data are from [Frantti et al. \(2000\)](#), earlier VCA results are from [Ramer and Rappé \(2000\)](#).

	a (Å)	c (Å)	c/a	Tiz	O1z	O2z	Pb-O2 (Å)	Ti-O1 (Å)	Ti-O2 (Å)
CASTEP	4.0481	4.1283	1.020	0.5573	0.6112	0.0926	2.600	1.918	2.036
exp.	4.0303	4.1449	1.028	0.5649	0.6110	0.0921	2.508	1.960	2.024
VCA	3.9760	4.1050	1.033	-	-	-	-	-	-

Table 2. Structure of the $R3m$ rhombohedral phase of PZTO. Experimental data are from [Amin et al. \(1981\)](#), earlier VCA results are from [Ramer and Rappé \(2000\)](#).

	a (Å)	α (°)	Ox	Oy	Pbx	Tix	Pb-O (Å)	Ti-O (Å)
CASTEP	4.0749	89.535	-0.0040	0.5080	0.5586	0.0250	2.516	1.973, 2.115
exp.	4.0809	89.676	-0.0046	0.5092	0.5620	0.0216	2.537	1.994, 2.098
VCA	4.0215	90 (fixed)	-	-	-	-	-	-

Table 3. Structure of the $R3c$ rhombohedral phase of PZTO. Experimental data are from [Jirak and Kala \(1988\)](#), earlier VCA results are from [Ramer and Rappé \(2000\)](#).

	a (Å)	α (°)	Ox	Oy	Oz	Pbx	Tix	Pb-O (Å)	Ti-O (Å)
CASTEP	5.7726	59.589	0.4942	0.0284	-0.0180	0.0283	0.2632	2.565	1.979, 2.111
exp.	5.8240	59.600	0.4860	0.0330	-0.0190	0.0341	0.2620	2.487	2.024, 2.109
VCA	5.6790	60 (fixed)	-	-	-	-	-	-	-

Table 4. Energy differences between the three phases of PZTO, in meV per 5 atom cell. Earlier VCA results are from [Ramer and Rappé \(2000\)](#).

	$E(R3m) - E(P4mm)$	$E(R3c) - E(P4mm)$
CASTEP	-4.7	-6.3
VCA	9	6

These results indicate that the structural features are reproduced quite accurately within VCA. Note that the experimental data for rhombohedral phases are for Zr concentrations slightly different from 0.5, since these phases are not stable for the 1:1 composition. The energy differences between the phases are extremely small in recent studies and earlier work by [Ramer and Rappé \(2000\)](#). DFT energies cannot be trusted at this level of accuracy to judge the relative stability of the polymorphs. For example, the fact that the angles were fixed to 90 and 60° in the earlier VCA work suggests that after the full optimization, the rhombohedral phases are likely to become more stable than the tetrahedral phase, in agreement with the CASTEP results ([Table 4](#)).

The structure of leucite

Tetragonal leucite, $KAlSi_2O_6$, contains three different sites with a fully disordered distribution of Al and Si cations. The structure is only slightly distorted with respect to the cubic cell and the accuracy of reproduction of this distortion is a measure of the quality of the VCA description. The results presented below ([Table 5](#)) show exceptionally good agreement with the experimental data. Furthermore, atomic positions are also predicted very accurately. The highest deviation from the experimental data for any

individual fractional coordinate is 0.001 in the CASTEP calculations, compared with maximum deviations of up to 0.007 in the forcefield modeling.

Table 5. Lattice parameters of leucite compared to experimental data ([Mazzi et al., 1976](#)) and the results of forcefield calculations ([Winkler et al., 1991](#)).

	a (Å)	c (Å)	c/a
CASTEP	13.1497	13.8318	1.052
exp.	13.09	13.75	1.050
empirical	12.9884	13.8000	1.062

Geometry optimization

CASTEP supports two schemes for geometry optimization: BFGS and damped molecular dynamics.

BFGS geometry optimization

The main advantage of the BFGS minimizer ([Pfrommer et al., 1997](#)) is the ability to perform cell optimization, including optimization at fixed external stress. The BFGS scheme uses a starting Hessian which is recursively updated during optimization. The CASTEP implementation involves a Hessian in the mixed space of internal and cell degrees of freedom, so that both lattice parameters and atomic coordinates can be optimized.

The LBFGS algorithm (low-memory BFGS) is expected to perform better for large systems. This approach uses only a limited number of inverse Hessian updates to construct a new Hessian; this scheme has been shown to scale linearly in memory, while BFGS scales as a square of the system size ([Aarons, 2011](#)). The LBFGS algorithm also implements a universal sparse preconditioner that accelerates geometry optimization by a factor of two for small systems and a factor of ten for very large ones ([Packwood et al., 2016](#)).

When cell optimization is required, use of a finite basis set correction term is recommended. Calculating the term is not too costly (10-30% of the self-consistent electronic minimization at the first iteration) relative to the advantages that it provides. Cell optimization runs may be problematic if the finite basis set correction is not used or if the energy cutoff is so low that the correction is not accurate. In these circumstances, the optimization run may stop with a message which states that the energy has converged, but that the stress is still non-zero. The minimizer attempts to find the energy minimum rather than the stress zero-point, since the former is more meaningful under the circumstances.

Another potential pitfall is the use of the [Fixed Basis Size Cell optimization](#) setting when the starting geometry is very different from the final one. The finite basis set correction depends on the cell size and shape, although this dependence is disregarded by the minimizer. In addition, the effective cutoff energy changes when the cell geometry is modified with the above setting (it is the number of plane waves that is kept fixed). If this change takes the $dE_{\text{tot}}/d(\ln E_{\text{cut}})$ function far away from the point that was used to evaluate the finite basis set correction, the results will not be accurate. Therefore, you should compare the starting and final geometries and perform a completely new run starting from the final configuration if the difference between the two structures is large.

Constraints

CASTEP can perform geometry optimization with constraints applied. The simplest type of constraint is to fix the atom positions. In CASTEP, this means fixing the fractional coordinates of the atoms.

Note: Atoms on special positions need not be fixed manually as the [symmetry treatment](#) in CASTEP ensures the correct behavior of such atoms.

It is also possible to fix lattice parameters. Once again, it is only necessary to do this for parameters that are not fixed by symmetry. This type of constraint is often useful in phase stability studies when, for example, you want to fix the angles to 90° ([Winkler and Milman, 1997](#)).

It is also possible to impose more general [linear constraints](#) on atomic coordinates. These constraints are specified using a matrix that transforms the Cartesian coordinates of all atoms to the subspace of unconstrained coordinates. This facility is intended for fixing, for example, the z-coordinates of atoms in slab calculations of surface processes.

Non-linear constraints

[Non-linear constraints](#) refer to constraints on interatomic distances (bonds), angles, and torsions. Such constraints can be imposed using the delocalized internals optimizer.

Estimated compressibility

You can facilitate cell optimization convergence by making a reasonable initial estimate of the bulk modulus for the material. The initial changes to lattice vectors are calculated on the basis of this value (and, of course, based on the calculated stress tensor). When the estimated bulk modulus is too high, the steps become smaller than is ideal for the minimizer; therefore, it is conceivably possible that you could reduce the number of geometry optimization steps by reducing this value. On the other hand, too small a bulk modulus for a hard material could result in an oscillating behavior, where the first step is too big. Thus, prior knowledge of the hardness of the material could help to reduce the number of steps required for calculations. The effect of a judicious choice of the initial bulk modulus value is illustrated in the table below (times are given relative to that of the calculation using an initial value of 500 GPa).

Compound	Estimated bulk modulus (GPa)	Number of steps	Relative time
Cubane	5.000	15	0.98
	50.00	15	0.87
	250.0	15	0.82
	500.0	20	1.00
	1000.0	24	1.29
Glycine	5.000	46	1.29
	50.00	42	1.03
	250.0	39	0.92
	500.0	37	1.00
	1000.0	54	1.24
YBa ₂ Cu ₃ O ₇	5.000	12	0.81
	50.00	13	0.74
	250.0	12	0.81
	500.0	17	1.00
	1000.0	13	0.81

TPSD geometry optimization

The BFGS algorithm as implemented in CASTEP uses the assumption that the potential is quadratic to determine an optimal step length per iteration. When this is not the case the BFGS algorithm does not perform well and may take a long time to optimize the structure. A more robust Barzilai-Borwein ([1988](#)) Two-Point Steepest Descent (TPSD) algorithm allows a larger range of problems to be solved. It is specifically more efficient when cell optimization with user-supplied constraints is requested. This scenario describes, for example, optimization of solid-solid interfaces strained to a substrate: that is, the lateral cell parameters and all cell angles are fixed, only the cell dimension in the direction normal to the interface is allowed to relax.

The TPSD algorithm requires only the gradient and position of the system at the current and previous iteration, meaning that a relatively small amount of memory is consumed. From the difference of each value between the iterations, a step size is calculated for use in the direction of the most negative gradient from the current iteration. TPSD optimization has been found to converge reliably in a number of situations where the BFGS algorithm takes too long to converge.

Damped molecular dynamics

Damped [molecular dynamics](#) presents an alternative method for geometry minimization that involves only internal coordinates (the cell parameters have to be fixed). The method uses the critical damping regime as a way of dealing with the ground state. The regime can be implemented either by using one damping coefficient for all degrees of freedom (coupled modes) or by using different coefficients for different degrees of freedom (independent modes). The latter approach allows you to freeze all modes, both fast and slow, simultaneously. Alternatively, you can perform steepest descents damping with a fixed coefficient. However, this is a less efficient approach. Indeed, it is not, strictly speaking, a molecular dynamics technique, since it solves first-order equations of motion and not second-order equations.

Both independent modes and coupled modes damped molecular dynamics runs can be performed with a bigger time step than undamped molecular dynamics simulations. When the system gets close to equilibrium, the time step can be increased even further, since the fast modes freeze out before the slow ones. CASTEP can automatically adjust the time step, leading to increased efficiency of the algorithm. It is also recommended that you recalculate the damping coefficients periodically during a damped molecular dynamics run. A full description of the method implemented in CASTEP can be found elsewhere ([Probert, 2003](#)).

Dynamics

Molecular dynamics (MD) involves the stepwise integration of Newton's equations from a given starting point. It is the most natural method of performing equilibrium statistical-mechanical calculations using a simulation. Additionally, MD may be used to explore conformations, such as molecular adsorption sites on a surface. If frictional forces are added to the equations of motion, Langevin dynamics becomes possible, as does geometry optimization using damped MD. Finally, extended Lagrangian methods allow thermostatic control of the temperature.

Molecular dynamics in total-energy DFT schemes is implemented in essentially the same way as in conventional forcefield based methods. The main difference is that the energy and atomic forces are derived by solving DFT equations rather than from empirical potentials of interatomic interactions. Electrons are kept on the Born-Oppenheimer surface by means of explicit electronic structure optimization after each MD step. A side effect of this is that evaluation of force and energy from first principles is always the most computationally expensive part of *ab initio* MD. As a result, the efficiency of the MD step itself has no impact on the speed of the calculation.

MD in CASTEP is based on the velocity Verlet algorithm for integration of the equation of motion. The default time step can be as high as 1 fs with this algorithm because of its numerical stability and the conservation of the constant of motion.

The efficiency of the method is due in large part to the introduction of wavefunction extrapolation between MD steps ([Arias et al., 1992](#)). In addition, charge density extrapolation ([Alfe, 1999](#)) has been introduced.

Wavefunctions and density extrapolation

The main idea behind the interpolation schemes is to provide a good starting model of the electronic structure for the SCF optimization, after the geometry change. This can be achieved by using the multi-linear extrapolation as proposed by Arias et al. ([1992](#)).

The problem with wavefunction interpolation is that wavefunctions may be multiplied by an arbitrary phase factor or ordered in different ways in two contiguous steps. So, before the extrapolation is performed, the two subspaces $\{\psi_{n,\mathbf{k}}(t)\}$ and $\{\psi_{n,\mathbf{k}}(t-dt)\}$ are aligned so that $\sum_{n,\mathbf{k}} |\psi_{n,\mathbf{k}}(t) - \psi_{n,\mathbf{k}}(t-dt)|$ is minimized.

Then the wavefunctions at the next time step, $t+dt$, can be written as:

Eq. CASTEP 31

$$\Psi_{n,\mathbf{k}}(t + dt) = \Psi_{n,\mathbf{k}}(t) + \alpha [\Psi_{n,\mathbf{k}}(t) - \Psi_{n,\mathbf{k}}(t - dt)] + \beta [\Psi_{n,\mathbf{k}}(t - dt) - \Psi_{n,\mathbf{k}}(t - 2dt)]$$

and similarly for the charge density:

Eq. CASTEP 32

$$\rho(t + dt) = \rho(t) + \alpha [\rho(t) - \rho(t - dt)] + \beta [\rho(t - dt) - \rho(t - 2dt)]$$

The coefficients α and β are calculated by determining the best quadratic extrapolation of the atomic positions. This extrapolation scheme not only speeds up the calculation but also improves conservation of the constant of motion and dramatically reduces the "electronic drag" effect ([Payne et al., 1992](#)).

An improvement suggested by Alfe ([1999](#)) recognizes the fact that the charge density is mostly determined by the superposition of the atomic charge densities. Therefore one can write:

Eq. CASTEP 33

$$\rho(t) = \rho_{at}(t) + \delta\rho(t)$$

where $\rho(t)$ is the self-consistent charge density at time t , and $\rho_{at}(t)$ is the sum of the atomic charge densities. The charge at time $t+dt$ is simply extrapolated as:

Eq. CASTEP 34

$$\rho(t + dt) = \rho_{at}(t + dt) + \delta\rho(t + dt)$$

where the change of $\delta\rho$ is given by:

Eq. CASTEP 35

$$\delta\rho(t + dt) = \delta\rho(t) + \alpha [\delta\rho(t) - \delta\rho(t - dt)] + \beta [\delta\rho(t - dt) - \delta\rho(t - 2dt)]$$

The atomic charge density can be calculated exactly and cheaply using the same methods as for [Mulliken population analysis](#). The resultant scheme includes extrapolation of wavefunctions using [Eq. CASTEP 31](#), extrapolation of charge density *difference* using [Eq. CASTEP 35](#) and recalculation of the atomic charge densities.

Experience shows that the second-order extrapolation scheme described above is not necessarily the best or the fastest algorithm. CASTEP therefore offers a selection of extrapolation schemes that differ in the way the coefficients are selected: 1st order extrapolation with variable coefficients; 2nd order

extrapolation with variable coefficients; alternating first and second order extrapolation steps with variable coefficients; and similar combinations of 1st and 2nd order schemes with fixed coefficients. The actual setting is controlled by the values of the `MD_EXTRAP_FIT` keywords in the `.param` file. The fixed coefficient scheme is based essentially on a Taylor expansion, while the variable coefficients schemes are based on the best fit between extrapolated and MD-predicted atomic coordinates. It has been shown that the accuracy of wavefunction extrapolation improves greatly when the coefficients are chosen based on the extrapolation of atomic coordinates.

An alternative to using wavefunction extrapolation is to use extended Lagrangian formulation, XL-BOMD (Steneteg 2010, Niklasson 2011). The XL-BOMD scheme allows simultaneous propagation of nuclear and electronic degrees of freedom and shows good energy conservation at time steps that are unusually high for first principles calculations.

Ensembles

Integrating Newton's equations of motion allows you to explore the constant-energy surface of a system. However, most natural phenomena occur under conditions where the system is exposed to external pressure and/or exchanges heat with the environment. Under these conditions, the total energy of the system is no longer conserved and extended forms of molecular dynamics are required.

Several methods are available for controlling temperature and pressure. Depending on which state variables (the energy E , enthalpy H (that is, $E + PV$), number of particles N , pressure P , stress S , temperature T , and volume V) are kept fixed, different statistical ensembles can be generated. A variety of structural, energetic, and dynamic properties can then be calculated from the averages or the fluctuations of these quantities over the ensemble generated.

Both isothermal (where heat is exchanged with a temperature bath to maintain a constant thermodynamic temperature) and adiabatic (where no heat exchange occurs) ensembles are available:

Table 1. Thermodynamic ensembles handled by CASTEP

Ensemble
Constant temperature, constant pressure (NPT)
Constant energy, constant volume (NVE)
Constant pressure, constant enthalpy (NPH)
Constant temperature, constant volume (NVT)

NVE ensemble

The constant-energy, constant-volume ensemble (NVE), also known as the *microcanonical ensemble*, is obtained by solving the standard Newton equation without any temperature and pressure control. Energy is conserved when this (adiabatic) ensemble is generated. However, because of rounding and truncation errors during the integration process, there is always a slight fluctuation, or drift in energy.

True constant-energy conditions (that is, without temperature control) are not recommended for the equilibration phase of the simulation because, without the energy flow facilitated by temperature control, the desired temperature cannot be achieved.

However, during the data collection phase, if you are interested in exploring the constant-energy surface of the conformational space, or if for some other reason you do not want the perturbation introduced by temperature- and pressure-bath coupling, this is a useful ensemble.

Nosé NVT dynamics

The Nosé thermostat ([Nosé, 1984](#)) generates deterministic dynamics, with the temperature controlled by a fictitious additional coordinate, s , added to the Lagrangian of the system. The thermostat employs a feedback loop between the instantaneous kinetic energy and the required temperature. The rate of feedback is determined by the mass parameter, Q . This parameter should be chosen so that the natural oscillation frequency of the Nosé coordinate is close to the characteristic frequency of the actual system.

The mass parameter is related to the thermostat relaxation time by:

Eq. CASTEP 36

$$Q = g \frac{k_B T}{\tau^2}$$

Where:

g is the number of degrees of freedom (usually $3N - 3$, where N is the number of atoms)

k_B is the Boltzmann constant

T is the thermostat temperature

τ is the relaxation time.

An improvement on the standard Nosé thermostat (or Nosé-Hoover thermostat) is the Nosé-Hoover chain method, described in detail by [Tuckerman et al. \(2001\)](#). In this method the kinetic energy fluctuations of the thermostat variable are controlled by coupling it to another thermostat variable. The kinetic energy fluctuations of the second thermostat are, in turn, controlled by coupling to a third thermostat, and so on, to form a chain of M thermostats. This new coupling (the Nosé-Hoover "chain" thermostatting mechanism) leads to a more general canonical dynamics method.

Langevin NVT dynamics

The Langevin thermostat generates stochastic dynamics using a Brownian motion model, implemented using the fluctuation-dissipation theorem. It is controlled by the damping time parameter, which controls the rate of decay of fluctuations in the temperature. In practice, this should be chosen such that it is larger than the time scale of any motions of interest. An advantage of the Langevin description is that it can be proved to provide ergodic results. The Nosé thermostat, on the other hand, provides good short term dynamics, but fails to give ergodicity.

Nosé-Hoover-Langevin thermostat

The Nosé-Hoover-Langevin (NHL) thermostat suggested by Leimkuhler et al. ([2009](#)) combines the advantages of the Nosé-Hoover chain method with the ergodicity of Langevin dynamics. In practical terms this thermostat converges to equilibrium faster than the Nosé-Hoover chain method and offers much better conservation of the constant of motion.

NPT ensemble

The constant-temperature, constant-pressure ensemble (NPT) allows control over both the temperature and pressure. The unit cell vectors are allowed to change, and the pressure is adjusted by adjusting the volume of the unit cell.

Pressure is currently controlled in CASTEP using either the [Andersen](#) or [Parrinello-Rahman](#) method.

Note: Only the size, and not the shape, of the unit cell can be changed with the Andersen method.

Temperature can be controlled using either the Nosé or the Langevin thermostat.

NPT is the ensemble of choice when the correct pressure, volume, and densities are important in the simulation. This ensemble can also be used during equilibration to achieve the desired temperature and

pressure, before changing to the constant-volume or constant-energy ensemble when data collection starts.

Andersen method of pressure control

In the [Andersen \(1980\)](#) method of pressure control, the volume of the cell can change, but its shape is preserved by only allowing the cell to change isotropically.

The Andersen method is useful for liquid simulations since the box could become quite elongated in the absence of restoring forces if the shape of the cell were allowed to change. A constant shape also makes the dynamics analysis easier.

However, this method is not very useful for studying materials under anisotropic stress or undergoing phase transitions, which involve changes in both cell lengths and cell angles (in these situations, the [Parrinello-Rahman method](#) should be used where available).

The basic idea is to treat the volume V of the cell as a dynamic variable in the system. The Lagrangian of the system is modified so that it contains a kinetic energy term with a user-defined mass M and a potential term which is the pV potential derived from an external pressure P_{ext} acting on volume V of the system.

Parrinello-Rahman method of pressure and stress control

The Parrinello-Rahman method of pressure and stress control can allow simulation of a structure under externally applied stress. This is useful for studying the stress-strain relationship of materials. Both the shape and the volume of the cell can change, so that the internal stress of the system can match the externally applied stress.

The method is discussed in more detail in [Parrinello and Rahman, 1981](#) and is only summarized here.

The Lagrangians of the system are modified such that a term representing the kinetic energy of the cell depends on a user-defined mass-like parameter \mathbf{W} . An elastic energy term $p\Omega$ is related to the pressure and volume or the stress and strain of the system. The equations of motion for the atoms and cell vectors can be derived from this Lagrangian. The motion of the cell vectors, which determines the cell shape and size, is driven by the difference between the target and internal stress.

With hydrostatic pressure only:

Eq. CASTEP 37

$$L = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{s}}_i' \mathbf{G} \dot{\mathbf{s}}_i - \sum_{i=1}^N \sum_{j>1}^N \phi(\mathbf{r}_{ij}) + \frac{1}{2} W \text{Tr} [\dot{\mathbf{h}}' \dot{\mathbf{h}}] - p\Omega$$

Where:

$\mathbf{h} = \{\mathbf{a} \cdot \mathbf{b} \cdot \mathbf{c}\}$ is the cell vector matrix

$\mathbf{G} = \mathbf{h}' \mathbf{h}$

$\mathbf{r}_i = \mathbf{h} \mathbf{s}_i$

ϕ is the interaction potential

Ω is the volume of the cell

Tr is the trace of a matrix

The dots above some symbols indicate time derivatives and the primes indicate matrix transposition.

With stress, the elastic term $p\Omega$ is replaced by:

Eq. CASTEP 38

$$p(\Omega - \Omega_0) + \Omega_0 \text{Tr} [(\mathbf{S} - p\mathbf{I})\boldsymbol{\varepsilon}]$$

Where:

S is the applied stress

Ω_0 is the initial volume

ε is the strain

ε is also a tensor, defined as:

$$\frac{(h_0'^{-1} \mathbf{G} h_0^{-1} - \mathbf{1})}{2}$$

Note: It is the user-defined variable \mathbf{W} , which determines the rate of change of the volume/shape matrix.

A large \mathbf{W} means a heavy, slow cell. In the limiting case, infinite \mathbf{W} reverts to constant-volume dynamics. A small \mathbf{W} means fast motion of the cell vectors. Although that may mean that the target stress can be reached faster, there may not be enough time for equilibration.

NPH ensemble

The constant-pressure, constant-enthalpy ensemble ([Andersen, 1980](#)) is the analogue of constant-volume, constant-energy ensemble, where the size of the unit cell is allowed to vary.

Constraints

CASTEP supports linear constraints defined using the matrix \mathbf{A}_{ij} :

Eq. CASTEP 39

$$\sum_i^{N_i} \sum_j^{N_c} \mathbf{A}_{ij} \cdot \mathbf{R}_i = C$$

The summations are over N_i ions and N_c constraints. Vector \mathbf{R}_i is the Cartesian position of the i^{th} atom and C is a constant. These constraints can be used to, for example:

- Fix some of the Cartesian coordinates of the atom
- Fix the x-separation between a pair of atoms
- Constrain an atom to lie in a plane
- Constrain the center of mass to be fixed

Example

The example below ([Figure 1](#)) shows the results of an NVE calculation for a nitrogen diatomic molecule with using a time step of 1 fs. The energy conservation is excellent, the energy drift over 500 steps (0.5 ps) is less than 0.1 kcal/mole. The power spectrum of the trajectory gives the vibrational frequency as 2340 cm^{-1} , which is within 1% of the experimental value of 2360 cm^{-1} .

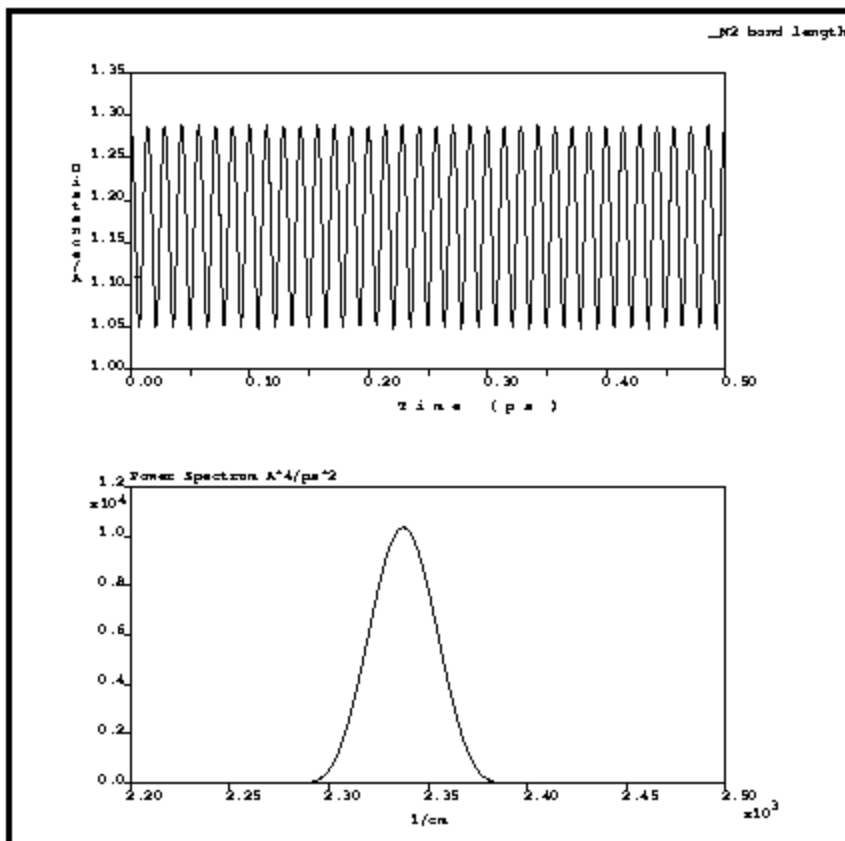


Figure 1. Bond length of the N₂ molecule and power spectrum of the trajectory

Core level spectroscopy

CASTEP can calculate spectroscopic properties of solids that are due to electronic transitions from a core level of an ion to the conduction band (X-ray absorption) and from the valence band to a core level (X-ray emission). This can be used to describe a wide variety of experimental results connected to such processes. Core holes can be created by X-ray or electron incident radiation.

The core level is localized, so core level spectroscopy provides a detailed element-specific picture of the local electronic structure around a given atomic site. There is no contribution from the other atoms in the system, so the electronic states for a specific atom can be investigated.

In the case of anisotropic systems, angular-dependent experiments enable the separation of states with different symmetries for the involved orbitals. An important consequence is that symmetry states, which result solely from chemical bonding, can be studied.

Emission spectroscopy

X-ray emission spectroscopy (XES) is a classical technique used to study the electronic structure of bulk samples. It is ideally suited to these systems due to the large information depth (around 0.1 μm for soft X-rays). In XES the core hole created by an X-ray absorption process is filled by the decay of a valence electron. For this process energy is conserved by the emission of an x-ray photon of matching energy. A selective, resonant excitation of a core hole state at the atomic center of an adsorbate can be used to probe surfaces.

Absorption spectroscopy

Electron energy-loss near-edge structure (ELNES or EELS) and x-ray absorption near-edge structure (XANES) spectroscopies provide information on the unoccupied electronic states by exciting one electron from a core level into an unoccupied state. Scanning transmission electron microscopes with an electron energy-loss spectrometer attached have been used extensively in the study of nanoscale materials, providing information on local composition, structure, and electronic structure. However, the probing electron or x-ray interacts with a system that has been perturbed by the probe itself. The system being studied has had an inner-shell electron removed, leaving a core hole.

Core hole effects

The relaxation of a system with a core hole will affect the observed core level excitation spectra so that interpretation of the experimental spectrum becomes a more challenging task. A satisfactory theory of optical spectra or core excited spectra should calculate two particle electron-hole interactions in a reliable and accessible way. In the core level excitation process, the core hole is localized on a single atomic site. Using an atom with a reduced occupation in the core level in a supercell approximation has been a good and popular description for the calculation of core level spectroscopy using standard density functional theory (DFT).

Recent developments in core-level spectroscopy calculations using the Bethe-Salpeter equation or time-dependent DFT (or a combination of the two) provide more rigorous approaches for a core-level spectra calculation. In these methods many-body effects, such as the broadening of spectra due to electron-hole lifetime, can be taken into account in a natural way. While good agreement with experimental results has been achieved, this necessarily comes with a much greater computational burden in comparison to standard ground state calculations.

A systematic observation of core hole effects and a quantitative estimation of the core hole strength in materials can assist in the simulation and interpretation of core level spectra. Applying empirical rules, a core-level spectrum is not likely to be heavily influenced by core-hole effects, so information on the ground electronic structure of a material can be inferred directly from the experimental spectrum. In this case, traditional ground state calculations should predict the main features of experimental results and allow interpretation of the spectrum. If this is not the case, inclusion of the influence of the core hole is essential in the theoretical simulation. Analysis of experimental results should take into account that near-edge fine structure includes influences in the core excitation processes beyond the ground state electronic structure.

There is an open question regarding the best way of handling the charge of core holes; depending on the nature of the system it might be appropriate to treat the system either as having lost an electron and thus having a charge of 1 or as neutral. Materials Studio assumes the former treatment.

Energy broadening

The ELNES calculation can be performed with an energy resolution far better than that used to obtain experimental results. Therefore, the calculated ELNES must be broadened before comparing it with the experiment. The broadening observed in the experimental spectra has three origins: the lifetime of the core hole, the lifetime of the excited state, and instrumental broadening. A good description of this subject was given by Hebert ([2007](#)).

Instrumental broadening is easiest to simulate: it can be modeled by a Gaussian with a FWHM given by the instrument. For a TEM equipped with a field emission gun, this is usually about 0.6-0.7 eV. Some instruments are equipped with a monochromator to improve energy resolution to about 0.1 eV. In nearly all cases the energy distribution can be modeled by a Gaussian curve.

The broadening by the core hole lifetime depends on the atom and the edge. Values for lifetime broadening are tabulated and can be found in the literature, see Fuggle and Inglesfield ([1992](#)).

Broadening due to the lifetime of the core hole is, however, relatively low for edges accessible in EELS (about 0.2 eV for the Ni or Cu L3 edge). The broadening of core hole lifetimes can be modeled by a Lorentzian ([Fuggle and Inglesfield, 1992](#)).

The broadening by the excited state lifetimes is more complicated. At the edge onset (where the lifetime of the excited state approaches infinity) the broadening is zero and increases with increasing energy. Different methods have been employed to obtain the broadening factor, see Hebert ([2007](#)) for a comparative review. An empirical linear function $\Gamma(E) = 0.1 E$ (where E is the energy above the threshold) gives good results when compared to the experiment - this is the option employed in CASTEP.

Spin-orbit splitting

Experimental spectra record transitions involving core states that are split as a result of the spin-orbit interactions; so one should distinguish between states such as $p_{1/2}$ and $p_{3/2}$ and so on. The CASTEP implementation lacks spin-orbit terms, so the calculations can only produce "generic" spectra for p , d , or f states. In spectroscopic terms this means producing (for example) $L_{2,3}$ spectra rather than just L_2 . The simplest, albeit slightly approximate, way to model experimental spectra is to modify the calculated spectrum as follows:

- Find the experimental value of the spin-orbit splitting of the core states.
- Generate an approximate L_3 spectrum by shifting the L_2 spectrum.
- Apply intensity scaling based on the occupancy of the respective electronic shell. The intensity ratios for L spectra are 2:4 and for M spectra 4:6, and so on.
- Add the two shifted and scaled spectra together.

For a more general discussion of the core level spectroscopy and details of its implementation see S.-P. Gao et al. ([2008](#)) and references.

Phonon density of states

Phonon density of states (or vibrational density of states) is defined in exactly the same way as the electronic densities of state, see the DOS equation. The integral over the Brillouin zone goes over all $3N$ phonon bands, where N is the number of atoms in the cell. There are two popular conventions regarding normalization of the phonon DOS. Either it can be normalized to unity or to the total number of vibrational modes, $3N$.

The partial (or projected) phonon density of states is determined as a contribution from the given atom to the total phonon DOS. This is a useful concept that allows one to understand the nature of various branches in the phonon spectrum. The contribution to the partial density of states on atom i , from each phonon band, is evaluated using:

Eq. CASTEP 41

$$N_i(E) = \int \frac{d\mathbf{k}}{4\pi^3} |e_j(i)|^2 \delta(E - E_j(\mathbf{k}))$$

where e_j is the eigenvector (normalized to unit length) associated with the mode of energy E_j . The projected density of states is then obtained by summation of these contributions over all phonon bands. By construction all the projected phonon DOS sum up to the true phonon DOS.

Electron localization function

Formulation of electron localization function

The electron localization function (ELF) was introduced by Becke and Edgecombe as a "simple measure of electron localization in atomic and molecular systems" ([Becke and Edgecombe, 1990](#)). Becke and Edgecombe associated the localization of an electron with the probability density for finding a second

like-spin electron near the reference point. For small probability densities, $D(\mathbf{r})$ is also small and the electron is more localized.

Eq. CASTEP 87

$$D(\mathbf{r}) = \sum_i^{\sigma} |\nabla \Psi_i(\mathbf{r})|^2 - \frac{1}{4} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

The Pauli repulsion between two like-spin electrons, described by the size of $D(\mathbf{r})$, is taken as a measure of the electron localization. Using the corresponding factor found for a uniform electron gas, $D_h(\mathbf{r})$, Becke and Edgecombe, defined ELF as:

Eq. CASTEP 88

$$\eta(\mathbf{r}) = \frac{1}{[1 + \chi_{BE}^2(\mathbf{r})]}$$

where

Eq. CASTEP 89

$$\chi_{BE}(\mathbf{r}) = \frac{D(\mathbf{r})}{D_h(\mathbf{r})}$$

$$D_h(\mathbf{r}) = \frac{3}{5} (6\pi^2)^{2/3} \rho(\mathbf{r})^{5/3}$$

Becke and Edgecombe attributed the ratio $\chi_{BE}(\mathbf{r})$ to a dimensionless localization index, calibrated with respect to the uniform electron gas. This reference was chosen arbitrarily, so ELF is only a relative measure of the electron localization. High ELF values show that at the examined position the electrons are more localized than in a uniform electron gas of the same density. For example, when $\eta(\mathbf{r}) = 1/2$ the effect of the Pauli repulsion is the same as in a uniform electron gas of the same density.

The ELF formulation originates from the Hartree-Fock description of electron gas. A formulation for ELF in DFT has been developed by Savin et al. (1992). This DFT-ELF approach evaluates the Pauli kinetic energy density based on the diagonal elements of the one-particle density matrix (the electron density). The Pauli kinetic energy is the energy due to the redistribution of the electrons in accordance with the Pauli principle and is the integral of the Pauli kinetic energy density:

Eq. CASTEP 90

$$t_p(\mathbf{r}) = t(\mathbf{r}) - \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

The Pauli kinetic energy density itself does not resolve the bonding situation. It is an arbitrary division of $t_p(\mathbf{r})$ by the kinetic energy density of a uniform electron gas of the same electron density, this yields all the information:

$$t_h(\mathbf{r}) = c_F \rho(\mathbf{r})^{5/3}$$

where c_F is the Fermi constant:

$$c_F = \frac{3}{10} (3\pi^2)^{2/3}$$

For a closed shell system the ratio:

$$\chi_S(\mathbf{r}) = \frac{t_P(\mathbf{r})}{t_h(\mathbf{r})}$$

is formally identical to the ratio $\chi_{BE}(\mathbf{r})$ in the HF approximation. The same applies for an open shell system, where the kinetic energy densities are computed for the corresponding spin part only. So the ELF formulas based on $\chi_{BE}(\mathbf{r})$ and $\chi_S(\mathbf{r})$ are identical. In the interpretation of Savin and coworkers (1992) ELF is a measure of the influence of Pauli principle as given by the Pauli kinetic energy density, relative to a uniform electron gas of the same density. Similarly, for the original definition ELF does not mirror $t_P(\mathbf{r})$.

How to interpret ELF

The values of ELF are fairly straightforward to calculate but may not be easy to interpret. The ELF website (<http://www.cpfs.mpg.de/ELF/index.php?content=06interpr.txt>) provides a very useful article on physical meanings of ELF and, in particular, on what ELF is not.

Note: ELF is was developed for all electron descriptions. ELF in CASTEP is calculated for valence electrons only, so it might be less meaningful. In particular, ELF values from CASTEP do not span the full range from 0 to 1 - extremely localized or delocalized electrons may be poorly described.

Mulliken population analysis

Mulliken charges and bond populations are calculated according to the formalism described by Segall et al. (1996a and 1996b).

Introduction

A disadvantage of the use of a plane wave (PW) basis set is that, due to the delocalized nature of the basis states, it provides no information regarding the localization of the electrons in the system. In contrast, a Linear Combination of Atomic Orbitals (LCAO) basis set provides a natural way of specifying quantities such as atomic charge, bond population, charge transfer, and so on.

Population analysis in CASTEP is performed using a projection of the PW states onto a localized basis using a technique described by Sanchez-Portal et al. (1995). Population analysis of the resulting projected states is then performed using the Mulliken formalism (Mulliken, 1955). This technique is widely used in the analysis of electronic structure calculations performed with LCAO basis sets.

Formalism

The eigenstates $|\psi_\alpha(\mathbf{k})\rangle$, obtained from the PW calculation when sampling at a given wavevector \mathbf{k} , are projected onto Bloch functions formed from a LCAO basis set $|\phi_\mu(\mathbf{k})\rangle$. In general, such a localized basis set will be neither orthonormal nor complete. Therefore, care must be taken when performing the projection.

The overlap matrix of the localized basis set, $\mathbf{S}(\mathbf{k})$, is defined as:

Eq. CASTEP 63

$$S_{\mu\nu}(\mathbf{k}) = \langle \phi_\mu(\mathbf{k}) | \phi_\nu(\mathbf{k}) \rangle$$

The quality of the projection may be assessed by calculating a *spilling parameter*:

Eq. CASTEP 64

$$\sigma = \frac{1}{N_\alpha} \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\alpha} \langle \psi_\alpha(\mathbf{k}) | (1 - \hat{p}(\mathbf{k})) | \psi_\alpha(\mathbf{k}) \rangle$$

Where:

N_α is the number of PW states

$w_{\mathbf{k}}$ are the weights associated with the calculated k-points in the Brillouin zone

$p(\mathbf{k})$ is the projection operator of Bloch functions with wavevector \mathbf{k} generated by the atomic basis set:

Eq. CASTEP 65

$$\hat{p}(\mathbf{k}) = \sum_{\mu} |\phi_{\mu}(\mathbf{k})\rangle \langle \phi_{\mu}(\mathbf{k})|$$

where $|\phi_{\mu}(\mathbf{k})\rangle$ are the duals of the LCAO basis, such that:

Eq. CASTEP 66

$$\langle \phi_{\mu}(\mathbf{k}) | \phi_{\nu}(\mathbf{k}) \rangle = \langle \phi^{\mu}(\mathbf{k}) | \phi_{\nu}(\mathbf{k}) \rangle = \delta_{\mu\nu}$$

The spilling parameter varies between one, when the LCAO basis is orthogonal to the PW states, and zero, when the projected wavefunctions perfectly represent the PW states.

The density operator may be defined:

Eq. CASTEP 67

$$\hat{p}(\mathbf{k}) = \sum_{\alpha}^{occ} n_{\alpha} |\chi_{\alpha}(\mathbf{k})\rangle \langle \chi^{\alpha}(\mathbf{k})|$$

where n_{α} are the occupancies of the PW states, $|\chi_{\alpha}(\mathbf{k})\rangle$ are the projected PW states $p(\mathbf{k})|\psi_{\alpha}(\mathbf{k})\rangle$ and $|\chi^{\alpha}(\mathbf{k})\rangle$ are the duals of these states. From this operator the density matrix for the atomic states may be calculated as follows:

Eq. CASTEP 68

$$P_{\mu\nu}(\mathbf{k}) = \langle \phi^{\mu}(\mathbf{k}) | \hat{p}(\mathbf{k}) | \phi^{\nu}(\mathbf{k}) \rangle$$

The density matrix $\mathbf{P}(\mathbf{k})$ and the overlap matrix $\mathbf{S}(\mathbf{k})$ are sufficient to perform population analysis of the electronic distribution. In Mulliken analysis ([Mulliken, 1955](#)) the charge associated with a given atom, A , is determined by:

Eq. CASTEP 69

$$Q(A) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\mu}^{onA} \sum_{\nu} P_{\mu\nu}(\mathbf{k}) S_{\nu\mu}(\mathbf{k})$$

and the overlap population between two atoms, A and B , is:

Eq. CASTEP 70

$$n(AB) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\mu}^{onA} \sum_{\nu}^{onB} 2P_{\mu\nu}(\mathbf{k}) S_{\nu\mu}(\mathbf{k})$$

The weight of a band on a given orbital may be calculated by simply projecting the band onto the selected orbital. So, the weight of band α on orbital μ is given by:

Eq. CASTEP 71

$$W_{\alpha\mu}(\mathbf{k}) = \langle \psi_{\alpha}(\mathbf{k}) | \phi_{\mu}(\mathbf{k}) \rangle \langle \phi^{\alpha}(\mathbf{k}) | \psi_{\alpha}(\mathbf{k}) \rangle$$

The contribution of each band α to the density of states is multiplied by the weight $W_{\alpha\mu}(\mathbf{k})$ to get the projected density of states for orbital μ .

The LCAO Basis Set

In this case, the natural choice of basis set is that of pseudo-atomic orbitals, generated from the pseudopotentials used in the electronic structure calculation. These are generated automatically when population analysis is performed. The orbitals are calculated by solving for the lowest energy eigenstates of the pseudopotential in a sphere, using a spherical Bessel basis set.

By default, the basis set used on an atom of a given species is that of the orbitals in the closed valence shell of that species. This is usually a sufficiently good basis set for the purposes of population analysis and partial density of states projection. If the spilling parameter indicates that the basis set does not represent the PW states with sufficient accuracy, the number of orbitals in the atomic basis set may be increased. A spilling parameter in the region of a few percent or less is sufficiently good for population analysis and partial density of states projection. Care should be exercised when increasing the basis set dramatically, as this can lead to artificial transfers of charge.

Implementation details

The elements of the overlap matrix $\mathbf{S}(\mathbf{k})$ are computed in reciprocal space, as the imposition of periodic boundary conditions implies that the orbitals need only be evaluated on a discrete reciprocal space grid. The overlaps between orbitals on different atomic sites are calculated on the same grid with the application of a phase factor. The overlaps between the plane wave states and the basis functions:

Eq. CASTEP 72

$$T_{\alpha\mu}(\mathbf{k}) = \langle \psi_{\alpha}(\mathbf{k}) | \phi_{\mu}(\mathbf{k}) \rangle$$

are also calculated in reciprocal space as this is the natural representation of the plane wave states.

The duals of the orbitals are constructed as follows:

Eq. CASTEP 73

$$|\phi^{\mu}(\mathbf{k})\rangle = \sum_{\nu} S_{\mu\nu}^{-1}(\mathbf{k}) |\phi_{\nu}(\mathbf{k})\rangle$$

The duals of the projected wavefunctions are generated in a similar manner:

Eq. CASTEP 74

$$|\chi^{\alpha}(\mathbf{k})\rangle = \sum_{\beta} \mathbf{R}_{\alpha\beta}^{-1}(\mathbf{k}) |\chi_{\beta}(\mathbf{k})\rangle$$

where $\mathbf{R}(\mathbf{k})$ is the overlap matrix between projected states:

Eq. CASTEP 75

$$R_{\alpha\beta}(\mathbf{k}) = \langle \chi_{\alpha}(\mathbf{k}) | \chi_{\beta}(\mathbf{k}) \rangle = \sum_{\mu\nu} T_{\alpha\nu}(\mathbf{k}) S_{\nu\mu}^{-1}(\mathbf{k}) T_{\beta\mu}^{*}(\mathbf{k})$$

Two auxiliary matrices can be defined for efficiency, namely:

Eq. CASTEP 76

$$\mathbf{U}(\mathbf{k}) = \mathbf{T}(\mathbf{k})\mathbf{S}^{-1}(\mathbf{k})$$

and

Eq. CASTEP 77

$$\mathbf{V}(\mathbf{k}) = \mathbf{R}^{-1}(\mathbf{k})\mathbf{U}(\mathbf{k})$$

These matrices are used to calculate the spilling parameter:

Eq. CASTEP 78

$$\sigma = 1 - \frac{1}{N_\alpha} \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\alpha} \sum_{\mu\nu} T_{\alpha\mu}(\mathbf{k}) S_{\mu\nu}^{-1}(\mathbf{k}) T_{\alpha\mu}^*(\mathbf{k}) = 1 - \frac{1}{N_\alpha} \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\alpha} \sum_{\nu} U_{\alpha\mu}(\mathbf{k}) T_{\alpha\nu}^*(\mathbf{k})$$

Similarly, the density matrix may be straightforwardly calculated as:

Eq. CASTEP 79

$$P_{\mu\nu}(\mathbf{k}) = \sum_{\alpha\beta} \sum_{\kappa\lambda} n_{\alpha}(\mathbf{k}) S_{\mu\nu}^{-1}(\mathbf{k}) T_{\alpha\nu}^*(\mathbf{k}) R_{\alpha\beta}^{-1}(\mathbf{k}) T_{\beta\lambda}(\mathbf{k}) S_{\lambda\nu}^{-1}(\mathbf{k}) = \sum_{\alpha} U_{\alpha\mu}^*(\mathbf{k}) V_{\alpha\nu}(\mathbf{k})$$

In the case of spin dependent systems, the populations of the two spin components are calculated separately and the sum and difference of the atomic and overlap populations are calculated to find the net charge and spin, respectively.

Interpreting the results

It is widely accepted that the absolute magnitude of the atomic charges yielded by population analysis have little physical meaning, since they display a high degree of sensitivity to the atomic basis set with which they were calculated ([Davidson and Chakravorty, 1992](#)). However, consideration of their relative values can yield useful information ([Segall et al., 1996a](#); [Segall et al., 1996b](#); [Winkler et al., 2001](#)), provided a consistent basis set is used for their calculation.

The spilling parameter should be in the region of a few percent or less in order to ensure that the results are reliable. If this is not the case, the number of orbitals in the basis set should be increased with care. If this does not significantly improve the spilling parameter, it may be that atomic orbitals do not provide a good representation of some of the states in the system.

In addition to providing an objective criterion for bonding between atoms, the overlap population may be used to assess the covalent or ionic nature of a bond. A high value of the bond population indicates a covalent bond, while a low value indicates an ionic interaction. A further measure of ionic character may be obtained from the effective ionic valence, which is defined as the difference between the formal ionic charge and the Mulliken charge on the anion species. A value of zero indicates a perfectly ionic bond, while values greater than zero indicate increasing levels of covalency. See Segall et al. ([1996b](#)) for more details.

Care should be taken when interpreting the bond order values for small unit cells. The results will be incorrect whenever an atom is bonded to a number of periodic images of itself. For example, bond orders for the primitive cell of silicon are reported as 3.0, while the same calculation for the conventional cell gives 0.75. The factor of four appears because CASTEP sums up the bond orders for the four bonds that link the Si atom at the origin with the periodic images of itself, in the primitive cell. A manual analysis of the multiplicities is required in such cases, specifically: determine the number of bonds to periodic images of the same atom and divide the bond order by that number.

Note: The physical meaning of Mulliken charges or bond populations for metallic systems is unclear. This calculation is allowed, but the scientific interpretation of the results will be left to the user.

Hirshfeld charge analysis

Hirshfeld charges ([Hirshfeld, 1977](#)) are defined relative to the deformation density, this is the difference between the molecular and unrelaxed atomic charge densities.

For quantitative descriptions of charge distributions in molecules or solids it is convenient to divide a system into well-defined atomic fragments. A general and natural choice is to share the charge density at each point between the atoms, in proportion to their free-atom densities at the corresponding distances from the nuclei. This prescription yields well-localized bonded-atom distributions each of

which closely resembles the molecular density in its vicinity. Integration of the atomic deformation densities - bonded minus free atoms - defines the net atomic charges and multipole moments which concisely summarize the molecular charge reorganization. This permits calculation of the external electrostatic potential and the interaction energy between molecules or between parts of the same molecule.

Calculating NMR shielding tensors using pseudopotentials

A uniform external magnetic field, \mathbf{B} , applied to a sample induces an electric current. In an insulating non-magnetic material, only the orbital motion of the electrons contributes to this current. In addition, for the field strengths typically used in NMR experiments, the induced electric current is proportional to the external field, \mathbf{B} . This first-order induced current, $\mathbf{j}^{(1)}(\mathbf{r})$, produces a non-uniform magnetic field:

Eq. CASTEP 42

$$\mathbf{B}_{in}^{(1)}(\mathbf{r}) = \frac{1}{c} \int d^3r' \mathbf{j}^{(1)}(\mathbf{r}') \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}$$

The shielding tensor, $\sigma(\mathbf{r})$, connects the induced magnetic field to the applied magnetic field:

Eq. CASTEP 43

$$\mathbf{B}_{in}^{(1)}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}$$

and the isotropic shielding is given by:

Eq. CASTEP 44

$$\sigma(\mathbf{r}) = \frac{\text{Tr} \left[\overleftrightarrow{\sigma}(\mathbf{r}) \right]}{3}$$

All-electron magnetic response with pseudopotentials

Information about $\sigma(\mathbf{r})$ at nuclear positions can be obtained from NMR experiments. In CASTEP, the first-order induced current, $\mathbf{j}^{(1)}(\mathbf{r})$, is calculated and then used to evaluate the induced magnetic field, $\mathbf{B}^{(1)}$ through Eq. 42. Calculations are performed with the gauge-including projector augmented-wave method (GIPAW) developed by Pickard and Mauri (2001). The projector augmented-wave formalism originally introduced by Blöchl (1994) makes it possible to obtain expectation values of all-electron operators in terms of pseudo-wavefunctions coming from a pseudopotential calculation and the GIPAW formalism reconciles the requirement of translational invariance of the crystal in a uniform magnetic field with the localized nature of Blöchl's projectors. The theory was initially applied with Troullier-Martins norm-conserving pseudopotentials (Pickard and Mauri, 2001) and has been extended subsequently to the case of ultrasoft pseudopotentials (Yates, 2007).

The first-order perturbation wavefunction, $\Psi^{(1)}$:

Eq. CASTEP 45

$$\left| \bar{\Psi}_n^{(1)} \right\rangle = G(\epsilon_n) \bar{H}^{(1)} \left| \bar{\Psi}_n^{(0)} \right\rangle$$

is proportional to the magnetic perturbation, $H^{(1)}$, which, in pseudopotential calculations, contains a contribution due to the non-locality of the pseudopotential, in addition to the usual term:

Eq. CASTEP 46

$$\frac{1}{2c} \mathbf{L} \cdot \mathbf{B}$$

Calculation of perturbed wavefunctions

In order to obtain the first-order perturbation wavefunction $\Psi^{(1)}$, the application of the Green function in [Eq. 46](#) is performed in CASTEP by solving a system of linear equations:

Eq. CASTEP 47

$$\left(\epsilon_n - \bar{H}^{(0)} \right) \left| \bar{\Psi}_n^{(1)} \right\rangle = Q \bar{H}^{(1)} \left| \bar{\Psi}_n^{(0)} \right\rangle$$

where Q is the projection operator onto the unoccupied Hilbert subspace. The system is solved by a conjugate gradient minimization scheme, whereby the tedious summation over unoccupied states is avoided. The method is, thus, comparable in computational cost to the calculation of the ground-state electronic structure.

NMR properties of molecules and crystals

The calculation of the induced current involves evaluation of expectation values of the position operator, whose definition for extended systems is not straightforward. Two approaches have been developed ([Pickard and Mauri, 2001](#)) and implemented in CASTEP. For translationally invariant systems with well-defined Bloch vectors, \mathbf{k} , the application of the position operator can be reduced to calculating the gradient in k-space. Alternatively, for finite systems, which are represented by supercell structures (a molecule in a box) in CASTEP, one can apply a real-space representation of the position operator. The artificial periodicity imposed on the system causes the position operator to acquire a sawtooth shape. Thus, in the vicinity of the box boundaries, the position operator is distorted. Because of this, a sufficiently large supercell must be constructed so that the electronic density does not reach the regions where the position operator behaves unphysically. This condition is easily satisfied by the usual physical requirement that the molecules in neighboring boxes do not interact.

NMR shielding tensor

Finally, the induced magnetic field, $\mathbf{B}^{(I)}$, is calculated from the induced current and its value at the nuclear position determines the NMR shielding tensor. The calculated tensor is rather sensitive to numerical errors in both the unperturbed wavefunction, $\Psi^{(0)}$, and its first-order perturbation, $\Psi^{(1)}$, so the convergence requirements for NMR calculations are more stringent than, for example, routine band structure calculations. To obtain reliable results, the convergence of the wavefunction with respect to the number of basis functions (plane waves) must be ensured and a well-converged conjugate gradient procedure put in place to determine the coefficients of the plane waves. Apart from that, in calculating solid-state NMR properties (a small unit cell as opposed to a molecule in a box) the convergence of the k-space sum over the Brillouin zone must be achieved. The NMR observables are not particularly sensitive to uncertainties in the ground-state density distribution in the system, which determines the unperturbed Hamiltonian. Here, the usual convergence criteria for self-consistent DFT calculations are sufficient.

Chemical shift (or shielding) can be calculated for paramagnetic materials where the total spin is zero, even if a spin-polarized treatment is applied. This opens the possibility of using the DFT+U method as implemented by Shih and Yates ([2017](#)). The nonlocal Hubbard correction potential has been reexamined in order to comply with the gauge-including projector augmented-wave transformation under an external uniform magnetic field. The resulting expression is suitable for chemical shift calculations using both norm-conserving and ultrasoft pseudopotentials in the projector augmented-wave scheme. As a result more accurate results can be obtained for transition metal and rare earth oxides.

Note: It is important to examine the results and establish that the solution is indeed paramagnetic. If the total spin of the final state is non-zero, or the spin arrangement is antiferromagnetic, the results are likely to be meaningless.

Sensitivity of NMR to calculation parameters

NMR properties calculations are very sensitive to the number of k-points in the Brillouin zone. It is hard to construct a general rule for the number of k-points required, so it is recommended that you carry out convergence tests. An example convergence test for gallium phosphide is given below (these results are obtained for the experimentally observed structure of cubic GaP, ultra-fine settings, on the fly generated ultrasoft pseudopotentials, PBE functional).

Table 1. Convergence test for GaP

	k-point mesh	chemical shift (ppm)
P	2 × 2 × 2	-578.60
	4 × 4 × 4	302.72
	8 × 8 × 8	376.18
	12 × 12 × 12	375.45
	16 × 16 × 16	375.34
Ga	2 × 2 × 2	920.61
	4 × 4 × 4	1335.72
	8 × 8 × 8	1352.50
	12 × 12 × 12	1352.21
	16 × 16 × 16	1352.20

It follows from [Table 1](#) that a grid of at least 12 × 12 × 12 is required to achieve convergence of the chemical shift to within 1-2 ppm, and finer grids might be needed to achieve higher accuracy.

NMR properties are very sensitive to atomic positions, which makes NMR such a useful experimental tool for structure analysis. This implies that it is highly recommended to perform a geometry optimization run prior to the NMR calculation. If the structure of a crystal or molecule under investigation is obtained from an experimental study, it is advisable to optimize positions of hydrogen atoms first of all. If the forces on heavy atoms as reported by CASTEP are high (in excess of 1 eV/Å) then complete structure optimization is recommended.

NMR J-couplings

NMR J-coupling or nuclear spin-spin coupling is an indirect interaction of the nuclear magnetic moments mediated by the bonding electrons. It is manifested as the fine structure in NMR spectra, providing a direct measure of bond strength and a map of the connectivities of the system.

The J-coupling mechanism is an essential component of many NMR experiments. Joyce *et al.* (2007) developed a method to calculate J-coupling constants from first-principles in extended systems in a planewave-pseudopotential density functional theory framework, using the projected augmented wave method (PAW) to reconstruct the all-electron properties of the system. This method has been validated for a small number of systems containing light atoms against quantum chemical calculations and against experimental data (see for example, [Joyce et al., 2008](#)). This technique has been further developed by

Green and Yates (2014) to incorporate scalar relativistic effects in the ZORA (zeroth-order regular approximation) approach and hence to provide a highly efficient method for predicting J-coupling in extended systems containing heavy ions at negligible extra computational cost compared to the non-relativistic method.

A general review of the formalism is given by Yates (2010), this discusses various aspects of the calculations which should be taken into account when comparing results with solid-state NMR experiments including anisotropy and orientation of the J tensors, the reduced coupling constant, and the relationship between the J-coupling and crystal structure.

J-coupling interactions can be decomposed into four mechanisms:

- two due to interactions of the electron spins with the nuclear moments
- two due to electron currents induced by the nuclear moments

When spin-orbit coupling is neglected these can be treated separately.

The spin term can be decomposed into an analog of a spin-dipole interaction plus a Fermi-contact term, which is due to the finite probability of the presence of an electron at the nucleus.

Induced current operators can be decomposed into diamagnetic and paramagnetic current operators.

Joyce *et al.* (2007) found that the Fermi-contact contribution to be consistently the largest component, while the diamagnetic and spin-dipolar contributions were very small for all the cases studied.

Experimental interest is focused primarily on the isotropic coupling constant which is obtained from the trace of the J-coupling tensor and is measured in Hertz. Recent extensive validation studies (for example, by Green and Yates 2014) demonstrate that the pseudopotential PAW approach for J-coupling calculations gives results in good qualitative and quantitative agreement with experiment both for light and heavy elements.

It is important to note that solid state calculations of J-couplings using CASTEP correctly account for long-range effects in the periodic systems and reproduce the differences between solution and solid-state values (Joyce *et al.*, 2008).

Note: Induced magnetization density and current density are expected to be short-ranged. This forms the basis of using J-coupling as a tool for probing the strength of interatomic bonds. However, in a periodic calculation the perturbing nucleus can be viewed as similar to a defect in a defect calculation. Hence, sometimes it might be necessary to construct a supercell which is large enough to inhibit the interaction between the periodic defects or perturbations. Convergence with respect to the cell size should represent an important test in establishing accuracy of J-coupling calculations in either periodic systems or in molecule in a box calculations.

EPR G-tensor

Electron Spin Resonance (EPR - also known as Electron Paramagnetic Resonance) is a powerful experimental probe of the structure of defects in solids. EPR spectra of spin $\frac{1}{2}$ centers are made up of two contributions:

- the hyperfine parameters
- the g-tensor

The g-tensor arises from the interaction of the electronic spin with external magnetic field. This term plays a somewhat similar role to the shielding in NMR; induced electronic currents in the sample modify the g tensor from its vacuum value.

EPR spectrum can be modeled using the following effective Hamiltonian, bilinear in the total electron spin S , and the applied uniform magnetic field or nuclear spins, B and I_I , respectively:

$$H_{eff} = \frac{\alpha}{2} S \cdot g \cdot B + \sum_I S \cdot A_I \cdot I_I$$

where:

atomic units are used

α is the fine structure constant

the summation I runs over the nuclei

The tensors A_I are the hyperfine parameters, and the tensor g is the EPR g-tensor.

The Gauge Including Projector Augmented Waves (GIPAW) approach has been used to compute g tensors in several crystalline materials including defects in α -quartz and zirconia.

The hyperfine tensor can be obtained from the ground state charge density. In CASTEP it is computed using the PAW approach of Van de Walle and Blöchl (1993). The calculation of the g-tensor is more involved, requiring the linear response currents. These are computed using the GIPAW approach of Pickard and Mauri (2001). The total g-tensor is obtained as:

$$g = g_e + \Delta g_{Z-KE} + \Delta g_{SO} + \Delta g_{SOO} = g_e + \Delta g$$

Where the contributions to the total change in the g-tensor are the electron Zeman kinetic energy, spin-orbit, and the spin-other-orbit correction. The calculation of these terms follows the approach of Pickard and Mauri (2002) extended for the use of ultrasoft potentials by Yates *et al.* (2007). The GIPAW approach has been used to compute g-tensors in several crystalline materials including defects in quartz and zirconia by Pietrucci *et al.* (2006).

Optical properties

Definition of optical constants

CASTEP can calculate the optical properties of solids that are due to electronic transitions.

In general, the difference in the propagation of an electromagnetic wave through vacuum and some other material can be described by a complex refractive index, N :

Eq. CASTEP 48

$$N = n + ik$$

In vacuum N is real, and equal to unity. For transparent materials it is purely real, the imaginary part being related to the *absorption coefficient* by:

Eq. CASTEP 49

$$\eta = \frac{2k\omega}{c}$$

The absorption coefficient indicates the fraction of energy lost by the wave when it passes through the material, so that the intensity at the distance x from the surface is:

$$I(x) = I(0) \exp(-\eta x)$$

where $I(0)$ is the intensity of the incident light.

The *reflection coefficient* can be obtained for the simple case of normal incidence onto a plane surface by matching both the electric and magnetic fields at the surface:

Eq. CASTEP 50

$$R = \left| \frac{1 - N}{1 + N} \right|^2 = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

However, when performing calculations of optical properties it is common to evaluate the complex dielectric constant and then express other properties in terms of it. The complex dielectric constant, $\varepsilon(\omega)$, is given by:

Eq. CASTEP 51

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2$$

and hence the relation between the real and imaginary parts of the refractive index and dielectric constant is:

Eq. CASTEP 52

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

Another frequently used quantity for expressing optical properties is the *optical conductivity*, $\sigma(\omega)$:

Eq. CASTEP 53

$$\sigma = \sigma_1 + i\sigma_2 = -i\frac{\omega}{4\pi}(\varepsilon - 1)$$

Optical conductivity is usually used to characterize metals, however CASTEP is aimed more toward the optical properties of insulators and semiconductors. The main difference between the two is that intraband transitions play important role in the IR part of the optical spectra of metals and these transitions are not considered at all in CASTEP.

A further property that can be calculated from the complex dielectric constant is the energy loss function. It describes the energy lost by an electron passing through a homogeneous dielectric material and is given by:

Eq. CASTEP 54

$$Im \left(\frac{-1}{\varepsilon(\omega)} \right)$$

Connection to experimental observables

Experimentally, the most accessible optical parameters are the absorption, $\eta(\omega)$, and the reflection, $R(\omega)$, coefficients. In principle, given the knowledge of both of these, the real and imaginary parts of N can be determined, through [Eq. CASTEP 49](#) and [Eq. CASTEP 50](#). [Eq. CASTEP 51](#) allows expression in terms of the complex dielectric constant. However, in practice, the experiments are more complicated than the case of normal incidence considered above. Polarization effects must be accounted for and the geometry can become quite complex (for example, transmission through multilayered films or incidence at a general angle).

CASTEP supports spin-polarized calculations of optical properties for magnetic systems. Only transitions between the states with the same spin are allowed. For a more general discussion of the analysis of optical data see Palik ([1985](#)).

Connection to electronic structure

The interaction of a photon with the electrons in the system is described in terms of time dependent perturbations of the ground state electronic states. Currently CASTEP provides two approaches to optical properties calculations; one is based on standard DFT Kohn-Sham orbitals and the other uses more accurate but much more time-consuming time-dependent DFT (TD-DFT) theory.

DFT optics

In this approach excited states are represented as unoccupied Kohn-Sham states. Transitions between occupied and unoccupied states are caused by the electric field of the photon (the magnetic field effect is weaker by a factor of v/c). When these excitations are collective they are known as plasmons (which are most easily observed by the passing of a fast electron through the system rather than a photon, in a technique known as Electron Energy Loss Spectroscopy, described by [Eq. CASTEP 54](#), since transverse photons do not excite longitudinal plasmons). When the transitions are independent they are known as single particle excitations. The spectra resulting from these excitations can be thought of as a joint density of states between the valence and conduction bands, weighted by appropriate matrix elements (introducing selection rules).

Evaluation of the dielectric constant

CASTEP calculates the imaginary part of the dielectric constant, which is given by:

Eq. CASTEP 55

$$\varepsilon_2(\mathbf{q} \rightarrow O_{\hat{u}}, \hbar\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{\mathbf{k}, \nu, c} |\langle \Psi_{\mathbf{k}}^c | \mathbf{u} \cdot \mathbf{r} | \Psi_{\mathbf{k}}^\nu \rangle|^2 \delta(E_{\mathbf{k}}^c - E_{\mathbf{k}}^\nu - \hbar\omega)$$

where \mathbf{u} is the vector defining the polarization of the incident electric field.

This expression is similar to Fermi's Golden rule for time dependent perturbations, and $\varepsilon_2(\omega)$ can be thought of as detailing the real transitions between occupied and unoccupied electronic states. Since the dielectric constant describes a causal response, the real and imaginary parts are linked by a Kramers-Kronig transform. This transform is used to obtain the real part of the dielectric function, $\varepsilon_1(\omega)$.

Details of the calculation

Evaluation of matrix elements

The matrix elements of the position operator that are required to describe the electronic transitions in [Eq. CASTEP 55](#) may normally be written as matrix elements of the momentum operator allowing straightforward calculation in reciprocal space. However, this depends on the use of local potentials ([Read and Needs, 1991](#)), while in CASTEP nonlocal potentials are more often used. The corrected form of the matrix elements is:

Eq. CASTEP 56

$$\langle \Psi_{\mathbf{k}}^c | \mathbf{r} | \Psi_{\mathbf{k}}^\nu \rangle = \frac{1}{i\omega m} \langle \Psi_{\mathbf{k}}^c | \mathbf{P} | \Psi_{\mathbf{k}}^\nu \rangle + \frac{1}{\hbar\omega} \langle \Psi_{\mathbf{k}}^c | [V_{nl}(r), \mathbf{r}] | \Psi_{\mathbf{k}}^\nu \rangle$$

Ultrasoft pseudopotentials produce an additional contribution to optical matrix elements that is also included in CASTEP results.

Drude correction

The intraband contribution to the optical properties affects mainly the low energy infrared part of the spectra. It can be described sufficiently accurately using a semiempirical Drude term in the optical conductivity:

Eq. CASTEP 57

$$\epsilon_D(\omega) = 1 - \frac{\omega_P^2}{\omega(i\gamma_D + \omega)}$$

in terms of the plasma frequency ω_P and damping parameter γ_D which depends on many details of the material and is usually obtained from experiment. The Drude damping parameter describes the broadening of the spectra due to effects not included in the calculation. Examples of processes that contribute to this broadening are electron-electron scattering (including Auger processes), electron-phonon scattering, and electron-defect scattering. This last contribution is usually the most important. As a result an a priori determination of the broadening would require knowledge as to the concentrations and kinds of defects present in the sample under study.

Polarization

For materials that do not display full cubic symmetry, the optical properties will display some anisotropy. This can be included in the calculations by taking the polarization of the electromagnetic field into account. As mentioned above, the unit vector \mathbf{u} defines the polarization direction of the electric field. When evaluating the dielectric constant there are three options:

- *polarized*: requires a vector to define the direction of the electric field vector for the light at normal incidence to the crystal.
- *unpolarized*: requires a vector to define the direction of propagation of incident light at normal incidence to the crystal. The electric field vector is taken as an average over the plane perpendicular to this direction.
- *polycrystal*: no direction need be specified, the electric field vectors are taken as a fully isotropic average.

Scissors operator

As discussed below, the relative position of the conduction to valence bands is erroneous when the Kohn-Sham eigenvalues are used. In an attempt to fix this problem, inherent in DFT, a rigid shift of the conduction band with respect to the valence band is allowed. This procedure of artificially increasing the band gap is known as a *scissor operator*.

Limitations of the method

Local field effects

The level of approximation used here does not take any local field effects into account. These arise from the fact that the electric field experienced at a particular site in the system is screened by the polarizability of the system itself. So, the local field is different from the applied external field (that is, the photon electric field). This can have a significant effect on the spectra calculated (see the example of bulk silicon calculation below) but it is prohibitively expensive to calculate for general systems at present.

Quasiparticles and the DFT bandgap

In order to calculate any spectral properties it is necessary to identify the Kohn-Sham eigenvalues with quasiparticle energies. Although there is no formal connection between the two, the similarities between the Schrödinger-like equation for the quasiparticles and the Kohn-Sham equations allow the two to be identified. For semiconductors, it has been shown computationally (by comparing GW and DFT band structures) that most of the difference between Kohn-Sham eigenvalues and the true excitation energies can be accounted for by a rigid shift of the conduction band upward with respect to the valence band ([Godby et al., 1992](#)). This is attributed to a discontinuity in the exchange-correlation potential as the system goes from (N)-electrons to (N+1)-electrons during the excitation process. There

can, in some systems, be considerable dispersion of this shift across the Brillouin zone, and the scissor operator used here will be insufficient.

Excitonic effects

In connection with the absence of local field effects, excitonic effects are not treated in the present formalism. This will be of particular importance for ionic crystals (for example NaCl) where such effects are well known.

Other limitations

- The nonlocal nature of the GGA exchange-correlation functionals is not taken into account when evaluating the matrix elements but it is expected that this will have a small effect on the calculated spectra.
- Phonons and their optical effects have been neglected.
- Finally, there is an intrinsic error in the matrix elements for optical transition due to the fact that pseudowavefunctions have been used (that is they deviate from the true wavefunctions in the core region). However, the selection rules will not be changed when going from pseudo- to all-electron wavefunctions.

Sensitivity of optical properties to calculation parameters

Number of conduction bands

This parameter defines the energy range covered in the calculation, and it also determines the accuracy of the Kramers-Kronig transform. It is clear from [Figure 1](#) that $\epsilon_2(\omega)$ converges rapidly with the number of conduction bands included.

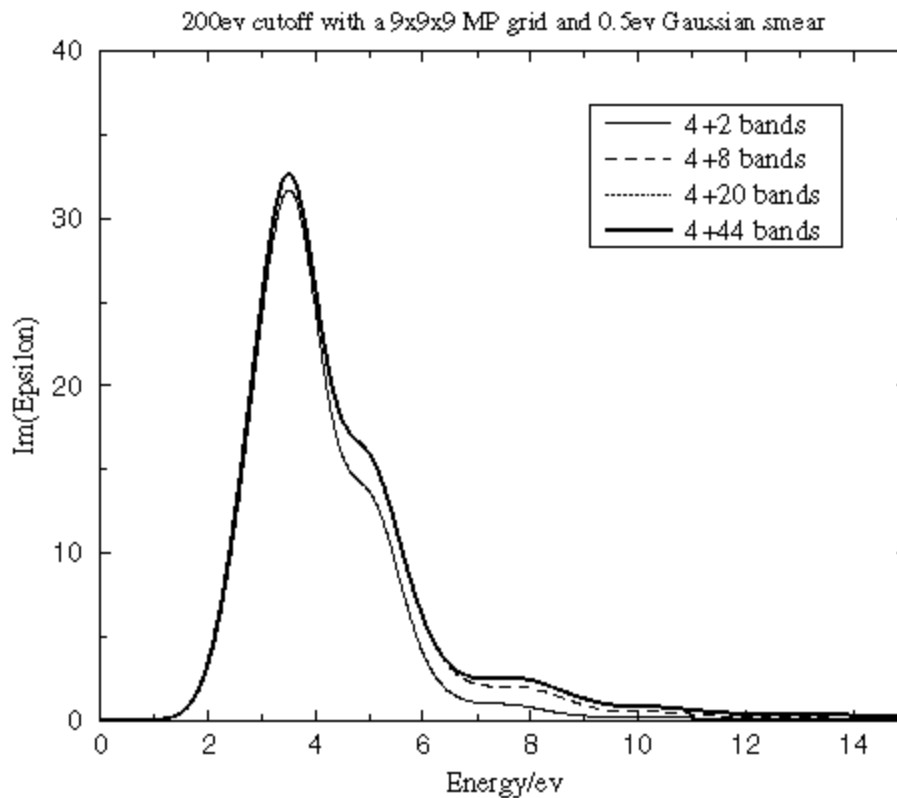


Figure 1. Convergence of the dielectric function with the number of conduction bands

Energy cutoff

The value of the energy cutoff that was used in the original SCF calculation of the ground state electron density is an important factor that determines the accuracy of the calculated optical properties. A bigger basis set provides more accurate self-consistent charge density and more variational freedom when searching for wavefunctions of unoccupied states. [Figure 2](#) shows that while it is important to converge the calculation with respect to the planewave cutoff to obtain the correct energies for the spectral features, the shape of those features is reached rapidly.

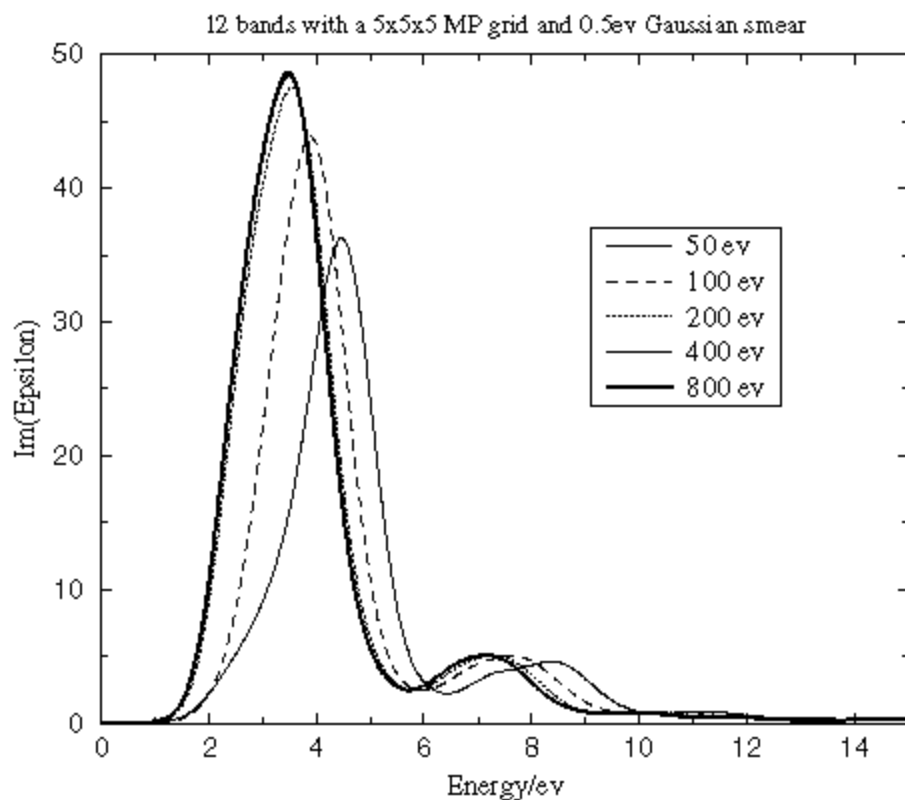


Figure 2. Convergence of the dielectric function with the cutoff energy

Number of k-points in the SCF calculation

The accuracy of the ground state electron density depends on the number of k-points used in the SCF run as well as on the basis set quality. [Figure 3](#) reveals that the optical properties converge rapidly with the number of k-points used in the SCF run, which implies low sensitivity to the details of the charge density.

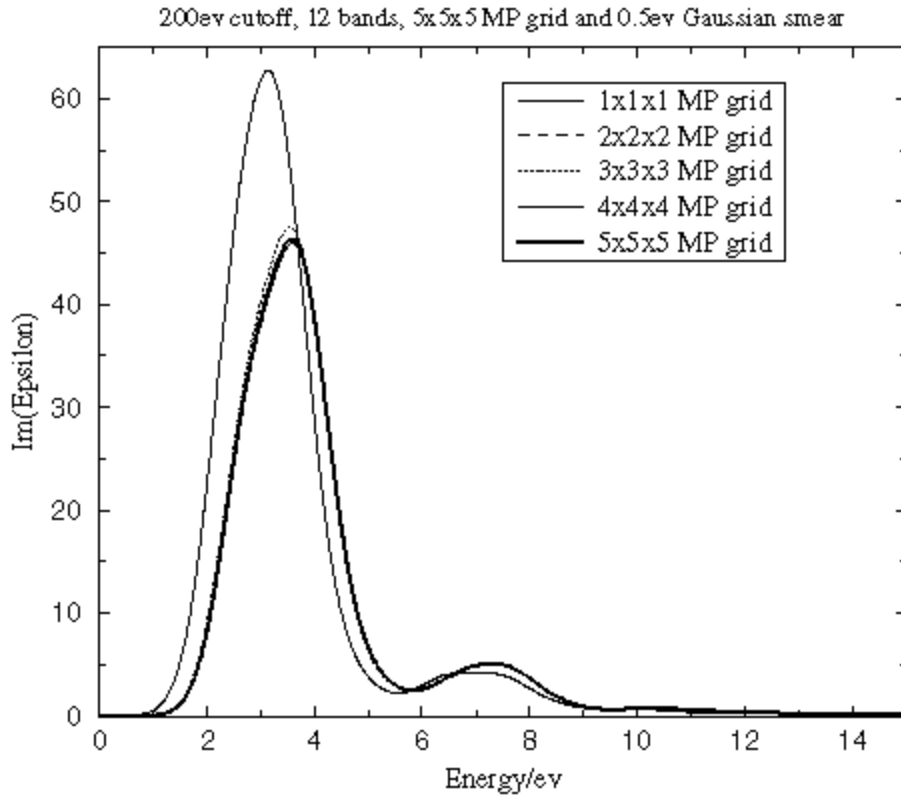


Figure 3. Convergence of the dielectric function with the number of k-points in the SCF calculation

Number of k-points for Brillouin zone integration

It is important to use a sufficient number of k-points in the Brillouin zone when running optical matrix element calculations. The matrix element changes more rapidly within the Brillouin zone than electronic energies themselves. Therefore, one requires more k-points to integrate this property accurately than are needed for an ordinary SCF calculation. [Figure 4](#) clearly demonstrates the importance of converging the Brillouin zone integration for the optical properties with respect to the k-point density. Both energies and spectral features are strongly affected by the accuracy of this integration.

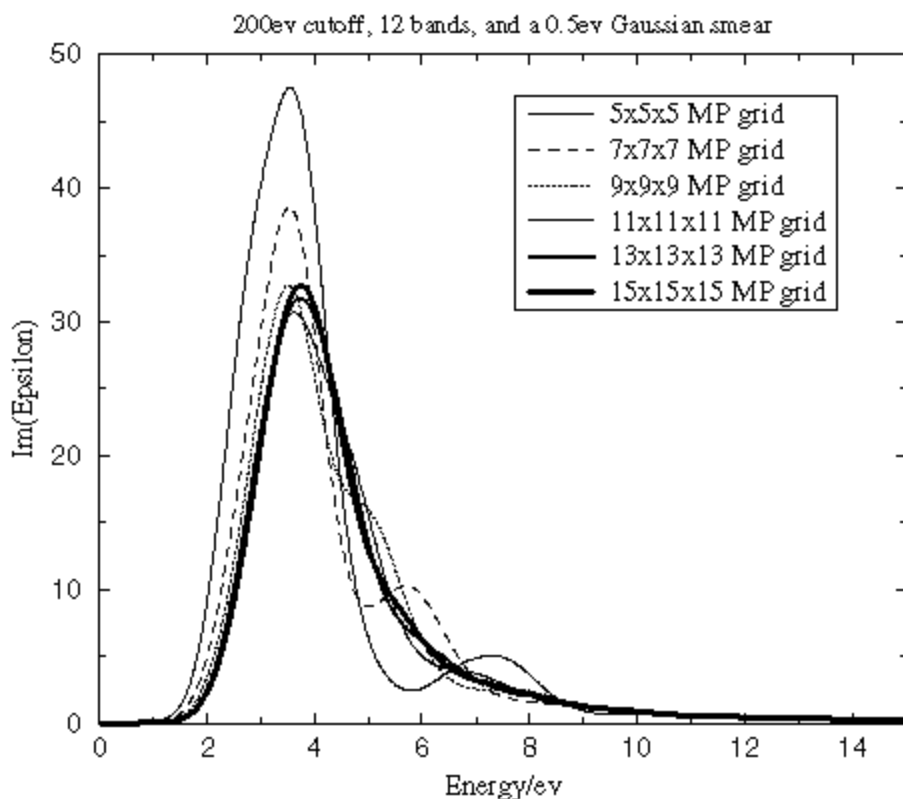


Figure 4. Convergence of the dielectric function with the number of k-points in the optical matrix elements calculation

TD-DFT optics

TD-DFT is a formally exact treatment of electronic excited states. The implementation in CASTEP follows the work of Hutter (2003), which takes a linear response approach to computing excitation energies directly. A benefit of this method is that the response wavefunctions for excited states are calculated and can then be used to derive further properties such as optical matrix elements and atomic forces. In the case of atomic forces, a geometry optimization or molecular dynamics run can be performed for a chosen excitation.

Hutter reformulated the equations of time-dependent Hartree-Fock in the Tamm-Dancoff approximation applied to TD-DFT (Hirata and Head-Gordon, 1999) so that they could be efficiently implemented in a plane-wave basis set. This self-consistent eigenvalue problem is solved in CASTEP by the user's choice of conjugate gradient or block-Davidson minimizers. The result is a set of electronic excitation energies and linear response wavefunctions.

A technical report on the implementation details of the TD-DFT minimizers can be found at <http://www.hector.ac.uk/cse/distributedcse/reports/castep02/>.

A second report on the implementation of excited state forces can be found at <http://www.hector.ac.uk/cse/distributedcse/reports/castep03/>.

Phonons

The basic theory of phonons, or lattice vibrations, in crystals is well understood and has been described in detail in text books such as those by Born and Huang (1954) and Ashcroft and Mermin (1976). The importance of the phonon interpretation of lattice dynamics is illustrated by the large number of physical properties that can be understood in terms of phonons: infrared, Raman, and neutron

scattering spectra; specific heat, thermal expansion, and heat conduction; electron-phonon interactions and, thus, resistivity and superconductivity, and so on.

A number of approximations are made in order to arrive at the phonon description of lattice vibrations. First of all, it is assumed that the mean equilibrium position of each ion, i , is a Bravais lattice site, \mathbf{R}_i . Secondly, it is assumed that the amplitude of atomic displacements is small compared to interatomic distances. This leads to a harmonic approximation which is sufficiently accurate to describe most of the lattice dynamical effect of interest. However, further refinement, in the form of anharmonic theory, is required to explain physical properties at elevated temperatures when the harmonic approximation breaks down.

The N -ion harmonic crystal can be considered as $3N$ independent harmonic oscillators, whose frequencies are those of $3N$ classical normal modes. Thus, at each wave vector, \mathbf{q} , in the Brillouin zone there are $3N$ vibrational modes. There are two equivalent descriptions of this system, either in terms of normal modes or phonons. Phonons are the quanta of the ionic displacement field that describe classical sound; they are similar to photons, the quanta of the radiation field that describe classical light.

The properties of phonons can be described using a harmonic approximation based on the knowledge of just one fundamental quantity, the force constants matrix:

Eq. CASTEP 58

$$D_{\mu\nu}(\mathbf{R} - \mathbf{R}') = \left. \frac{\partial^2 E}{\partial u_\mu(\mathbf{R}) \partial u_\nu(\mathbf{R}')} \right|_{\mathbf{u}=0}$$

Here u refers to the displacement of a given atom and E is the total energy in the harmonic approximation. This force constants matrix (or Hessian matrix) can also be represented in reciprocal space and the result is commonly referred to as the dynamical matrix:

Eq. CASTEP 59

$$D_{\mu\nu}(\mathbf{q}) = \frac{1}{N_{\mathbf{R}}} \sum_{\mathbf{R}} D_{\mu\nu}(\mathbf{R}) \exp(-i\mathbf{q}\mathbf{R})$$

Classical equations of motion can be written in the language of dynamical matrices, as an eigenvalue problem. Each atomic displacement is described in the form of plane waves:

Eq. CASTEP 60

$$\mathbf{u}(\mathbf{R}, t) = \boldsymbol{\varepsilon} e^{i(\mathbf{q}\mathbf{R} - \omega(\mathbf{q})t)}$$

where the polarization vector of each mode, $\boldsymbol{\varepsilon}$, is an eigenvector with the dimension of $3N$ of the eigenvalue problem:

Eq. CASTEP 61

$$M\omega^2(\mathbf{q})\boldsymbol{\varepsilon} = D(\mathbf{q})\boldsymbol{\varepsilon}$$

The dependence of the frequency, ω , on the wave vector is known as the phonon dispersion.

Each lattice always has three *acoustic* modes. Their dispersion relation at small values (near the Γ point) is linear, which is characteristic of sound waves. The rest of the vibrational modes, $3N - 3$, in a Bravais lattice with basis are known as *optical* modes because the long wavelength optical modes in ionic crystals can interact with electromagnetic radiation and are therefore responsible for much of the characteristic optical behavior of such crystals. The frequencies of optical modes are finite at $\mathbf{q} = 0$. A simplistic characterization of acoustic and optical branches ([Ashcroft and Mermin, 1976](#)) would be: All ions in a primitive cell move essentially in phase in an acoustic mode and the dynamics is determined by the interaction between cells; an optical mode is one in which the ions within each cell exhibit a

molecular vibration mode which is broadened into a band of frequencies due to intercellular interactions.

A popular way of classifying lattice vibrations is based on the relationship between the orientation of the polarization vector, ϵ , and the propagation direction, \mathbf{q} . In an isotropic medium for the case of a monatomic primitive cell it is always possible to choose three solutions for a given \mathbf{q} so that one branch (*longitudinal*) is polarized along the propagation direction and the other two branches (*transverse*) are polarized perpendicular to this direction. This simple relationship does not hold for an arbitrary \mathbf{q} -vector in an anisotropic crystal, nor for a Bravais lattice with basis. It is still common to classify vibrational modes along high symmetry directions in simple lattices based on the transverse and longitudinal description.

Long wavelength vibrations in polar materials deserve a special mention. The long range character of the Coulomb forces gives rise to macroscopic electric fields for longitudinal optic (LO) phonons at the Γ -point in polar semiconductors and insulators. The coupling between longitudinal phonons and the nonperiodic electric field gives rise to LO-TO splitting at the Γ -point. The value of the splitting is determined by the static dielectric constant of the crystal and by the Born effective charge of the ions. The Born effective charge tensor of the s^{th} ion is the partial derivative of the macroscopic polarization with respect to a periodic displacement of all the periodic images of that ion at zero macroscopic electric field. A good review of the practical methods of dealing with this effect is given by [Baroni et al., \(2001\)](#).

Thermodynamic properties of crystals can be evaluated in a fairly straightforward way based on a knowledge of the phonon frequencies across the Brillouin zone (see [Ashcroft and Mermin, 1976](#); [Baroni et al., 2001](#)). These quasiharmonic results are quite accurate at moderate temperatures and only small corrections to calculated phase transition properties can be found at temperatures as high as 1000-2000 K ([Kern et al., 1999](#)).

Practical schemes for phonon calculations

A good review of the existing schemes can be found in [Baroni et al., \(2001\)](#). The theoretical study of phonon properties has to rely on one of the three available methods for determining the force constants matrix: analytical calculations, supercell calculations, or linear response calculations. The analytical approach is only viable when the energy model is sufficiently simple to allow a direct evaluation of the second derivatives of the energy with respect to atomic displacements (for example, empirical pair potential models). Therefore, it is unsuitable for first principles calculations. Further alternatives such as extracting vibrational properties from molecular dynamics runs ([Arias et al., 1992](#)) are less transparent and noticeably more computationally expensive.

The supercell method involves perturbing the positions of the atoms slightly and calculating the reaction forces ([Ackland et al., 1997](#)). It is necessary to use supercells of the original cell when interatomic interaction in the system is long ranged. The main advantage of this method (and of the closely related frozen phonon technique) is that there is no need for a new formalism; any total energy scheme like CASTEP can be used to evaluate the forces at a number of carefully selected distorted configurations. The original frozen phonon scheme requires a displacement with the given wave vector and has been successfully used since the early 1980s ([Yin and Cohen, 1982](#); [Ho et al., 1984](#)). The force constants matrix evaluation in this formalism has been used to calculate interplanar force constants ([Wei and Chou, 1994](#)) and, thus, phonon dispersion along high symmetry directions. More recent applications are based on the full reconstruction of the force constants matrix ([Ackland et al., 1997](#); [Parlinski et al., 1997](#); and references in [Baroni et al., 2001](#)).

Linear response calculations seek to evaluate the dynamical matrix directly for a set of \mathbf{q} -vectors. The starting point of the linear response approach is evaluation of the second-order change in the total energy induced by atomic displacements. The main advantage of the scheme is that there is no need to artificially increase the cell size in order to accommodate small values of the \mathbf{q} -vectors, as in the frozen phonon method, or to overcome the long range interaction problem (force constants matrix from

supercell calculations). A more detailed description of the linear response method can be found in [Baroni et al., \(2001\)](#). The CASTEP implementation is described in the [Linear response](#) topic.

Interpolation schemes

The force constant matrix ([Eq. CASTEP 58](#)) for non-polar insulators and most metals decays proportionally to r^{-5} or even faster. This fact allows the introduction of an effective interpolation scheme to accelerate phonon calculations within both the finite displacement and linear response formalisms through the introduction of a cutoff radius, R_c , beyond which all the elements of the force constant matrix can be treated as zero. If an approximation for the force constant is available, the dynamical matrix for any given reciprocal vector can be calculated using [Eq. CASTEP 59](#).

Finite displacement: supercell method

In the supercell method, finite displacement calculations are carried out in the supercell, circumventing the sphere described by the cutoff radius, which directly give all the non-zero elements of the force constant matrix.

Linear response: Fourier interpolation

In the Fourier interpolation method, calculations are performed on the regular reciprocal mesh (with a spacing corresponding to the real space cutoff radius). The set of dynamical matrices obtained in these calculations can be used to construct the force constant matrix using Fourier transformation.

Symmetry analysis of vibrations

Symmetry considerations in vibrational analysis are useful for various reasons. For example, the use of symmetry in the CASTEP implementation reduces computational time and the automatic assignment of spectroscopic labels allows you to interpret experimentally measured modes at Γ -points with greater confidence. Symmetry analysis and the subsequent enforcing of symmetry is carried out along the lines suggested by [Warren and Worlton \(1974\)](#). The nomenclature suggested by these authors for labeling symmetry elements is adopted in the CASTEP output. The notation for irreducible representation labels that are common in spectroscopic analysis is specified by [IUPAC recommendations \(1997\)](#).

Infrared spectra

In the infrared energy range (typically below 1 eV), vibrations are an important component of optical spectra. In the case of metals, this process is screened considerably by the plasmon ([intraband](#)) electronic contribution, while for semiconductors and insulators, it is vibrations that are mainly responsible for absorbing light energy.

Theoretically, infrared absorption intensities are described in terms of a [dynamical matrix](#) (also known as a Hessian) and Born effective charges (also known as atomic polarizability tensors, ATP). The Born effective charge tensor of an ion is the partial derivative of the macroscopic polarization with respect to a periodic displacement of all the periodic images of that ion at zero macroscopic electric field. A good review of the practical methods of dealing with this effect is given by Baroni et al. ([2001](#)). The Born effective charge tensor is calculated within the [linear response formalism](#) by applying a [Gonze approximation](#). Once these data are known, it is straightforward to calculate IR intensities (see [Calculating vibrational frequencies](#)). IR absorption intensities are printed in the CASTEP output file for any run where phonons at the Γ -point and LO-TO splitting are calculated.

The concept of IR absorption intensities is mostly used in the analysis of molecules. CASTEP can be used to model isolated molecules if the molecule in question is assumed to be contained within a box (see [Setting up a calculation on an isolated molecule](#)). This approach allows accurate prediction of IR absorption intensities. Figure 1 compares the results of such calculations obtained using DMol³ and CASTEP for a variety of molecules.

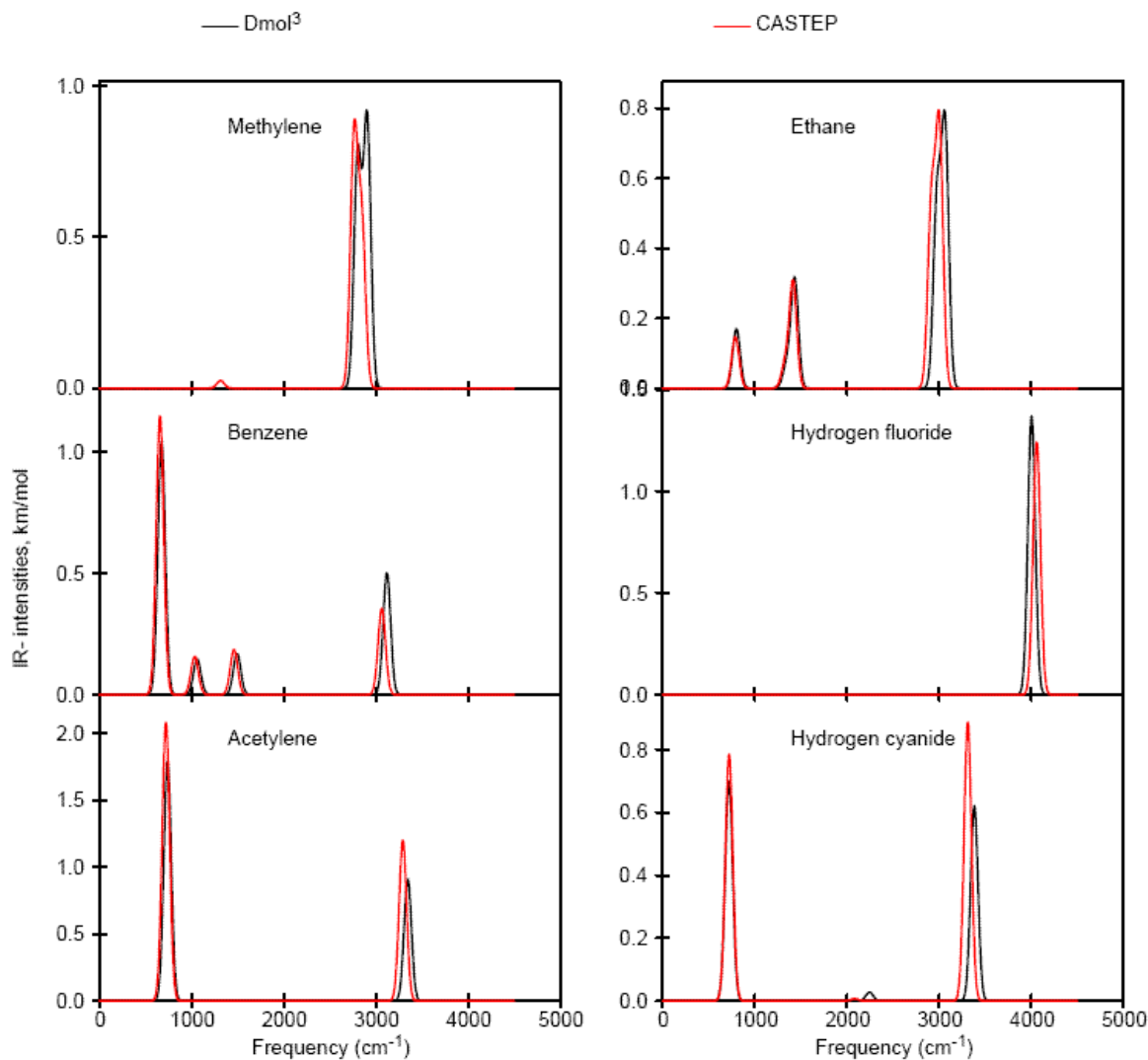


Figure 1. Comparison of IR spectra calculated using DMol³ and CASTEP for a range of molecules

Linear response

Linear response, or density functional perturbation theory (DFPT), is one of the most popular methods of *ab initio* calculation of lattice dynamics ([Baroni et al. 2001](#)). However, the applicability of the method extends beyond the study of vibrational properties. Linear response provides an analytical way of computing the second derivative of the total energy with respect to a given perturbation. Depending on the nature of this perturbation, a number of properties can be calculated. A perturbation in ionic positions gives the dynamical matrix and phonons; in magnetic field - NMR response; in unit cell vectors - elastic constants; in an electric field - dielectric response, and so on.

The force constants matrix can be obtained by differentiating the Hellmann-Feynman forces on atoms, with respect to ionic coordinates. This procedure reveals that the force constants matrix depends on the ground state electron charge density and on its linear response to a distortion of atomic positions. Due to the variational principle of the density functional formalism, the second order change in energy depends on the first order change in the electron density.

The DFPT formalism is, in many ways, very similar to the density functional theory (DFT) itself. DFT states that the total energy is the functional of the electron density; thus one can solve the DFT equations by minimizing the total energy. Similarly, the DFPT problem can be solved by minimizing the second order perturbation in the total energy, which gives the first order changes in density, wavefunctions and potential ([Gonze et al. 1994](#), [Gonze 1997](#)).

This variational technique for solving DFPT problems is a more robust and accurate method than the original Green's function, iterative scheme suggested by [Baroni et al. 1987](#). Both methods should converge to the same solution but the Green's function method does not rely on the variational principle and its convergence properties are thus inferior. Moreover, once the first order change in wavefunctions, $\psi^{(1)}$, is evaluated, then the Green's function scheme evaluates the second order energy, which is not stationary with respect to first-order errors in $\psi^{(1)}$. Thus, the variational scheme of [Gonze 1997](#) is expected to be more accurate.

The electronic second order energy, which is minimized in this approach, as implemented in CASTEP, is:

Eq. CASTEP 62

$$E^{(2)} = \sum_{\mathbf{k},n} \left[\left\langle \Psi_{\mathbf{k},n}^{(1)} \left| H^{(0)} - \varepsilon_{\mathbf{k},n}^{(0)} \right| \Psi_{\mathbf{k},n}^{(1)} \right\rangle + \left\langle \Psi_{\mathbf{k},n}^{(1)} \left| V^{(1)} \right| \Psi_{\mathbf{k},n}^{(0)} \right\rangle + \left\langle \Psi_{\mathbf{k},n}^{(0)} \left| V^{(1)} \right| \Psi_{\mathbf{k},n}^{(1)} \right\rangle \right] + \frac{1}{2} \int \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') + \sum_{\mathbf{k},n} \left\langle \Psi_{\mathbf{k},n}^{(0)} \left| V^{(2)} \right| \Psi_{\mathbf{k},n}^{(0)} \right\rangle$$

where the superscripts refer to the ground state (0) and first (1) and second (2) order changes, respectively. Similar terms have to be evaluated for the ionic terms in the total energy. The preconditioned conjugate gradients minimization scheme can be used to find the minimum of this functional with respect to the first order wavefunctions. The dynamical matrix for a given \mathbf{q} is then evaluated from the converged first order wavefunctions and densities ([Gonze 1997](#)).

Raman spectra

Raman spectroscopy is used to study the vibrational, rotational, and other low-frequency modes in a system. It is based on the Raman effect of inelastic scattering of monochromatic light. This interaction with vibrations results in the energy of incident photons being shifted up or down. The energy shift is defined by the vibrational frequency and the proportion of the inelastically scattered light is defined by the spatial derivatives of the macroscopic polarization, technical details are described by Porezag and Pederson ([1996](#)).

Spatial derivatives of the macroscopic polarization are calculated numerically along eigenvectors of each Raman active phonon mode by calculating the polarization for each displacement using a [linear response](#) formalism. Once these derivatives are known, it is straightforward to calculate the Raman cross-section through appropriate space averaging.

Raman activities defined by Porezag and Pederson ([1996](#)) characterize phonon mode contributions to the intensity of peaks in Raman spectra. These intensities depend on some other factors such as the temperature and incident light wavelength. It is important to specify these parameters in order to simulate a realistic Raman spectrum that can be compared to experimental results.

The Raman susceptibility tensor from which the Raman intensity can be calculated is defined as:

$$A_{\alpha\beta}^m = \sqrt{V} \sum_{I\gamma} \frac{d\chi_{\alpha\beta}^{(1)}}{dR_{I\gamma}} \frac{v_{I\gamma}^m}{\sqrt{M_I}}$$

where:

$\chi^{(1)}$ is the first order dielectric susceptibility

v is a phonon eigenvector (the direction in which atoms, I , at equilibrium positions R , move under

excitation of a phonon mode, m in a unit cell with volume V)

Greek subscripts denote Cartesian directions

The derivative of $\chi^{(1)}$ inside the sum can be calculated in CASTEP using a finite difference approach, making small atomic displacements corresponding to the eigenvectors of each Raman active mode. However, the derivative can be written in full as:

$$\frac{d\chi_{\alpha\beta}^{(1)}}{dR_{I\gamma}} = -\frac{1}{V} \frac{d^3 E}{d\epsilon_\alpha d\epsilon_\beta dR_{I\gamma}}$$

where:

ϵ is the electric field of a photon in a Raman experiment exciting the phonon

E is the total energy of the system.

We can use the $(2n+1)$ theorem in quantum mechanics to evaluate this in a more direct manner, see Miwa (2011). This theorem states that, under a perturbation, if the perturbed wavefunctions are known to order n then we can evaluate the perturbed energy up to order $2n+1$. In particular, in a CASTEP phonon calculation, we need to evaluate the perturbed wavefunctions up to first order and therefore we should have access to the 3rd order energy perturbation, $E^{(3)}$, from which we can compute the susceptibility derivatives.

For Raman intensities, the full expression for this third derivative is given by equations (28)-(31) of Miwa (2011). These expressions are implemented in CASTEP for norm-conserving pseudopotentials.

The finite difference method and the "2n+1" linear response method lead to the same Raman susceptibility tensor, however the mathematical, and hence computational, routes are rather different. In the finite difference method, the phonon eigenvectors are calculated during a phonon task, and are then used to calculate the third order derivative for each mode one at a time. This means that there is a separate Raman intensity calculation for each Raman active mode to obtain its intensity. Computationally, this is usually the most time consuming part of a Raman intensity calculation.

Alternatively, in the linear response method, we first precompute the 9 second order derivatives with respect to electric field: equation 19 of Miwa (2011) and then construct the full set of Raman tensors during the phonon perturbations: equation (28) of Miwa (2011). Computationally, this means that in the linear response Raman intensity method there is an initialization stage and each phonon perturbation calculation has slightly more work to do than in the finite difference method. However, the computational work is then complete, unlike in the finite difference method where additional electric field perturbations are required for every Raman intensity.

For small cells the linear response method will be slower as the initialization stage and the extra cost of each phonon perturbation does not outweigh the effort of calculating the finite difference Raman tensor. For example, a linear response calculation for the primitive cell of boron nitride in the diamond structure takes about twice as long as the finite displacement calculation. However, the linear response method quickly becomes significantly more efficient as the number of degrees of freedom increases. Calculations for molecular crystals containing 50-100 atoms per unit cell can be an order of magnitude faster using the linear response method compared to the finite difference method.

Note: It is important to remember that Raman intensities are effectively third order derivatives, so to obtain reasonable results very accurate calculations are required. Both the energy cutoff and k-point sampling can contribute significantly to a convergence error, so a careful convergence test is necessary to obtain reliable Raman intensities.

Thermodynamic calculations

The results of a calculation of phonon spectra can be used to compute energy (E), entropy (S), free energy (F), and lattice heat capacity (C_V) as functions of temperature. The CASTEP total energy yields the

total electronic energy at 0 K. The vibrational contributions to the thermodynamic properties are evaluated to compute E , S , F , and C_v at finite temperatures as discussed below.

Note: Thermodynamic calculations can be performed only if the system is in the ground state, that is, geometry optimization is fully converged. This means that all the phonon eigenfrequencies must be real and non-negative.

When you perform a vibrational analysis with CASTEP the results of the thermodynamic calculations can be visualized using the [thermodynamic analysis](#) tools.

The formulas below are based on work by [Baroni et al. \(2001\)](#).

The temperature dependence of the energy is given by:

Eq. CASTEP 80

$$E(T) = E_{tot} + E_{zp} + \int \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} F(\omega) d\omega$$

where E_{zp} is the zero point vibrational energy, k is the Boltzmann constant, \hbar is the Planck constant and $F(\omega)$ is the phonon density of states. E_{zp} can be evaluated as:

Eq. CASTEP 81

$$E_{zp} = \frac{1}{2} \int F(\omega) \hbar\omega d\omega$$

The vibrational contribution to the free energy, F , is given by:

Eq. CASTEP 82

$$F(T) = E_{tot} + E_{zp} + kT \int F(\omega) \ln \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right] d\omega$$

The vibrational contribution to the entropy, S , can be obtained using:

Eq. CASTEP 83

$$S(T) = k \left\{ \int \frac{\frac{\hbar\omega}{kT}}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} F(\omega) d\omega - \int F(\omega) \ln \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right] d\omega \right\}$$

The lattice contribution to the heat capacity, C_v , is:

Eq. CASTEP 84

$$C_v(T) = k \int \frac{\left(\frac{\hbar\omega}{kT}\right)^2 \exp\left(\frac{\hbar\omega}{kT}\right)}{\left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right]^2} F(\omega) d\omega$$

A popular representation of the experimental data on heat capacity is based on the comparison of the actual heat capacity to that predicted by the Debye model. This leads to the concept of the temperature dependent Debye temperature, $\Theta_D(T)$. Heat capacity in Debye model is given by ([Ashcroft and Mermin, 1976](#)):

Eq. CASTEP 85

$$C_v^D(T) = 9Nk \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

where N is the number of atoms per cell. Thus, the value of the Debye temperature, Θ_D , at a given temperature, T , is obtained by calculating the actual heat capacity, [Eq. CASTEP 84](#), then inverting [Eq. CASTEP 85](#) to obtain Θ_D .

Dialogs in CASTEP

The following topics describe the dialogs in CASTEP:

- [CASTEP Calculation dialog](#)
- [CASTEP Analysis dialog](#)

Use the Save settings... option to save the current dialog settings.

CASTEP Calculation dialog

The Calculation dialog allows you to set up and run a CASTEP calculation.

It contains the following tabs:

- [Setup](#): Allows you to choose the type and quality of calculation that CASTEP will perform, along with other basic input options, including exchange-correlation functional, spin polarization, and total charge.
- [Electronic](#): Allows you to set the parameters associated with the electronic Hamiltonian. These include the basis set, pseudopotentials, SCF convergence criteria, and integration accuracy.
- [Properties](#): Allows you to select the properties that will be computed as part of a CASTEP calculation. These include electronic properties (such as band structure, density of states, and population analysis), optical properties, vibrational properties, and stress.
- [Job Control](#): Allows you to specify settings for the CASTEP job.

Run: Runs a job using the settings specified. The results are placed in a subfolder of the current Materials Studio project directory.

Note: This button is enabled only when the current 3D model document contains a periodic structure.


Run | Copy Script: Converts the current settings to a script and copies the script to the clipboard. Refer to the Generating scripts topic for more information on using sections of scripts generated from a dialog.

Files...: Provides access to the [CASTEP Job Files](#) dialog which allows you to save input files for a CASTEP calculation without running the job, or to run a job using an existing set of input files.

This functionality is provided for users who need to run the CASTEP server program in standalone mode, or who wish to edit the CASTEP input files in order to gain access to features not supported by the CASTEP interface.

Help: Displays the Help topic for the current tab.

Access methods

Menu	<i>Modules CASTEP Calculation</i>
Toolbar	 <i>Calculation</i>

Setup tab

The *Setup* tab allows you to choose the type and quality of calculation that CASTEP will perform along with other basic input options such as exchange-correlation functional, spin polarization, and total charge.

Task: Select the type of calculation that CASTEP will perform from the dropdown list. Available options are:

- [Energy](#) - performs a single-point energy calculation
- [Geometry Optimization](#) - searches for a minimum energy structure
- [Dynamics](#) - performs a molecular dynamics calculation
- [Elastic Constants](#) - performs an elastic constants calculation
- [TS Search](#) - performs a transition state search
- [TS Confirmation](#) - produces a refined reaction path based on a TS search
- [Properties](#) - calculates properties based on the results obtained from one of the other tasks

More...: Provides access to further options for the selected task: opening the [CASTEP Geometry Optimization](#), [CASTEP Dynamics](#), [CASTEP Elastic Constants](#), [CASTEP Transition State Search](#), or [CASTEP TS Confirmation](#) dialogs.

Quality: Set the overall quality of a single-point energy, geometry optimization, or dynamics calculation. This quality affects the basis set, k-point, and SCF convergence criteria, along with the convergence criteria for the Geometry Optimization, Elastic Constants, and TS Search tasks. Available options are:

- [Express](#)
- [Coarse](#)
- [Medium](#)
- [Fine](#)
- [Ultra-fine](#)

Tip: Use the [Coarse](#) quality setting for a quick assessment of the calculation. Use the [Express](#) quality setting to achieve a good compromise between speed and accuracy which is appropriate for most calculations. Use [Fine](#) and [Ultra-fine](#) quality settings for calculations that require very high accuracy, at the expense of longer calculation times. Carry out convergence testing for highly sensitive calculations by increasing the quality setting and possibly by increasing accuracy of the basis set and the k-point sampling.

The *Quality* setting affects all relevant task parameters that control the precision of the simulation. If any parameter is set to a value different from that specified by the overall quality level, the *Quality* is displayed as [Customized](#).

Functional: Select the type of DFT exchange-correlation potential to be used in the calculation. Choose the class of functional from the first dropdown list, then select the specific functional from the second dropdown list.

- **LDA:** local functional
 - **CA-PZ:** [Ceperley and Alder, 1980](#); data as parameterized by [Perdew and Zunger, 1981](#)
- **GGA:** gradient-corrected functionals
 - **PBE:** [Perdew et al., 1996](#)
 - **RPBE:** [Hammer et al., 1999](#)
 - **PW91:** [Perdew et al., 1992](#)
 - **WC:** [Wu and Cohen, 2006](#)
 - **PBESOL:** [Perdew et al., 2008](#)
 - **BLYP:** exchange from [Becke, 1988](#); correlation from [Lee, Yang, Parr, 1988](#)

Nonlocal potentials:

- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

Note: Nonlocal exchange can only be used for insulators using [All Bands/EDFT Electronic minimizer](#) for [Energy](#) and [Geometry Optimization](#) (without cell optimization) tasks. It is not compatible with stress, NMR, phonon, or polarizability calculations. The formalism cannot be used with mixture atoms and only norm conserving potentials can be used. Note that stress calculations, and hence cell optimization and the [Elastic Constants](#) task, are supported for screened exchange versions, sX and sX-LDA.

Note: There is an important difference between standard DFT calculations with local exchange-correlation potentials and the nonlocal exchange case. The potential used in the latter scenario depends on the wavefunctions at SCF k-points, while in the former case, the potential depends only on electron density. This difference can make calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Use method for DFT-D correction: When checked, the selected method will be used for dispersion corrections. Available options are:

- [TS](#) for GGA PBE, PBESOL, RPBE, BLYP, PW91; also for PBE0 and B3LYP
- [Grimme](#) for GGA PBE and B3LYP
- [OBS](#) for GGA PW91 and LDA
- [MBD*](#) for GGA PBE; also for HSE03, HSE06, and PBE0

Note: The option selected will automatically update the *Use custom DFT-D parameters* setting on the [DFT-D tab](#) of the CASTEP Electronic Options dialog.

Spin polarized: When checked, indicates that the calculation will be performed using different wavefunctions for different spins. This is known as a 'spin-polarized' or 'spin-unrestricted' calculation. If unchecked, the calculation uses the same orbitals for alpha and beta spins. This is known as a 'non-spin-polarized' or 'spin-restricted' calculation. Default = [unchecked](#).

Use formal spin as initial: When checked, indicates that the initial value for the number of unpaired electrons for each atom will be taken from the formal spin specified for each atom. This starting value will be subsequently optimized during the calculation. Default = [checked](#).

Note: This option is enabled only if the *Spin polarized* checkbox is checked.

Note: Atom-resolved initial spin is used only if either the *Electronic minimizer* control is set to [Density mixing](#) on the [SCF](#) tab of the CASTEP Electronic Options dialog or the LDA+U calculation (see below) is chosen.

Initial spin: Specify the initial value for the number of unpaired electrons in a spin-polarized calculation. This starting value will be subsequently optimized during the calculation.

Note: This option is enabled only if the *Spin polarized* checkbox is checked and the *Use formal spin as initial* checkbox is unchecked.

Use LDA+U: When checked, indicates that LDA+U formalism is to be used. Actual values of U can be set up through the Hubbard U tab of the Electronic Configuration dialog.

Note: This option is only enabled if the *Spin polarized* checkbox is checked.

Note: The LDA+U formalism is not compatible with NMR or polarizability calculations. The formalism cannot be used with mixture atoms or real-space pseudopotentials.

Include spin-orbit coupling: When checked, indicates that [spin-orbit coupling](#) will be added to the Hamiltonian.

Note: The formalism is currently implemented only for tabulated norm-conserving pseudopotentials, with no LDA+U corrections, and is not supported for nonlocal exchange-correlation functionals. Additionally, it is not yet compatible with calculations of:

- NMR
- Dipole corrections
- Electron localization function
- Linear response, including polarizability calculation
- Optical properties
- Electronic excitations
- Partial density of states
- Hirshfeld population analysis


Visualization of the electrostatic potential is also not yet implemented.

Metal: When checked this indicates that the system is metallic so that empty bands can be created and edited. When unchecked the *Fix occupancy* checkbox on the [SCF](#) tab of the CASTEP Electronic Options dialog is checked. When unchecked the [k-point separations](#) used by default are coarser. Default = [checked](#).

Note: In some calculations is not sufficient to use fixed orbital occupancies if the system under investigation should actually have a band gap according to DFT results. This applies to calculations that use the linear response formalism for vibrational properties and to calculations of electric field responses (polarizability and IR and Raman spectra). Attempting to study a metallic systems using fixed orbital occupancies will result in poor convergence and usually in unphysical results for IR and Raman intensities and for polarizability. If this is the case, check whether your system is metallic by running either [density of states](#) or [band structure](#) calculations.

Charge: Specify the total charge on the unit cell.

Access methods

Menu	Modules CASTEP Calculation Setup
Toolbar	 Calculation Setup

CASTEP Geometry Optimization dialog


The Geometry Optimization dialog allows you to set up and display the parameters that control the [Geometry Optimization](#) task.

It contains the following tabs:

- [Minimizer](#): Provides access to the parameters that specify the convergence level of the minimization and the external pressure and allows you to control cell optimization.
- [Options](#): Provides access to the parameters that control the minimization algorithm.
- [Stress](#): Provides access to the parameters that control the external stress or hydrostatic pressure on the structure.

Help: Displays the Help topic for the current tab.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More...</i>
Toolbar	 <i>Calculation Setup More...</i>

Minimizer tab

The *Minimizer* tab allows you to specify the convergence level of the minimization and the external pressure, and to control cell optimization.

Quality: Set the geometry optimization convergence thresholds for energy change, maximum force, maximum stress, and maximum displacement between optimization cycles. The optimization will stop when all of these criteria are satisfied.

Four sets of convergence thresholds are available:

- [Coarse](#)
- [Medium](#)
- [Fine](#)
- [Ultra-fine](#)

The values of the convergence thresholds in each set are given in the table below:

Value	Coarse	Medium	Fine	Ultra-fine
<i>Energy</i> (eV/atom)	5×10^{-5}	2×10^{-5}	1×10^{-5}	5×10^{-6}
<i>Max. force</i> (eV/Å)	0.1	0.05	0.03	0.01
<i>Max. stress</i> (GPa)	0.2	0.1	0.05	0.02
<i>Max. displacement</i> (Å)	0.005	0.002	0.001	5×10^{-4}

Alternatively, thresholds can be specified independently for *Energy*, *Max. force*, *Max. stress*, and *Max. displacement*. If you enter your own values for any of these settings, the *Quality* is displayed as [Customized](#) on both the *Minimizer* tab and the [Setup](#) tab of the CASTEP Calculation dialog.

Note: When the [main quality](#) is set to [Express](#) the geometry optimization quality is also set to [Express](#). In this case energy tolerance will be displayed in eV/cell rather than eV/atom, the default value is 0.001 eV/cell. All other tolerances are ignored and geometry optimization runs stop when the energy change is less than the tolerance regardless of the values of forces or displacements.

Energy: Specify the convergence threshold for the maximum energy change, in eV/atom, during the geometry optimization. The units are eV/cell if the *Quality* is set to [Express](#).

Max. force: Specify the convergence threshold for the maximum force, in eV/Å, during the geometry optimization. If the *Quality* is set to [Express](#), this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. stress: Specify the convergence threshold for the maximum stress, in GPa, during the geometry optimization. If the *Quality* is set to [Express](#), this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. displacement: Specify the convergence threshold for the maximum displacement, in Å, during the geometry optimization. If the *Quality* is set to [Express](#), this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. iterations: Specify the maximum number of geometry optimization cycles. If this number of cycles is reached, then the calculation will stop, even if the convergence criteria are not satisfied.

Cell optimization: Specify whether the cell should be optimized and how. Default = [None](#). Options are:

- [None](#) - No cell optimization is requested and the *Basis set for variable cell* and *Compressibility* options are not available.
- [Full](#) - Complete optimization of the cell.
- [Fixed Volume](#) - The cell is optimized while keeping the volume fixed, cell angles and cell lengths are varied.
- [Fixed Shape](#) - The cell is optimized while keeping the cell angles and cell length ratios fixed, the cell volume is varied.

Basis set for variable cell: Specify the desired behavior of the basis set when the cell size changes. Default = [Fixed Basis Quality](#). Options are:

- [Fixed Basis Quality](#) - The number of plane waves changes to maintain the fixed cutoff energy (finite basis set correction is required)
- [Fixed Basis Size](#) - The number of plane waves is kept constant, so the effective cutoff energy changes (finite basis set correction is not required)

Tip: [Fixed Basis Quality](#) is the recommended option.


Compressibility: Specify an estimated compressibility value for the crystal under investigation in order to accelerate the geometry optimization. Each entry in the dropdown list is interpreted as a preset value:

- [Soft](#) - 25 GPa, suitable for soft materials like molecular crystals
- [Medium](#) - 200 GPa, suitable for most transition metals
- [Hard](#) (default) - 500 GPa, suitable for minerals, ceramics, and hard metals

Note: CASTEP geometry optimization will respect constraints on the fractional coordinates of atoms. These constraints may be imposed using the controls on the Atom tab of the Edit Constraints dialog.

Nonlinear constraints are respected only for P1 structures that do not contain mixture atoms and only when the delocalized internals optimizer is used, that is, the *Use delocalized internals* checkbox is checked on the [Options](#) tab of the CASTEP Geometry Optimization dialog.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More... Minimizer</i>
Toolbar	 <i> Calculation Setup More... Minimizer</i>

Options tab

The *Options* tab allows you to specify the minimization algorithm and the parameters controlling the algorithm.

Algorithm: Specify the minimization algorithm. These algorithms are supported by CASTEP:

- [LBFGS](#)
- [BFGS](#)
- [Damped MD](#)
- [TPSD](#)

The [BFGS](#) algorithm is generally recommended. The [LBFGS](#) algorithm (low-memory BFGS) is expected to perform better for large systems. The latter algorithm also implements a universal sparse preconditioner that accelerates geometry optimization ([Packwood et al., 2016](#)). However, if there are constraints TPSD might be a better choice (see the [Geometry optimization](#) theory topic for further details).

The [TPSD geometry optimization](#) algorithm is a viable alternative for systems where the potential energy surface deviates significantly from the quadratic form. TPSD offers robust convergence and is particularly recommended when user-supplied constraints on lattice parameters are applied during cell optimization (for example, when optimizing a solid-solid interface in a direction perpendicular to the interface plane).

Note: The [Damped MD](#) algorithm is not used when cell optimization is performed.

Use line search: When checked, indicates that optimization should use the advanced line search algorithm.

Note: This checkbox is checked by default, except when the [main quality](#) is set to [Express](#). If you specify the [Express](#) quality setting and then request line search, the *Quality* is displayed as [Customized](#) on both the [Minimizer](#) tab and the [Setup](#) tab of the CASTEP Calculation dialog. In the latter scenario, you must set convergence criteria for gradients and displacements to sensible values, as the line search algorithm cannot function using only the energy change criterion.

Use delocalized internals: When checked, indicates that delocalized internal coordinates should be used during geometry optimization, instead of Cartesian coordinates. This setting typically speeds up the calculation by 2-3 times.

Note: The *Use delocalized internals* option is enabled only if the [BFGS](#) algorithm is selected.

Note: The delocalized internals minimizer does not currently support cell optimization. As a result, CASTEP will automatically switch over to Cartesian coordinates when the cell is allowed to vary.

The delocalized internals minimizer respects nonlinear constraints only for P1 structures that do not contain mixture atoms.

Damping algorithm: Specify the algorithm for the Damped MD method. The supported algorithms are:

- **Independent** - the damping constant is chosen independently for each mode, so that all modes lose energy at the same rate.
- **Coupled** - the same damping constant is used for all modes at each step.
- **Steepest Descent**

The **Independent** damping algorithm is recommended (see the [Geometry optimization](#) theory topic for details).

Damping coefficient recalculation frequency: During the damped MD optimization, the damping coefficients are recalculated occasionally to improve the damping rate. This value specifies the number of MD steps between these recalculations.

Note: The *Damping coefficient recalculation frequency* value is not used by the steepest descent algorithm.

Wavefunction extrapolation: Specify the method to be used for wavefunction extrapolation between MD steps.


- **None** - no extrapolation is performed.
- **1st VV** - first-order extrapolation with variable coefficients.
- **2nd VV** - second-order extrapolation with variable coefficients.
- **2/1 VV** - alternate second- and first-order extrapolation with variable coefficients.
- **1st CC** - first-order extrapolation with constant coefficients.
- **2nd CC** - second-order extrapolation with constant coefficients.
- **2/1 CC** - alternate second- and first-order extrapolation with constant coefficients.

Time step: Specify the time step to be used in the damped MD geometry optimization.

Auto-update time step: When checked, indicates that the time step will be automatically updated to speed up the geometry optimization.

Note: The *Time step* and *Auto-update time step* controls are enabled only if the **Damped MD** algorithm is selected.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More... Options</i>
Toolbar	 <i>Calculation Setup More... Options</i>

Stress tab

The *Stress* tab allows you to specify an external stress or hydrostatic pressure on the structure for geometry optimization.

Note: The options on this tab are applicable only when cell optimization has been requested.

External stress: Specify any element of the external stress tensor on the structure, in GPa.


Equivalent hydrostatic pressure: Specify the hydrostatic pressure on the structure.

The hydrostatic pressure is one third of the trace of the stress tensor. When a value is specified here, the diagonal elements of the stress tensor are modified so as to leave any anisotropic term unchanged.

Note: A positive value of external stress and hydrostatic pressure indicates that the structure is compressed.

Reset external stress to zero: Sets all elements of the stress tensor to zero.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More... Stress</i>
Toolbar	 <i>Calculation Setup More... Stress</i>

CASTEP Dynamics dialog


The CASTEP Dynamics dialog allows you to set up and display the parameters that control the [Dynamics](#) task.

It contains the following tabs:

- [Dynamics](#): Provides access to the main parameters that specify the dynamics, including choice of ensemble, temperature, pressure, and the length of the run.
- [Options](#): Provides access to the parameters that control the details of the dynamics algorithm, including thermostat, barostat and wavefunction extrapolation settings.
- [Stress](#): Provides access to the parameters that control the external stress or hydrostatic pressure on the structure.

Help: Displays the Help topic for the current tab.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More...</i>
Toolbar	 <i>Calculation Setup More...</i>

Dynamics tab

The *Dynamics* tab allows you to specify the main parameters for controlling dynamics simulations.

Ensemble: Specify the ensemble to be used in the dynamics simulation.

- [NVE](#) - dynamics at fixed volume and constant energy.
- [NVT](#) - dynamics at fixed volume with a thermostat to maintain a constant temperature.
- [NPH](#) - dynamics at constant enthalpy with a barostat to maintain a constant pressure.
- [NPT](#) - dynamics with a thermostat to maintain a constant temperature and with a barostat to maintain a constant pressure.

Initial velocities: Select the method of velocity initialization to be used for the dynamics calculation. The available options are:

- [Random](#) - set initial velocities to random value (default).
- [Current](#) - set initial velocities to values currently defined on the structure.

Temperature: Specify the temperature of the dynamics simulation. For the [NVE](#) ensemble, the initial random velocities of the atoms are scaled to this temperature.

Pressure: Specify the external pressure for the dynamics simulation in the [NPH](#) or [NPT](#) ensemble. For [Parrinello](#) barostat full stress tensor can be specified on the [Stress](#) tab.

Time step: Specify the time step for the dynamics simulation.

Total simulation time: Specify the total time for the dynamics simulation. When modified the number of steps is adjusted appropriately for the current time step.


Number of steps: Specify the total number of steps for the dynamics simulation.

Basis set for variable cell: Specify the desired behavior of the basis set when the cell size changes.

- [Fixed Basis Quality](#) - the number of plane waves changes to maintain the fixed cutoff energy (finite basis set correction is required).
- [Fixed Basis Size](#) - the number of plane waves is kept constant, so the effective cutoff energy changes (finite basis set correction is not required).

Tip: [Fixed Basis Quality](#) is the recommended option.

Access methods

Menu	Modules CASTEP Calculation Setup More... Dynamics
Toolbar	 Calculation Setup More... Dynamics

Options tab

The *Options* tab allows you to specify parameters which control the details of the dynamics algorithm.

Thermostat: Specify the thermostat to be used for NVT or NPT dynamics. Available options are:

- [Langevin](#)
- [Nose](#)
- [NHL](#)

Note: This option is enabled only if the [NVT](#) or [NPT](#) ensemble is selected on the [Dynamics](#) tab. The Nosé-Hoover-Langevin (NHL) thermostat is only available for the [NVT](#) ensemble.

Barostat: Specify the barostat to be used for NPH or NPT dynamics. Available options are:

- [Andersen](#) - scales the cell uniformly
- [Parrinello](#) - allows variation in the cell shape

Note: This option is enabled only if the [NPT](#) or [NPH](#) ensemble is selected on the [Dynamics](#) tab.

Langevin constant: Specify the damping time of temperature fluctuations during Langevin NVT dynamics. This time should normally be larger than the time scale of any motions of interest.

Nose Q ratio: Specify a scaling factor for the fictitious mass Q of the Nosé thermostat for Nosé or Nosé-Hoover-Langevin NVT dynamics. A larger Q ratio implies increased damping of temperature fluctuations.

Cell time constant: Specify the characteristic cell time, which is used to estimate the mass associated with the barostat. A larger value implies increased damping of pressure fluctuations.


Wavefunction extrapolation scheme: Specify the method to be used for wavefunction extrapolation between molecular dynamics steps. This selection is not available when *Use Extended Lagrangian (XL-BOMD)* is selected.

- **None** - no extrapolation is performed.
- **1st VV** - 1st order extrapolation with variable coefficients.
- **2nd VV** - 2nd order extrapolation with variable coefficients.
- **2/1 VV** - Alternate 2nd and 1st order extrapolation with variable coefficients.
- **1st CC** - 1st order extrapolation with constant coefficients.
- **2nd CC** - 2nd order extrapolation with constant coefficients.
- **2/1 CC** - Alternate 2nd and 1st order extrapolation with constant coefficients.

Use eXtended Lagrangian (XL-BOMD): When checked, indicates that the extended Lagrangian molecular dynamics ([Steneteg 2010](#), [Niklasson 2011](#)) is used instead of the wavefunction extrapolation schemes. The extended Lagrangian formulation allows significantly higher time step values to be used, while conserving the constant of motion. This option is available only for fixed-cell (NVE and NVT) ensembles. Default = [checked](#).

Fix center of mass: When checked, indicates that the center of mass will be fixed during the dynamics simulation. Default = [unchecked](#).

Access methods

Menu	<i>Modules CASTEP Calculation Setup More... Options</i>
Toolbar	 <i>Calculation Setup More... Options</i>

Stress tab

The *Stress* tab allows you to specify an external stress or hydrostatic pressure on the structure for molecular dynamics.

Note: The options on this tab are available only when the [NPT](#) or [NPH](#) ensemble is selected on the [Dynamics tab](#).

External stress: Specify any element of the external stress tensor on the structure, in GPa.

Equivalent hydrostatic pressure: Specify the hydrostatic pressure on the structure.


The hydrostatic pressure is one third of the trace of the stress tensor. When a value is specified here, the diagonal elements of the stress tensor are modified so that any anisotropic term remains unchanged.

Note: A positive value of external stress and hydrostatic pressure indicates that the structure is compressed.

Note: When the [Andersen](#) barostat is selected on the [Options tab](#) only hydrostatic pressure is used by CASTEP.

Reset external stress to zero: Sets all elements of the stress tensor to zero.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More... Stress</i>
Toolbar	 <i>Calculation Setup More... Stress</i>


CASTEP Elastic Constants dialog

The CASTEP Elastic Constants dialog is accessed from the *More...* button on the [Setup tab](#), when the [Elastic Constants](#) option is selected from the *Task* dropdown list.

It contains the following tabs:

- [Elastic Constants](#): Allows you to specify the strains applied to the crystal, used for calculating elastic constants.
 - [Options](#): Allows you to set the convergence level of the elastic constants calculation.
- Help:** Displays the Help topic for the current tab.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More...</i>
Toolbar	 <i>Calculation Setup More...</i>

Elastic Constants tab

The *Elastic Constants* tab allows you to set parameters that define how the elastic constants will be calculated.

Number of steps for each strain: Specify the number of distorted structures generated for each strain pattern. An odd value implies that the undistorted structure will be among those generated. Even values are, therefore, recommended.

Maximum strain amplitude: Set the maximum distortion used. Values in excess of 0.01 are not recommended, since the crystal is likely to be beyond linear elasticity. However, values of 0.001 and below will generate a set of structures that are very similar to one another. In these circumstances, computational noise may become significant when comparing the calculated stress values for similar structures.

Use volume-conserving strains: When checked indicates that the strain patterns will be modified to use volume-conserving strains, when possible. This option should only be used if the standard set of strains is producing unsatisfactory results.

Strain pattern: Displays a matrix showing the nonzero components of the strain tensor for each generated strain. For example, the line:


$$1 \quad 0 \quad 0 \quad 1 \quad 0 \quad 0$$

means that the *xx*, *yz* (and *zy*) components of the strain tensor will be non-zero.

Note: This matrix is not editable.

Note: For trigonal symmetry, the orientation standard where C lies along the z-axis and A is in the xz plane must be used. For further details on the lattice orientation standard and how to set it, see the [Viewing or changing the lattice parameters](#) topic.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More... Elastic Constants</i>
Toolbar	 <i>Calculation Setup More... Elastic Constants</i>

Options tab

The *Options* tab allows you to specify the convergence level of the elastic constants calculation.

Quality: Sets the convergence thresholds for energy change, maximum force, and maximum displacement between cycles. This is used for the geometry optimization runs that are required for the elastic constants calculation. The calculation will stop when all of these criteria are satisfied.

Four sets of convergence thresholds are available; [Coarse](#), [Medium](#), [Fine](#) and [Ultra-fine](#). The values of each convergence threshold in each set are given in the table below:

Quality	Energy (eV/atom)	Force (eV/Å)	Displacement (Å)
Coarse	1×10^{-5}	0.02	0.001
Medium	4×10^{-6}	0.01	4×10^{-4}
Fine	2×10^{-6}	0.006	2×10^{-4}
Ultra-fine	1×10^{-6}	0.002	1×10^{-4}
Customized	User defined	User defined	User defined

Alternatively, thresholds can be specified independently. If user defined values are used, the *Quality* displayed is [Customized](#).

Note: When the [main quality](#) is set to [Express](#) the elastic constants quality is also set to [Express](#). In this case energy tolerance will be displayed in eV/cell rather than eV/atom, the default value is 0.001 eV/cell. All other tolerances are ignored and geometry optimization runs stop when the energy change is less than the tolerance regardless of the values of forces or displacements.


Energy: Specify the convergence threshold for the maximum energy change, in eV/atom. The units are eV/cell if the *Quality* is set to [Express](#).

Max. force: Specify the convergence threshold for the maximum force, in eV/Å. If the *Quality* is set to [Express](#), this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. displacement: Specify the convergence threshold for the maximum displacement, in Å. If the *Quality* is set to [Express](#), this tolerance by default will be set to a very high value and will effectively be ignored in the calculation.

Max. iterations: Specify the maximum number of elastic constants cycles. If this number of cycles is reached, then the calculation will stop even if the convergence criteria are not satisfied.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More... Options</i>
Toolbar	 <i>Calculation Setup More... Options</i>

CASTEP Transition State Search dialog

The CASTEP Transition State Search dialog allows you to set up and display the parameters that control the [TS Search](#) task, including the protocol to be used and the quality of the search.

Note: CASTEP transition-state searches require a trajectory document (for example, an `.arc` or `.xtc` file) as input. You will not be able to start a transition-state search run unless a suitable document is in scope.

Note: When a transition state search is performed on a periodic system the unit cell is fixed.

Search protocol: Select the type of synchronous transit that will be performed from the dropdown list. Available options are:

- [LST Maximum](#) - performs a single linear synchronous transit (LST) maximization, bracketing the maximum between the reactants and product
- [Halgren-Lipscomb](#) - performs an LST maximization, followed by a single-line search minimization
- [LST/Optimization](#) - performs an LST maximization, followed by a full conjugate gradient minimization
- [Complete LST/QST](#) - performs an LST, followed by repeated conjugate gradient minimizations and quadratic synchronous transit (QST) maximizations until a transition state has been located
- [QST/Optimization](#) - starting from a QST, performs repeated maximizations and conjugate gradient minimizations until a transition state has been located

Quality: Set the TS search convergence thresholds for the root mean square (RMS) forces on the atoms. The search will stop when this criterion is satisfied.

Five quality settings are available:

- [Express](#)
- [Coarse](#)
- [Medium](#)
- [Fine](#)
- [Ultra-fine](#)

The value of the convergence threshold for each setting is given in the table below:

	Express	Coarse	Medium	Fine	Ultra-fine
<i>RMS convergence (eV Å⁻¹)</i>	0.1	0.5	0.25	0.05	0.01

RMS convergence: Specify the value, in eV Å⁻¹, at which convergence is considered to take place in terms of the RMS of the gradients.

Max. number QST steps: Specify the maximum number of QST maximization cycles. If this number of cycles is reached, then the calculation will stop, even if the convergence criteria are not satisfied.

Optimize reactants and products: Specifies that the input structure for the reactant and product in a TS search calculation should be optimized to a local minimum. Selecting this allows the TS search to start from a "raw" trajectory, where the reactant and product structures have not already been optimized.


Note: This choice may lead to reactant and product structures deviating substantially from the input structures, so it is recommended that you carefully check the final path.

Calculate partition functions: Specifies whether to calculate partition functions based on the Gamma-point dynamical matrix for the reactants, products, and the transition state. This data will be stored in the output 3D Atomistic Collection document.

Note: This is not available unless *Optimize reactants and products* is checked.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Setup More...</i>
Toolbar	 <i>Calculation Setup More...</i>

CASTEP TS Confirmation dialog

The CASTEP TS Confirmation dialog allows you to set up and display the parameters that control the simulation in a CASTEP [TS Confirmation](#) task.

Quality: Set the geometry optimization convergence thresholds for energy change, maximum force, and maximum displacement between optimization cycles. The optimization will stop when the energy convergence is satisfied along with either the displacement or gradient criteria.

Four sets of convergence thresholds are available:

- [Coarse](#)
- [Medium](#)
- [Fine](#)
- [Ultra-fine](#)

The values of the convergence thresholds in each set are given in the table below:

Value	Coarse	Medium	Fine	Ultra-fine
<i>Energy</i> (eV/atom)	1×10^{-4}	2×10^{-5}	1×10^{-5}	5×10^{-6}
<i>Max. force</i> (eV/Å)	0.5	0.1	0.05	0.02
<i>Max. displacement</i> (Å)	0.05	0.005	0.004	0.003

Alternatively, thresholds can be specified independently for *Energy*, *Max. force*, and *Max. displacement*. If you enter your own values for any of these settings, the *Quality* is displayed as [Customized](#) on both the CASTEP TS Confirmation dialog and the [Setup](#) tab of the CASTEP Calculation dialog.

Note: When the [main quality](#) is set to [Express](#) the transition state confirmation quality is also set to [Express](#). In this case the energy tolerance will be displayed in eV/cell rather than eV/atom, the default value is 0.002 eV/cell.

Energy: Specify the convergence threshold for the maximum energy change, in eV/atom, during the geometry optimization. The units are eV/cell if the *Quality* is set to [Express](#).

Max. force: Specify the convergence threshold for the maximum force, in eV/Å, during the geometry optimization.


Max. displacement: Specify the convergence threshold for the maximum displacement, in Å, during the geometry optimization.

Altering the value of any threshold is allowed and results in the *Quality* being set to [Customized](#).

Max. images: The number of intermediate NEB images used during the transition state confirmation.

Help: Displays the Help topic in a browser.

Access methods

Menu	Modules CASTEP Calculation Setup More...
Toolbar	 Calculation Setup More...

Electronic tab

The *Electronic* tab allows you to set the parameters associated with the electronic Hamiltonian. These include the basis set, pseudopotentials, SCF convergence criteria, and k-point set.

Energy cutoff: Select the precision used for the [plane wave basis set](#).

- [Coarse](#)
- [Medium](#)
- [Fine](#)
- [Ultra-fine](#)

The actual value of the energy cutoff corresponding to the selected quality for the current structure is also displayed.

Note: Calculation of the NMR parameters may require the *Energy cutoff* to be set to a higher value than for total energy or geometry optimization calculations. It is advisable to study the convergence of the results as the *Energy cutoff* parameter is increased. Generally, setting the cutoff to between 270 and 400 eV should produce convergence of the shielding constant to about 1 ppm, but in some cases, the cutoff has to be increased up to 550 eV.

SCF tolerance: Select the threshold used to determine whether an SCF has converged. Available options and associated convergence thresholds are:

- [Coarse](#) - 10^{-5} eV/atom
- [Medium](#) - 2×10^{-6} eV/atom
- [Fine](#) - 10^{-6} eV/atom
- [Ultra-fine](#) - 5×10^{-7} eV/atom

Note: When the [main quality](#) is set to [Express](#) the SCF tolerance is also set to [Express](#) which corresponds to 10^{-4} eV/cell.

Energy tolerances per: Specifies whether energy tolerances are calculated as the energy change per atom ([Atom](#) is the default setting) or per unit cell (the [Cell](#) value is enforced when the main quality, and hence the SCF tolerance quality, is set to [Express](#)).

k-point set: Define the number of integration points that will be used to integrate the wavefunction in reciprocal space. Available options are:

- [Gamma](#) - a single point at (0, 0, 0)
- [Coarse](#)
- [Medium](#)
- [Fine](#)

Pseudopotentials: Select the type of [pseudopotential](#) to be used. Two different types of pseudopotentials are available, ultrasoft and norm-conserving; both of them are available as either

[generated on the fly](#) (OTFG) potentials or as [tabulated potentials](#). OTFG potentials are generally preferred for reasons of accuracy and consistency. They are required for NMR calculations.

- **OTFG ultrasoft** (default) - the preferred option, ultrasoft pseudopotentials allow calculations to be performed with lower energy cutoffs. On-the-fly generation produces potentials that are consistent between solid state and pseudo-atom calculations since they use the same exchange-correlation functional throughout. The set of OTFG ultrasoft pseudopotentials introduced in Materials Studio 8.0 provides results in close agreement with all electron calculations and is very accurate for describing ground state structures.
- **OTFG norm conserving** - typically harder and therefore more computationally expensive than ultrasoft pseudopotentials. Norm-conserving potentials are currently required for linear response-based calculations of phonon properties and of polarizabilities and for calculations with nonlocal exchange-correlation functionals (for example, screened exchange).
- **Ultrasoft** - tabulated ultrasoft pseudopotentials, provided for compatibility with earlier versions of Materials Studio.
- **Norm conserving** - tabulated norm-conserving pseudopotentials, provided for compatibility with earlier versions of Materials Studio.

Note: It is not recommended to use PW91 exchange-correlation functional when requesting on the fly generation of pseudopotentials; PBE, RPBE, WC, BLYP, or PBESOL are better options when a GGA functional is required.

Note: When you specify the type of pseudopotential to be used in this way, the default pseudopotential of that type for each element will be used in the calculation.

Tip: Use the [Electronic Options dialog](#) to exercise more control over which pseudopotentials are used for each element.

Relativistic treatment: The way relativistic effects are incorporated into OTFG pseudopotentials. Options are:

- **Schroedinger**
- **Koelling-Harmon** (default)
- **ZORA**


Use core hole: Specify whether to include core holes in the calculation; core holes can be used in core level spectroscopy calculations and should be defined using the Core Hole tab of the Electronic Configuration dialog.

Note: For calculations exploiting core holes, on-the-fly pseudopotentials must be used. If the *Use core hole* checkbox is not checked, any core holes in the input system will not be preserved during the calculation.

Note: CASTEP calculations with core holes assume by default that an electron is removed from the system, so it is treated as having a charge of 1 (or one more than specified in the *Charge* field on the [Setup](#) tab of the CASTEP Calculation dialog). In some circumstances, for example when studying impurities, it might be more appropriate to consider the system as charge neutral. In order to achieve this you should specify the *Charge* of -1 on the [Setup](#) tab, in this way the CASTEP input file will have a zero charge. It is also possible to edit the `seedname.param` file to specify a fractional charge. The strength of the core hole can be adjusted by editing the `seedname.ce11` file and modifying the pseudopotential definition string (for example, change `{1s1}` to `{1s0.5}` to use a core hole with the charge of 0.5).

More...: Provides access to the [CASTEP Electronic Options dialog](#), which allows you to set up and display further details of the electronic Hamiltonian.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic</i>
Toolbar	 <i>Calculation Electronic</i>


CASTEP Electronic Options dialog

The CASTEP Electronic Options dialog allows you to set up and display the details of the electronic Hamiltonian used in CASTEP calculations. These parameters are relevant for the [Energy](#), [Geometry Optimization](#), [Dynamics](#), [Elastic Constants](#) and [TS Search](#) tasks.

It contains the following tabs:

- [Basis](#): Provides access to the plane-wave energy cutoff, FFT grid specification, and finite basis set correction.
 - [SCF](#): Provides access to the parameters that control the electronic minimization algorithm.
 - [k-points](#): Provides more detailed access to the k-point set.
 - [Potentials](#): Provides control over which pseudopotentials will be used for each element in the structure.
 - [DFT-D](#): Provides access to the parameters for van der Waals dispersion correction calculations.
- Help:** Displays the Help topic for the current tab.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More...</i>
Toolbar	 <i>Calculation Electronic More...</i>

Basis tab

The *Basis* tab provides access to basis set information, including the plane-wave energy cutoff, FFT grid specification and finite basis set correction.

Use custom energy cutoff: When checked, a custom value for the energy cutoff can be specified in the adjacent text box. Otherwise the text box displays the energy cutoff appropriate for the *Energy cutoff* quality parameter on selected on the [Electronic](#) tab.

Density: Specify the quality of the FFT grid. Three options are available:

- [Standard](#)
- [Fine](#)
- [Precise](#)

The FFT grid parameters are chosen such that they provide a good representation of the electron density. At the [Precise](#) level, an exact representation of the density is provided for the given energy-cutoff. At the [Standard](#) and [Fine](#) levels, a reduced FFT grid is used to speed up the calculation. Some aliasing will occur as a result but the effect on the SCF solution is usually small. The FFT grid parameters that will be used in the CASTEP calculation are displayed as derived using the current energy-cutoff and unit cell parameters.

Augmentation density scaling factor: Specify a finer grid for representation of the augmentation charge density in the atomic core region. By default the same grid is used as for the standard electron density; it is reasonable in some cases to increase the augmentation grid by a factor of up to 4 in order to improve the accuracy of calculations. This can be controlled by the *Quality* setting on the [Setup](#) tab of the CASTEP Calculation dialog.

Apply finite basis set correction: Specify when to use a finite basis set correction in the evaluation of energy and stress. This can be controlled by the *Quality* setting on the [Setup](#) tab of the CASTEP Calculation dialog.

This correction gives a volume dependent addition to the energy that may result in a significant correction to any calculated stress. It is particularly important where an accurate stress or cell geometry optimization is required. Three settings are available:

- **Smart** - apply the correction only when stress is required. This will include any cell geometry optimization.
- **Always** - apply the correction to all calculations.
- **Never** - do not apply a correction, even when stress is calculated. Any result for stress or cell geometry may be unreliable as a result.

Correction mode: Specify how the finite basis set correction should be calculated. The evaluation of the correction requires an estimate for the derivative of the total energy with respect to the logarithm of the plane-wave energy cutoff. The options are:

- **Automatic** - the energy derivative will be calculated automatically using numerical differentiation.
- **Manual** - the energy derivative is specified manually.


Numerical differentiation using: Specify the number of energy points to use in evaluating the energy derivative required for the finite basis set correction. A converged SCF energy will be evaluated at each point.

Note: This option is enabled only if the [Automatic Correction mode](#) is selected.

Energy derivative w.r.t. cutoff: Specify the value of the energy derivative required for the finite basis set correction.

Note: This option is enabled only if the [Manual Correction mode](#) is selected.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More... Basis</i>
Toolbar	 <i>Calculation Electronic More... Basis</i>

SCF tab

The *SCF* tab on the CASTEP Electronic Options dialog provides access to parameters that control the electronic minimization algorithm.

SCF tolerance: Specify the SCF convergence threshold. This will override the *SCF tolerance* option specified on the [Electronic](#) tab.

Note: When calculating linear response properties (for example phonons, polarizabilities, NMR properties), it is important that the SCF convergence threshold is sufficiently strict from the computational point of view to accurately calculate these properties. When the calculation of linear response properties is requested, CASTEP will use a convergence threshold of 10^{-8} eV atom⁻¹, unless the specified threshold is lower. To force CASTEP to use a less stringent threshold, the ELEC_ENERGY_TOL parameter should be manually inserted in the input parameters ([.param](#)) file for the property calculation.

Max. SCF cycles: Set the maximum number of SCF iterations allowed for an energy calculation. The energy calculation will end after the specified number of iterations, even if the SCF has not converged.

Convergence window: The convergence tolerance window for SCF. This is number of SCF iterations in a row for which convergence criteria are fulfilled. This parameter is required in order to avoid occasional oscillations.

Electronic minimizer: Specify the electronic minimization method to be used for the SCF calculation. Two options are available, [Density Mixing](#) and [All Bands/EDFT](#).

Tip: The [Density Mixing](#) option is recommended, particularly for variable occupancy calculations. The [All Bands/EDFT](#) method is usually slower and requires more memory. However, the EDFT scheme is recommended for metallic systems where converging electronic structure using [Density Mixing](#) option proves problematic.

Charge: Specify the amplitude for charge density mixing (that is, the amplitude of the output charge density to mix with the input charge density to obtain input for the next iteration).

Note: This option is enabled only if the [Density Mixing](#) minimization method is selected.

Spin: Specify the amplitude for spin density mixing, that is, the amplitude of the output spin density to mix with the input spin density to obtain input for the next iteration.

Note: This option is enabled only for spin-polarized calculations using the [Density Mixing](#) minimization method.

More...: Provides access to the [CASTEP Density Mixing Options](#) dialog, where more detailed control over the [Density Mixing](#) electronic minimization method is available.

Note: This option is enabled only if the [Density Mixing](#) minimization method is selected.

Fix occupancy: When checked, the electronic occupation numbers will be fixed during electronic minimization. Only the lowest, occupied states will be included in the calculation. Default = [checked](#).

More...: Provides access to the [CASTEP Occupancy Options](#) dialog, where more detailed control over the occupancies is available.

Apply dipole corrections: Select the type of dipole corrections to apply from the dropdown list. Available options are:

- [None](#) (default)
- [Non self-consistent](#)
- [Self-consistent](#)

[Self-consistent](#) is the most accurate option, as this affects the electrostatic potential as well as the total energy and its gradients. This is the only option that is suitable to investigate the effect of dipole corrections, for example on surface workfunctions.


Tip: It is recommended to use the [All Bands/EDFT](#) electronic minimization scheme when applying a self-consistent dipole correction to an elongated cell of a slab representing a metal surface; the [Density mixing](#) minimization scheme may fail to converge for such systems.

[Non self-consistent](#) is recommended for cases where it is hard to converge the SCF with *Apply dipole corrections* set. This option can only be used for *Energy* calculations and is not compatible with phonon calculations.

Note: Dipole corrections will be applied only if the system is either molecule in the box or a periodic slab with the vacuum layer of at least 8 Å.

Note: If dipole corrections are to be applied the symmetry of the system will be converted to P1 to bring the molecule (or slab) into the center of the unit cell.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More... SCF</i>
Toolbar	 <i> Calculation Electronic More... SCF</i>

CASTEP Density Mixing Options dialog

The CASTEP Density Mixing Options dialog allows you to specify the parameters that control the [Density Mixing](#) method of electronic minimization.

Mixing scheme: Specify the method used for mixing the input densities and output densities from the current iteration to obtain the input density for the next iteration in the iterative solution for the SCF. The supported methods are:

- [Linear](#) - the input density and the output density are mixed in a simple linear combination.
- [Kerker](#) - the input density and output density are mixed using a reduced mixing factor for the long length scale Fourier coefficients of the density.
- [Pulay](#) (default) - the output density is mixed with densities from a number of previous iterations, using the RMM-DIIS method, leading to more rapid convergence.
- [Broyden](#) - the output density is mixed with densities from a number of previous iterations, using the quasi-Newton relaxation method. The overall convergence is similar to that of Pulay mixing.

The [Pulay](#) or [Broyden](#) method is recommended. The [Linear](#) method is not usually suitable for large systems.

Charge mixing amplitude: Specify the amplitude of the output charge density to mix with the input charge density to obtain input for the next iteration.

Charge mixing cutoff: Specify the length scale used. Charge mixing is reduced for Fourier coefficients at reciprocal lattice vectors less than about this value.

Note: This option is enabled only if the [Kerker](#), [Broyden](#), or [Pulay](#) density mixing method is selected.

DIIS history list: Specify the number of previous iterations to be considered in the DIIS for the [Pulay](#) or [Broyden](#) density mixing method.

Note: This option is enabled only if the [Pulay](#) or [Broyden](#) density mixing method is selected.

Spin mixing amplitude: Specify the amplitude of the output spin density to mix with the input spin density to obtain input for the next iteration.


Note: This option is enabled only for spin-polarized calculations.

Spin mixing cutoff: Specify the length scale used. Spin mixing is reduced for Fourier coefficients at reciprocal lattice vectors less than about this value.

Note: This option is enabled only for spin-polarized calculations using the [Kerker](#), [Broyden](#), or [Pulay](#) density mixing methods.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More... SCF More...</i>
Toolbar	 <i>Calculation Electronic More... SCF More...</i>

CASTEP Occupancy Options dialog

The CASTEP Occupancy Options dialog provides access to parameters that control occupancies in CASTEP calculations.

By default, CASTEP calculations are performed with variable occupancy. The fixed occupancy option is only suitable for structures that are known to be insulators or closed shell systems at the level of theory used in the CASTEP calculation.

Empty bands: Specify the number of additional bands to be included in an electronic minimization as a percentage of the number of occupied bands.

Note: This option is enabled only for variable occupancy calculations.

Smearing: Specify the broadening to be applied to the electronic occupation.

Note: This option is enabled only for variable occupancy calculations.

Optimize total spin after: Specify the number of SCF iterations for which the total electronic spin will remain fixed before being allowed to vary.


Note: This option is enabled only for spin-polarized variable occupancy calculations.

Note: The spin will be fixed throughout the calculation (including possible steps of geometry optimization) if the checkbox is unchecked.

Tip: In spin-polarized systems there may be more than one stable SCF solution with different total spin values. By setting the initial spin on the [Setup](#) tab and by fixing the total spin value for a number of SCF iterations, it is possible to exert some control over which solution is found.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More... SCF More...</i>
Toolbar	 <i>Calculation Electronic More... SCF More...</i>

k-points tab

The *k-points* tab provides access to more detailed options for controlling the k-point set used in CASTEP calculations.

The Monkhorst-Pack k-point grid to be used in the calculation can be specified in several ways. For cubic cells and for the C direction of hexagonal cells the even and odd grids for the Monkhorst-Pack scheme give the same number of k-points. However, the even grid provides better sampling and will always be used automatically under these conditions. This ensures that a good grid with k-point separation at (or less than) the specified target can be achieved more economically. As a consequence, such lattices may have much finer separations than requested as odd grids have been excluded - even though they would have been closer to the specified separation - and the better even grids have been taken in preference.

Gamma point only: When selected, indicates that a single k-point at (0,0,0) will be used for the density of states calculation.

Quality: When selected, indicates that the k-point grid will be generated using a k-point separation appropriate to the specified quality level. Select the desired quality level from the dropdown list. Available options are:

- Coarse
- Medium
- Fine

The k-point separations associated with the three *Quality* settings depend on whether the *Metal* checkbox on the [Setup](#) tab is checked and are as follows:

Quality	k-point separation (\AA^{-1})	
	Metal checked	Metal unchecked
Coarse	0.07	0.1
Medium	0.05	0.08
Fine	0.04	0.07

Separation: When selected, indicates that the k-point grid will be generated according to the specified k-point separation. Specify the k-point separation, in \AA^{-1} , in the associated text box.

Note: When the *Separation* option is selected, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, indicates that the k-point grid will be generated using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in \AA^{-1} , resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.


Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

Note: The *Grid parameters* and *Origin shift* controls are enabled only if the *Custom grid parameters* option is selected.

Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

Note: The actual set of k-points that will be used in the calculations may be altered if the symmetry of the system changes or LDA+U calculation is requested.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More... k-points</i>
Toolbar	 <i>Calculation Electronic More... k-points</i>

Potentials tab

The *Potentials* tab allows you to control which pseudopotentials will be used for each element in the structure.

Scheme: Select the type of [pseudopotential](#) to be used. Two different types of pseudopotentials are available, ultrasoft and norm-conserving; both of them are available as either [generated on the fly](#) (OTFG) potentials or as [tabulated potentials](#). OTFG potentials are generally preferred for the reasons of accuracy, consistency, and finally these are required for NMR calculations:

- **OTFG ultrasoft** (default) - the preferred option, ultrasoft pseudopotentials allow calculations to be performed with lower energy cutoffs. On-the-fly generation produces potentials that are consistent between solid state and pseudo-atom calculations since they use the same exchange-correlation functional throughout. The set of OTFG ultrasoft pseudopotentials introduced in Materials Studio 8.0 provides results in close agreement with all electron calculations and is very accurate for describing ground state structures.
- **OTFG norm conserving** - typically harder and therefore more computationally expensive than ultrasoft pseudopotentials. Norm-conserving potentials are currently required for linear response-based calculations of phonon properties and of polarizabilities and for calculations with nonlocal exchange-correlation functionals (for example, screened exchange).
- **Ultrasoft** - tabulated ultrasoft pseudopotentials, provided for compatibility with earlier versions of Materials Studio.
- **Norm conserving** - tabulated norm-conserving pseudopotentials, provided for compatibility with earlier versions of Materials Studio.

Note: The latest set of OTFG settings introduced in Materials Studio 8.0 has been developed in order to minimize the error with respect to fully converged all-electron DFT calculations. The error achieved by this set is 0.5 meV/atom which puts CASTEP among the most accurate pseudopotential codes available. A full definition of the test framework and the meaning of the error is given by Lejaeghere et al. (2014) and on the website of the [Delta project](#). The files that correspond to this set have an `_80` suffix. Some of these files have been subsequently improved to eliminate ghost states. The recommended set of OTFG settings includes files with an `_2017R2` (ultrasoft) or an `_2017R2ncp` (norm-conserving) suffix.

Note: It is not recommended to use PW91 exchange-correlation functional when requesting on the fly generation of pseudopotentials; PBE, RPBE, WC, BLYP, or PBESOL are better options when a GGA functional is required.

Note: When you specify the type of pseudopotential to be used in this way, the default pseudopotential of that type for each element will be used in the calculation.

Representation: Choose between [Reciprocal space](#) and [Real space](#) representations of the pseudopotentials.

Tip: The real space representation may give a performance advantage for large systems.

More...: Provides access to the [CASTEP Real Space Potentials dialog](#), which allows you to specify details of the transformation of pseudopotentials to a real space representation.

Note: This button is enabled only if [Real space](#) is selected from the *Representation* dropdown list.

Selected potentials: Displays information about the selected pseudopotentials for each element in a grid.

There is a row in the grid for each element. The element type, current pseudopotential, energy, and valence (Z) are displayed. To select a different pseudopotential for a particular element, click in the appropriate pseudopotential grid cell and choose a new pseudopotential from the dropdown list.

If changes are made to the default pseudopotentials, the *Scheme* displayed is [Custom](#).

Show potentials for all elements: When checked, the *Selected potentials* list will display information about all elements in the periodic table for which pseudopotentials are available. Otherwise, only elements present in the current structure are displayed in the list. Default = [unchecked](#).

View: Displays a modal view on the selected pseudopotential file.

External Potential


Electric field: Specify the external electric field strength, in eV/Å/e.

Field direction (X Y Z): Vector specifying the direction of the electric field.

Note: Only systems that contain molecules or slabs are appropriate for electric field calculations. For slabs, the field must be along the surface normal. In both cases atoms should be positioned in the middle of the cell and the symmetry must be P1.

Note: The field direction is specified in Cartesian coordinates. The values of the X, Y, and Z direction components of the electric field are interrelated. The three field components are used to define a unit vector. When a job is launched the direction components are normalized to give a unit vector which is then multiplied by the field magnitude to give the actual field components. Entering a vector with all zero components has the same effect as entering a (111) vector.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More... Potentials</i>
Toolbar	 / <i>Calculation Electronic More... Potentials</i>

CASTEP Real Space Potentials dialog

The CASTEP Real Space Potentials dialog allows you to specify the parameters describing the transformation of pseudopotentials to a real space representation.

Core radius: Specify the real space core radius of the element displayed. Change the element type using the dropdown list.

Tip: Enter zero to reset the core radius for the displayed element to the default value.

Note: The real space core radius determines the radius of real space integration to be used in the calculation. It should be larger than the core radius used in pseudopotential generation, normally by a factor of 1.5 to 2.0, so as to overcome the aliasing problems inherent in the real space integration method.

Reset all core radii to defaults: Sets all core radii to the default values.

Use custom energy cutoff for transformation: When checked, a value may be specified for the energy cutoff used in the transformation to the real space form of pseudopotentials. Otherwise a value will be calculated automatically based on the plane-wave energy cutoff to be used in the calculation. Default = [unchecked](#).


Impose tolerance: When checked, the real space pseudopotential transformation will be tested to ensure it is of the quality specified in the dropdown list. Default = [checked](#).

If the transformation is not of the requested quality, then the CASTEP calculation will not proceed. This should ensure that the results obtained from a real space pseudopotential calculation accurately reproduce those of a similar calculation using reciprocal space pseudopotentials.

Note: If this option is unchecked, the CASTEP calculation will be performed regardless of the quality of the real space pseudopotential transformation.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Electronic More... Potentials More...</i>
Toolbar	 <i>Calculation Electronic More... Potentials More...</i>

DFT-D tab

The *DFT-D* tab allows you to set up customized parameters for van der Waals dispersion corrections. This can involve the definition of DFT-D corrections for exchange functionals that are not usually supported, the definition of support for additional elements, or changing existing parameters.

Use custom DFT-D parameters: Specify whether to use custom DFT-D parameters. When this checkbox is checked, select the van der Waals scheme to use from the dropdown list, options are:

- [TS](#) (default)
- [Grimme](#)
- [OBS](#)
- [MBD*](#)

Note: The option selected will automatically update the *Use method for DFT-D correction* setting on the [Setup tab](#) of the CASTEP Calculation dialog.

Note: The schemes that rely on calculated electron densities, namely TS and MBD*, may not work well in calculations with small unit cells, where diameter of van der Waals spheres is comparable with lattice parameters. The MBD* scheme is particularly sensitive to such situations. In such cases, the CASTEP output file contains a warning explaining the problem. The MBD* scheme can also fail if the geometry is far from equilibrium, in which case it is useful to perform a preliminary geometry optimization with the TS scheme. The main area of application of the MBD* scheme is molecular crystals, so it may experience problems with highly ionic systems.

Atomic parameters

This table allows you to edit the dispersion correction parameters for each of the atomic species. The type and number of parameters depend on the DFT-D scheme selected, please refer to the original literature for the meaning and usage of each parameter.

The units for all parameters are in eV for energies and in Å for lengths. The available columns are:

Atom: Denotes the element to be edited.

C6 (eV Å⁶): Available for TS, MBD*, and Grimme schemes.

R0 (Å): Available for TS, MBD*, and Grimme schemes.

alpha (Å³): Available for TS, MBD*, and OBS schemes.

I (eV): Available for the OBS scheme.

Rvdw (Å): Available for the OBS scheme.

Note: Only the elements in the currently active document are listed in the *Atomic parameters* table .

Note: Each scheme includes a radius (R0 for TS and Grimme, Rvdw for OBS) that must be non-zero for each of the active elements.

Scheme parameters

Scheme parameters are dimensionless numbers that define the functional form of each scheme.

Please refer to the original literature to for the meaning and usage of each parameter.

Depending on the van der Waals scheme selected for the *custom DFT-D parameters* setting, the *Scheme parameters* that can be specified are:


- TS: sR, d
- Grimme: s6, d
- OBS: lambda, n
- MBD*: sR

Note: The default values for these parameters depend on the exchange correlation functional selected on the [Setup tab](#) of the CASTEP Calculation dialog.

Note: Both scheme parameters must be non-zero for the calculations to start and for input files to be written.

Reset All: Restores the default settings for each element in the grid.

Access methods


Menu	<i>Modules CASTEP Calculation Electronic More... DFT-D</i>
Toolbar	 <i>Calculation Electronic More... DFT-D</i>

Properties tab

The *Properties* tab allows you to select the properties that will be computed as part of a CASTEP calculation.

Choose the properties you wish to compute by checking the appropriate checkboxes in the list. Once you select a properties checkbox, additional options may be displayed below the list.

Access methods

Menu	<i>Modules CASTEP Calculation Properties</i>
Toolbar	 <i>Calculation Properties</i>

Band structure selection

Checking the *Band structure* checkbox on the [Properties](#) tab displays options for calculating electronic energies along high symmetry directions in the Brillouin zone.

Energy range: Specify the maximum energy above the Fermi level for which band structure will be calculated. Default = 10 eV.


k-point set: Specify the quality of the k-point set for the band structure calculation. Each setting corresponds to a particular approximate separation between consecutive k-points on the reciprocal space path. Default = [Medium](#).

Quality	k-point separation (\AA^{-1})
Coarse	0.04
Medium	0.025
Fine	0.015

Separation: Specify the approximate separation between k-points in \AA^{-1} . The default depends on the selected *k-point set*.

More...: Provides access to the [CASTEP Band Structure Options dialog](#), which allows you to set additional parameters, including the reciprocal space path.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Band structure</i>
Toolbar	 <i>Calculation Properties Band structure</i>

CASTEP Band Structure Options dialog

The Band Structure Options dialog allows you to specify a custom reciprocal space path and the eigenvalue convergence criterion used for band structure calculations.

Use separate XC functional for band structure calculation: When checked, allows you to select a different exchange-correlation functional for the band structure calculation from the one used in the self-consistent calculation.

Tip: This feature is particularly useful for carrying out expensive, screened exchange calculations. Perform the main run with the LDA or GGA functional, then invoke screened or exact exchange in non self-consistent mode during the band structure calculation.

Note: There is an important difference between standard DFT calculations with local exchange-correlation potentials and the nonlocal exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Functional: Select the type of exchange-correlation potential to be used in the band structure calculation.

Choose the type of functional from the first dropdown list. Available options are:

- LDA
- GGA
- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

Then, if appropriate, select the specific functional from the second dropdown list. Depending on the functional type selected from the first dropdown list, some of the following options may be available:

- CA-PZ
- PBE
- RPBE
- PW91
- WC
- PBESOL
- BLYP

Note: This option is enabled only when *Use separate XC functional for band structure calculation* is checked.


Band energy tolerance: Specify the convergence criterion for electronic eigenvalues during the band structure calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

Note: More information about the symmetry labels used in the Band Structure Options dialog can be found in Bradley and Cracknell ([1972](#)).

Path...: Provides access to the Brillouin Zone Path dialog, which allows you to specify a custom reciprocal space path.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Properties More...</i>
Toolbar	 <i>Calculation Properties More...</i>

Core level spectroscopy selection

Checking the *Core level spectroscopy* checkbox on the [Properties](#) tab displays options for calculating core level spectra.


Energy range: Specify the energy limit above the Fermi level for which core level spectra will be calculated. Default = 25 eV.

k-point set: Specify the quality of the k-point set for the core level spectroscopy calculation. Each setting corresponds to a particular separation between consecutive k-points on the reciprocal space path. Default = [Medium](#).

Quality	k-point separation (\AA^{-1})
Coarse	0.04
Medium	0.025
Fine	0.015

More...: Provides access to the [CASTEP Core Level Spectroscopy Options dialog](#), which allows you to set additional parameters, including the k-point set specification.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Core level spectroscopy</i>
Toolbar	 <i>Calculation Properties Core level spectroscopy</i>

CASTEP Core Level Spectroscopy Options dialog

The CASTEP Core Level Spectroscopy Options dialog allows you to specify the density of the k-point set and the eigenvalue convergence criterion used for core level spectra calculations.

The Monkhorst-Pack k-point grid to be used in the calculation can be specified in one of four ways:

Gamma point only: When selected, indicates that a single k-point at (0,0,0) will be used for the density of states calculation.

Quality: When selected, indicates that the k-point grid will be generated using a k-point separation appropriate to the specified quality level. Select the desired quality level from the dropdown list. Available options are:

- Coarse
- Medium
- Fine

The k-point separations associated with the three *Quality* settings are as follows:

Quality	k-point separation (\AA^{-1})
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, indicates that the k-point grid will be generated according to the specified k-point separation. Specify the k-point separation, in \AA^{-1} , in the associated text box.

Note: When the *Separation* option is selected, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, indicates that the k-point grid will be generated using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in \AA^{-1} , resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

Note: The *Grid parameters* and *Origin shift* controls are enabled only if the *Custom grid parameters* option is selected.


Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

Note: The actual set of k-points that will be used in the calculations may be altered if the symmetry of the system changes.

Band energy tolerance: Specify the convergence criterion in eV for electronic eigenvalues during the core level spectroscopy calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Core level spectroscopy More...</i>
Toolbar	 / <i>Calculation Properties Core level spectroscopy More...</i>

Density of states selection

Checking the *Density of states* checkbox on the [Properties](#) tab displays options for calculating electronic energies on the Monkhorst-Pack mesh of k-points.


Energy range: Specify the maximum energy above the Fermi level for which density of states will be calculated. Default = 10 eV.

k-point set: Specify the quality of the k-point set for the density of states calculation. Each setting corresponds to a particular separation between neighboring k-points in the Monkhorst-Pack grid. Default = [Medium](#).

Calculate PDOS: When checked, indicates that the information required to generate partial and local densities of states will also be calculated.

More...: Provides access to the [CASTEP Density of States Options dialog](#), which allows you to set additional parameters, including the k-point set specification.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Density of states</i>
Toolbar	 / <i>Calculation Properties Density of states</i>

CASTEP Density of States Options dialog

The CASTEP Density of States Options dialog allows you to specify the k-point set and the eigenvalue convergence criterion used for density of states calculations.

The Monkhorst-Pack k-point grid to be used in the calculation can be specified in one of four ways:

Gamma point only: When selected, indicates that a single k-point at (0,0,0) will be used for the density of states calculation.

Quality: When selected, indicates that the k-point grid will be generated using a k-point separation appropriate to the specified quality level. Select the desired quality level from the dropdown list. Available options are:

- [Coarse](#)
- [Medium](#)
- [Fine](#)

The k-point separations associated with the three *Quality* settings are as follows:

Quality	k-point separation (\AA^{-1})
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, indicates that the k-point grid will be generated according to the specified k-point separation. Specify the k-point separation, in \AA^{-1} , in the associated text box.

Note: When the *Separation* option is selected, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, indicates that the k-point grid will be generated using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in \AA^{-1} , resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

Note: The *Grid parameters* and *Origin shift* controls are enabled only if the *Custom grid parameters* option is selected.

Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

Note: The actual set of k-points that will be used in the calculations may be altered if the symmetry of the system changes.

Use separate XC functional for DOS calculation: When checked, indicates that a different exchange-correlation functional will be used for the density of states calculation from the one used in the self-consistent calculation.

Tip: This feature is particularly useful for carrying out expensive screened exchange calculations: perform the main run with the LDA or GGA functional, then invoke screened or exact exchange in non-self-consistent mode during the density of states calculation.

Note: There is an important difference between standard DFT calculations with local exchange-correlation potentials and the non-local exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Functional: Select the type of DFT exchange-correlation potential to be used in the density of states calculation.

Choose the type of functional from the first dropdown list. Available options are:

- LDA
- GGA
- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

Then, if appropriate, select the specific functional from the second dropdown list. Depending on the functional type selected from the first dropdown list, some of the following options may be available:


- CA-PZ
- PBE
- RPBE
- PW91
- WC
- PBESOL
- BLYP

Note: The *Functional* control is enabled only if the *Use separate XC functional for DOS calculation* checkbox is checked.

Band energy tolerance: Specify the convergence criterion, in eV, for electronic eigenvalues during the density of states calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Density of states More...</i>
Toolbar	 <i>Calculation Properties Density of states More...</i>

Electron density difference selection

Checking the *Electron density difference* checkbox on the [Properties](#) tab displays options for calculating an electron density difference field.

Calculation of atomic difference with respect to the sum of the densities of a subsystem requires that sets of atoms have been created in the input structure. Only sets with [DensityDifference](#) as part of the set name will be taken into account, and only if they contain atoms (it is possible for such sets to contain other objects like bonds or monitors; only atoms will be considered in electron density difference calculations). Use the Edit Sets dialog, accessed by selecting *Edit | Edit Sets* from the menu bar, to create the required sets in the 3D Atomistic document.

Note: Sets of atoms should not overlap; that is, no atom can belong to more than one 'DensityDifference' set.


Tip: When only one set with the correct name is present in the structure, Materials Studio assumes that the rest of the atoms should be treated as a second set. Thus, in the case of a molecule-surface interaction, it is sufficient to create a single set that comprises all the atoms in the molecule.

Atomic densities: When selected, indicates that only the density difference with respect to the sum of atomic densities will be calculated.

Sets of atoms: When selected, indicates that only the density difference with respect to the sum of the densities of sets of atoms will be calculated.

Both atomic densities and sets of atoms: When selected, indicates that both kinds of density difference will be calculated.


Access methods

Menu	<i>Modules CASTEP Calculation Properties Electron density difference</i>
Toolbar	 <i>Calculation Properties Electron density difference</i>

Electron localization function selection

Checking the *Electron localization function* checkbox on the [Properties](#) causes ELF to be calculated as part of the CASTEP run.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Electron localization function</i>
Toolbar	 <i>Calculation Properties Electron localization function</i>

Electronic excitations (TD-DFT) selection

Checking the *Electronic excitations (TD-DFT)* checkbox on the [Properties](#) tab displays options for calculating electronic excitations.

Calculate energies of: Specify the number of excited states which will be calculated. Default = 6.


The excitation data will be reported in the <seedname>_TDDFT.castep output file.

Calculate optical properties: If checked, the transition probabilities for these states will be calculated to provide access to optical properties.

Optimize geometry for: Specify the excited state whose geometry should be optimized. Default = 1 (that is, the first excited state).

The optimized structure for the specified state will be saved in the <seedname>_TDDFT_GO.xsd output file.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Electronic excitations (TD-DFT)</i>
Toolbar	 / <i>Calculation Properties Electronic excitations (TD-DFT)</i>

NMR selection

Checking the *NMR* checkbox on the [Properties](#) tab displays options for calculating shielding tensors and electric field gradients.

Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Shielding: Determines the chemical shielding tensor for each atom in the system.

Note: The shielding tensor is ill-defined for spin-polarized calculations. NMR calculation is allowed in a spin-polarized setting for a paramagnetic system, but you should check that the final electronic state is indeed paramagnetic. Similarly such calculations are not recommended for metallic systems without a band gap; however, it is legitimate to use variable orbital occupancies and metallic settings while modeling an insulator.

EFG: Determines the electric field gradients for each atom in the system.

J-coupling: Determines the J-coupling between the selected atom(s) and all other atoms in the system. At least one atom must be selected in the input 3D Atomistic document.

Note: J-coupling can be calculated only for non-magnetic systems. The *Relativistic treatment* of the OTFG pseudopotentials (on the [Electronic](#) tab of the CASTEP Calculation dialog) must be set to either [Schrodinger](#) for non-relativistic treatment or [ZORA](#) for scalar-relativistic effects to be taken into account. J-coupling calculations are supported only for systems with P1 symmetry. If your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.

G-tensor: Calculates the change in the EPR g-tensor for a molecule in a box or a defect in a crystal.

Note: The g-tensor can only be calculated with spin-polarization turned on and for systems with P1 symmetry. If your crystal has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you continue.

System type: Specify the type of system used in the calculation. Options are:


- [Crystal](#)
- [Molecule](#)
- [Auto](#) - CASTEP will assess the system and treat it as a crystal or molecule as appropriate

Note: Calculations in the [Molecule](#) mode can only be performed for systems with P1 symmetry. If your crystal representing molecule in the box has symmetry other than P1, you will be prompted to convert the crystal symmetry to P1 before you can continue.

More...: Provides access to the [CASTEP NMR Options dialog](#), which allows you to specify the nuclear quadrupolar moment for each element.

Note: Calculation of the NMR parameters requires higher accuracy for the wavefunctions than total energy or geometry optimization calculations. This affects how you choose the *Energy cutoff* quality parameter on the [Electronic](#) tab, even choosing [Ultra-fine](#) may not be sufficient to obtain high quality NMR parameters. Therefore, it is advisable to study the convergence of the results as the *Energy cutoff* parameter is increased. Generally, setting the cutoff to between 270 and 400 eV should produce convergence of the shielding constant to about 1 ppm, but in some cases, the cutoff has to be increased up to 550 eV.

Access methods

Menu	<i>Modules CASTEP Calculation Properties NMR</i>
Toolbar	 <i>Calculation Properties NMR</i>

CASTEP NMR Options dialog

The CASTEP NMR Options dialog allows you to set additional parameters affecting a NMR calculations.

Maximum number of steps: Specify the maximum number of conjugate gradient steps taken for each electronic band in the electronic minimizer during an NMR calculation of the first-order perturbed wavefunctions. Default = [250](#).

Nuclear quadrupolar moment

This section allows you to specify the nuclear quadrupolar moment, Q , used for electric field gradient calculations. The value of the quadrupolar moment depends on the actual isotope. CASTEP makes a suggestion based on the most typical isotope used in solid state NMR experiments. The value of Q affects only the quadrupolar coupling constant, C_Q , calculated and printed out by CASTEP. If you find that the wrong value of Q was used you can rescale the generated C_Q constant using a different Q value. The list of default values is based on the compilation by [Pyykkö \(2008\)](#).

Note: CASTEP versions before Materials Studio 5.0 used an older compilation by [Harris \(1996\)](#), so some results for quadrupolar coupling constants may have changed in later versions.


Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Q moment: Specify the nuclear quadrupolar moment of the element displayed. Change the element type using the dropdown list.

Tip: To reset the nuclear quadrupolar moment for the displayed element to the default value, enter [0](#) for the *Q moment*.

Reset all Q values to defaults: Sets all nuclear quadrupolar moments for all elements to the default values.

Help: Displays the Help topic in a browser.

Menu	<i>Modules CASTEP Calculation Properties NMR More...</i>
Toolbar	 <i>Calculation Properties NMR More...</i>

Optical properties selection

Checking the *Optical properties* checkbox on the [Properties](#) tab displays options for calculating electronic intraband transitions.


Energy range: Specify the maximum energy above the Fermi level for which optical properties will be calculated. Default = 10 eV.

Note: It is important to include a significant number of empty bands when calculating optical properties. The exact number required will depend on the nature and size of the system under consideration.

k-point set: Specify the quality of the k-point set for the optical properties calculation. Each setting corresponds to a particular separation between neighboring k-points in the Monkhorst-Pack grid. Default = [Medium](#).

More...: Provides access to the [CASTEP Optical Properties Options dialog](#), which allows you to set additional parameters, including the k-point set specification.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Optical properties</i>
Toolbar	 <i>Calculation Properties Optical properties</i>

CASTEP Optical Properties Options dialog

The CASTEP Optical Properties Options dialog allows you to specify the density of the k-point set and the eigenvalue convergence criterion used for optical properties calculations.

The Monkhorst-Pack k-point grid to be used in the calculation can be specified in one of four ways:

Gamma point only: When selected, indicates that a single k-point at (0,0,0) will be used for the density of states calculation.

Quality: When selected, indicates that the k-point grid will be generated using a k-point separation appropriate to the specified quality level. Select the desired quality level from the dropdown list. Available options are:

- [Coarse](#)
- [Medium](#)
- [Fine](#)

The k-point separations associated with the three *Quality* settings are as follows:

Quality	k-point separation (\AA^{-1})
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, indicates that the k-point grid will be generated according to the specified k-point separation. Specify the k-point separation, in \AA^{-1} , in the associated text box.

Note: When the *Separation* option is selected, the Monkhorst-Pack parameters are derived to give the specified separation between neighboring grid points.

Custom grid parameters: When selected, indicates that the k-point grid will be generated using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in \AA^{-1} , resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.

Note: The *Grid parameters* and *Origin shift* controls are enabled only if the *Custom grid parameters* option is selected.

Display points...: Displays the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

Note: The actual set of k-points that will be used in the calculations may be altered if the symmetry of the system changes.

Use separate XC functional for optics calculation: When checked, indicates that a different exchange-correlation functional will be used for the optical properties calculation from the one used in the self-consistent calculation.

Tip: This feature is particularly useful for carrying out expensive, screened exchange calculations. Perform the main run with the LDA or GGA functional, then invoke screened or exact exchange in non self-consistent mode during the band structure calculation.

Note: There is an important difference between standard DFT calculations with local exchange-correlation potentials and the non-local exchange case. The potential used in the latter scenario depends on the SCF k-points, while in the former case, the potential depends only on electron density. This difference can make all properties calculations a lot more expensive in terms of memory usage and CPU time, so it is advisable to limit the number of SCF k-points that you use in such situations. This is particularly relevant for small unit cells, where the default settings may generate a very large k-point set.

Functional: Select the type of DFT exchange-correlation potential to be used in the optical properties calculation.

Choose the type of functional from the first dropdown list. Available options are:

- LDA
- GGA
- HF
- HF-LDA
- sX
- sX-LDA
- PBE0
- B3LYP
- HSE03
- HSE06

Then, if appropriate, select the specific functional from the second dropdown list. Depending on the functional type selected from the first dropdown list, some of the following options may be available:


- CA-PZ
- PBE
- RPBE
- PW91
- WC
- PBESOL
- BLYP

Note: The *Functional* control is enabled only if the *Use separate XC functional for optics calculation* checkbox is checked.

Band energy tolerance: Specify the convergence criterion, in eV, for electronic eigenvalues during the optical properties calculation. The calculation will stop when all electronic eigenvalues change by less than this value over a single iteration of the electronic structure.

Help: Displays the Help topic in a browser.

Access methods


Menu	Modules CASTEP Calculation Properties Optical properties More...
Toolbar	 Calculation Properties Optical properties More...

Orbitals selection

Checking the *Orbitals* checkbox on the [Properties](#) tab causes the orbitals (wavefunctions) to be calculated as part of the CASTEP run.

Note: Orbitals are required to calculate the STM profile.

Access methods

Menu	Modules CASTEP Calculation Properties Orbitals
Toolbar	 Calculation Properties Orbitals

Phonons selection

Checking the *Phonons* checkbox on the [Properties](#) tab displays options for calculating phonon properties.

Density of states: When checked, indicates that the phonon density of states will be computed as part of the CASTEP run.

Dispersion: When checked, indicates that the phonon dispersion will be computed as part of the CASTEP run.

Both: When selected both the phonon density of states and dispersion will be calculated during the CASTEP run.

Calculate LO-TO splitting: When checked, indicates that a non-analytical correction to the dynamical matrix will be applied. The LO-TO phonon frequency splitting at the Γ -point will be calculated along the directions connecting the Γ -point with the neighboring points along the reciprocal space path. Default = [checked](#).

Method: Select the technique to be used to calculate phonon frequencies from the dropdown list. Available options are:


- [Linear response](#)
- [Finite displacement](#)

Finite displacement phonons are available only at the commensurate q-points (at the cost of creating a supercell). However, in this case, the phonon frequencies can be obtained with no limitations on the settings or the physical properties of the system. The finite displacement technique can be used for metals, ultrasoft potentials, spin-polarized systems, and so on.

Note: If LO-TO splitting is requested, then the restrictions on the system type and settings (insulator, norm-conserving potentials, non-spin-polarized calculation) are the same for both the linear response and finite displacement techniques.

More...: Provides access to the [CASTEP Phonon Properties Setup dialog](#), which allows you to set additional parameters affecting a phonon calculation, including the convergence tolerance.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Phonons</i>
Toolbar	 <i>Calculation Properties Phonons</i>

CASTEP Phonon Properties Setup dialog

The CASTEP Phonon Properties Setup dialog allows you to set additional parameters affecting a phonon calculation.

Method: Select the technique to be used to calculate phonon frequencies from the dropdown list. Available options are:

- [Linear response](#)
- [Finite displacement](#)

The finite displacement technique can be used for metals, ultrasoft potentials, spin-polarized systems, and so on, and allows you to obtain phonon frequencies with no limitations on the settings or the physical properties of the system.

Note: If LO-TO splitting is requested (that is, by checking the *Calculate LO-TO splitting* checkbox on the Properties tab of the CASTEP Calculation dialog when [Phonons](#) is selected), then the restrictions on the system type and settings (insulator, norm-conserving potentials, non-spin-polarized) are the same for both the linear response and finite displacement techniques.

Use interpolation: When checked, indicates that the real space dynamical matrix will be calculated using the Monkhorst-Pack mesh defined by the separation parameter. When *Method* is set to [Finite](#)

[displacement](#) this will invoke the nondiagonal supercell approach of Lloyd-Williams and Monserrat (2015).

q-vector grid spacing for interpolation: Specify the q-point separation parameter, in \AA^{-1} , which represents the average distance between Monkhorst-Pack mesh q-points used in the real space dynamical matrix calculations. A smaller separation parameter produces a denser mesh, giving more accurate results at the expense of longer calculation times.

Note: The *q-vector grid spacing for interpolation* control is enabled only if the *Use interpolation* checkbox is checked.

Linear response

Convergence tolerance: Specify the convergence criterion, in eV \AA^{-2} , for the force constants during a phonon properties run.

Note: The *Convergence tolerance* control is enabled only if [Linear response](#) is selected from the *Method* dropdown list.

Finite displacement

Supercell defined by cutoff radius: Specify the real space cutoff radius, in \AA , for dynamical matrix calculations. This value will be used to construct an appropriate supercell. A larger cutoff radius produces more accurate results at the expense of longer calculation times.

If the cutoff radius specified creates a large supercell, its size is reported as a factor of the size of the current cell, indicating that the calculation may be computationally expensive. If the cutoff radius is reasonable, it is confirmed that the original cell is large enough. For non-3D periodic systems a reminder that a supercell cannot be constructed is displayed.

Note: The *Supercell defined by cutoff radius* control is enabled only if [Finite displacement](#) is selected from the *Method* dropdown list and the *Use interpolation* checkbox is unchecked.

Dispersion

Quality: Set the quality of the q-vector set for the phonon dispersion calculation. The quality level affects the approximate separation between consecutive q-vectors on the reciprocal space path. Available options and the corresponding q-vector separations are:

Quality	q-vector separation (\AA^{-1})
Coarse	0.04
Medium	0.025
Fine	0.015

Separation: Specify the approximate separation between q-vectors in \AA^{-1} . The default depends on the selected *Quality* of the q-vector.

Path...: Provides access to the Brillouin Zone Path dialog, which allows you to specify a custom reciprocal space path.

Density of states

Quality: Set the quality of the q-vector set for the phonon density of states calculation. The quality level affects the separation between neighboring q-vectors in the Monkhorst-Pack grid. Available options and

the corresponding q-vector separations are:


Quality	k-point separation (\AA^{-1})
Gamma	a single q-vector at (0,0,0) will be used
Coarse	0.07
Medium	0.05
Fine	0.04

Note: For [Linear response](#) calculations, if [Gamma](#) point is selected and the *Use interpolation* checkbox is checked frequencies will be calculated using interpolation method. This involves calculations of phonon frequencies at multiple q-vectors in the Brillouin zone and is therefore an expensive way of generating Gamma point phonons. Such calculations can be justified only as a way of testing the accuracy of interpolation scheme (directly calculated frequencies are more accurate). To run calculations only at the Gamma point you should uncheck the *Use interpolation* checkbox.

More...: Provides access to the [CASTEP Phonon Density of States Options dialog](#), which allows you to specify the q-vector set.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Phonons More...</i>
Toolbar	 <i>Calculation Properties Phonons More...</i>

CASTEP Phonon Density of States Options dialog

The CASTEP Phonon Density of States Options dialog allows you to specify the q-vector set for phonon density of states calculations.

The Monkhorst-Pack q-vector grid to be used in the calculation can be specified in one of four ways.

Note: The option selected here propagates from the *Quality* setting in the *Density of States* section on the [CASTEP Phonon Properties Setup dialog](#). As a result, altering the selection here will also change the setting on the CASTEP Phonon Properties Options dialog.

Gamma point only: When selected, indicates that a single q-vector at (0,0,0) will be used for the density of states calculation.

Quality: When selected, indicates that the q-vector grid will be generated using a q-vector separation appropriate to the specified quality level. Select the desired quality level from the dropdown list. Available options and the associated q-vector separations are:

Quality	k-point separation (\AA^{-1})
Coarse	0.07
Medium	0.05
Fine	0.04

Separation: When selected, indicates that the q-vector grid will be generated according to the specified q-vector separation. Specify the q-vector separation, in \AA^{-1} , in the associated text box.

Note: When the *Separation* option is selected, the Monkhorst-Pack parameters are derived so as to produce the specified separation between neighboring grid points.

Custom grid parameters: When selected, indicates that the q-vector grid will be generated using the Monkhorst-Pack grid parameters and the origin shift in fractional reciprocal space coordinates specified in the *Grid parameters* and *Origin shift* text boxes, respectively.

Grid parameters: Specify the Monkhorst-Pack grid parameters in each of the lattice directions.

Actual spacing: Displays the k-point separation, in \AA^{-1} , resulting from the currently specified Monkhorst-Pack grid parameters in each of the lattice directions.

Origin shift: Specify the offset of the Monkhorst-Pack grid in fractional reciprocal space coordinates.


Note: The *Grid parameters* and *Origin shift* controls are enabled only if the *Custom grid parameters* option is selected.

Display points...: Displays, in a new window, the number and fractional coordinates of the reciprocal space mesh points that would be generated using the currently specified parameters.

Note: The actual set of q-vectors that will be used in the calculation may be altered if the symmetry of the system changes.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Phonons More... More...</i>
Toolbar	 <i>Calculation Properties Phonons More... More...</i>

Polarizability, IR and Raman spectra selection

Checking the *Polarizability, IR and Raman spectra* checkbox on the [Properties](#) tab displays options for calculating dielectric permittivity and molecular polarizability.


System type: Select the option from the dropdown list that best describes the system being studied or choose [Auto](#) for automatic detection. Available options are:

- [Auto](#)
- [Crystal](#)
- [Molecule](#)
- [Linear](#)

Calculate Raman intensities: When checked, activities for Raman active vibrations will be calculated. Subsequently CASTEP analysis can be used to construct Raman mode intensities for a given temperature and laser wavelength from calculated activities.

More...: Provides access to the [CASTEP IR and Raman Options](#) dialog, which allows you to set additional parameters affecting a polarizability, IR and Raman calculation, including the convergence tolerance and Raman frequency range.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Polarizability, IR and Raman spectra</i>
Toolbar	 <i>Calculation Properties Polarizability, IR and Raman spectra</i>

CASTEP IR and Raman Options dialog

The CASTEP IR and Raman Options dialog allows you to set additional parameters affecting a polarizability, IR, and Raman calculation.

Convergence tolerance: Specify the value, in \AA^3 , of the required convergence for the second-order response to the electric field. Default = $1.0\text{e-}5 \text{\AA}^3$.

Scissors operator: Specify the value, in eV, of the scissors operator to be used in calculating the response to the electric field.

Method: Select the technique to use to calculate Raman intensities from the dropdown list. Available options are:


- [Linear response](#)
- [Finite displacement](#)

Initial frequency: Specify the value, in cm^{-1} , of the minimal frequency for which Raman modes are calculated. Default = 0 cm^{-1} .

Final frequency: Specify the value, in cm^{-1} , of the maximal frequency for which Raman modes are calculated. Default = 10000 cm^{-1} .

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Polarizability, IR and Raman spectra More...</i>
Toolbar	 <i>Calculation Properties Polarizability, IR and Raman spectra More...</i>

Population analysis selection


The *Population analysis* checkbox is checked by default. When this is checked the [Properties](#) tab displays options for controlling the calculation of Mulliken charges (including partial charges for each angular momentum component), Mulliken spins (for spin-polarized calculations), and Mulliken bond populations. Hirshfeld charges are always calculated when the *Population analysis* checkbox is checked.

Distance cutoff for bond populations: Specify the maximum interatomic distance, in \AA , to be considered in the bond population calculation. Default = 3.0\AA .

Calculate band populations: When checked, indicates that the contribution to Mulliken populations from each band will be calculated, in addition to the Mulliken charges.

Note: For disordered crystals population analysis cannot be performed and any these settings will be not be used.


Access methods

Menu	<i>Modules CASTEP Calculation Properties Population analysis</i>
Toolbar	 <i>Calculation Properties Population analysis</i>

Stress selection

Checking the *Stress* checkbox on the [Properties](#) tab causes the stress tensor to be calculated as part of the CASTEP run.

Access methods

Menu	<i>Modules CASTEP Calculation Properties Stress</i>
Toolbar	 <i>Calculation Properties Stress</i>

Job Control tab

CASTEP calculations run in the background on a server using the gateway. The *Job Control* tab allows you to select a server for the CASTEP calculation and to control some aspects of how the calculation will be performed.

Note: The options specified on the *Job Control* tab only apply to new jobs. They do not affect jobs that are already running.

Gateway location: Select a server for the CASTEP calculation from the list of available server machines. You can add servers to the list using the Server Console.

Queue: Specify the queue to which the job will be submitted. Select the desired queue from the dropdown list, which displays the available queues on the chosen gateway. See *Working with queues* for additional details.

Job description: Specify the name to be used to identify the job.

A default job description is automatically assigned. An alternative description can be chosen by unchecking the *Automatic* checkbox and entering the new name in the *Job description* text box.

Note: Do not use this field for *Properties* task since in this case CASTEP Analysis will not be able to associate results files with the original structure.

Automatic: When checked, indicates that a job description will be selected automatically. Default = [checked](#).

Run in parallel on: Indicates that the job will be run on the selected gateway using the specified number of computer cores. The text to the right of the *Run in parallel on* control indicates the maximum number of cores available on the selected gateway.

Note: It is recommended to use the number of cores which is commensurate with the number of k-points in the calculation. You can determine the number of k-points by using the *Display points...* button on the [k-points tab](#) of the *CASTEP Electronic Options* dialog.

Using up to: Specify the maximum number of threads allowed to be used by each MPI process. If the number of threads is greater than 1, the hybrid OpenMP/MPI parallelization will be invoked. The actual number of threads in use will depend on the details of the hardware configuration and the queuing system setup. For example, under UGE it is possible to set up the gateway to guarantee exclusive use of nodes when number of threads is greater than 1.

Note: This functionality is available only on Linux gateways. To ensure it works as expected when a gateway is using a queuing system, check that the queuing system is set up consistently. See *Working with queues* for additional details.

Note: Hybrid OpenMP/MPI parallelization can substantially decrease the amount of memory required for a job (though it could somewhat decrease speed).


Runtime optimization: Specify the strategy used to balance memory use and speed during the calculation. Available options are:

- **Default** - Balance speed and memory use. Wavefunction coefficients for all k-points in a calculation will be kept in memory during, rather than be paged to disk. Some large work arrays will be paged to disk.
- **Memory** - Minimize memory use. All wavefunctions and large work arrays are paged to disk.
- **Speed** - Maximize speed. No paging to disk.

Note: This option does not apply to calculations using the nonlocal exchange correlation potential. In this case paging does not save any memory and *Speed* optimization is enforced.

More...: Provides access to the [CASTEP Job Control Options](#) dialog which allows you to set additional options associated with monitoring and controlling the results of a CASTEP calculation.

Access methods

Menu	<i>Modules CASTEP Calculation Job Control</i>
Toolbar	 <i>Calculation Job Control</i>

CASTEP Job Control Options dialog

The CASTEP Job Control Options dialog allows you to set the options associated with monitoring and controlling the results of a CASTEP calculation.

Update structure: When checked, indicates that intermediate results will be used to update the displayed structure as the job progresses. Default = [unchecked](#).

Update graphs: When checked, indicates that intermediate results will be used to update the displayed graphs as the job progresses. Default = [checked](#).

Update textual results: When checked, indicates that intermediate results will be used to update textual results files as the job progresses. Default = [checked](#).

Tip: Intermediate updates are useful shortly after initiating a job to assess if it is progressing as expected.

Update every: Specify the time interval, in seconds, between requests for intermediate updates.

Note: The rate at which new results appear is limited by the time it takes for the CASTEP server to perform a single iteration step of the chosen task. This may be significantly longer than the chosen update interval.

Retain server files: When checked, indicates that the folder on the server containing the job files will be retained after the job is complete. Default = [unchecked](#).

If this checkbox is left unchecked, the job files on the server will be deleted. Regardless of whether it is checked or unchecked, copies of the results files will *always* be retrieved from the server, placed in the associated project on the local machine, and displayed in the Project Explorer.

Tip: It may be useful to retain the server files so that standalone CASTEP runs can be performed.

Automatically view output: When checked, the output files from the job will be opened automatically when the calculation is completed. Files opened may include a structure document and a CASTEP output (.castep) file for the main task performed by the job. Default = [checked](#).

Notify on job completion: When checked, indicates that a dialog will be displayed when the job is complete. Default = [checked](#).

Tip: If you run several short jobs in one session, you may find it useful to stop the automatic display of job completion notices and results files.


Return BibTeX list of references: When checked, indicates that a BibTeX formatted list of references used for this run will be returned when the job has completed.

Return complete check file: When checked, indicates that the full check file will be returned when the job has completed. Availability of this file (which can be very large) can accelerate the restart of a job.

Note: This option does not apply to calculations using the nonlocal exchange correlation potential. In this case the check file is always returned so that restarts are enabled.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Job Control More...</i>
Toolbar	 <i>Calculation Job Control More...</i>

CASTEP Job Files dialog

The CASTEP Job Files dialog allows you to save input files for a CASTEP calculation without running the job, or to run a job using an existing set of input files.

This functionality is provided for users who need to run the CASTEP server program in standalone mode, or who wish to edit the CASTEP input files in order to gain access to features not supported by the CASTEP interface.

Save Files: Saves the input files required to run the CASTEP job on the server but does not submit the job.

Note: The *Save Files* button is enabled only when the current 3D model document contains a suitable periodic structure.

The input files are placed in a subfolder of the current Materials Studio project directory and the primary CASTEP input ([.param](#)) file is displayed in the Project Explorer.

Run Files: Runs a CASTEP job using an existing set of input files.

Note: The *Run Files* button is enabled only when the current document is a CASTEP input ([.param](#)) file.

The job is submitted using the settings specified on the *Job Control* tab.


The results files will be placed in a subfolder of the current Materials Studio project directory.

When band structure, density of states or optical properties are requested, additional input files will be produced for each property. This is because these properties must each be calculated using a separate run of the CASTEP server. These additional input files are named according to the property they are intended to calculate.

In such situations, selecting the input file for the main task and pressing the *Run Files* button runs all of the input files in a single job.

Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Calculation Files...</i>
Toolbar	 <i>Calculation Files...</i>

CASTEP Analysis dialog


The Analysis dialog allows you to analyze the results of a CASTEP calculation.

A list of properties that may be analyzed is displayed at the top of the dialog.

Select the property you wish to analyze from the list. Options relating to analysis of that property are displayed at the bottom of the dialog.

Help: Displays the Help topic for the currently selected analysis.


Access methods

Menu	<i>Modules CASTEP Analysis</i>
Toolbar	 <i>Analysis</i>

Band structure selection

The following options are available when [Band structure](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the band structure information will be taken.

When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Energy units: Specify the energy units to be used for the dispersion graph. Available options are:

- eV
- Ha

Scissors: Specify the scissors operator to be used in plotting the band structure.

The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

Graph style: Specify the style to be used for the band structure graph. Available options are:

- Points
- Line

Show DOS: When checked, indicates that a density of states from the specified results file will be displayed, together with the band structure graph.

Full DOS: When selected, indicates that the total density of states will be displayed.

Partial: When selected, indicates that the partial density of states (PDOS) will be displayed.

The angular momenta to be included in the PDOS display can be controlled using the *s*, *p*, *d*, *f*, and *Sum* checkboxes.

Note: When the appropriate structure document is active and atoms are selected, the contribution to the density of states from the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.

Display DOS: Specify which spin components should be plotted in the density of states graph. For a spin-polarized calculation, the supported options are:

- Total - contributions from both spin-up and spin-down eigenstates are summed
- Alpha - contributions from spin-up eigenstates only
- Beta - contributions from spin-down eigenstates only
- Alpha and Beta - contributions from both spin-up and spin-down eigenstates are displayed in a butterfly plot
- Spin - difference between contributions from spin-up and spin-down eigenstates is displayed
- Total and Spin

When a non-spin-polarized CASTEP calculation is analyzed, only the **Total** option is available.

Function: Specify whether to plot the untreated DOS or the integrated density of states (the number of states).


More...: Provides access to the [CASTEP DOS Analysis Options](#) dialog which allows you to specify parameters controlling the density of states integration method.

Note: The *Full*, *Partial*, *Display DOS*, and *More...* options are enabled only if *Show DOS* is checked.

View: Displays the band structure using the options specified.


Note: If you have calculated DOS for a spin polarized system with a non-zero initial spin and the total spin is not optimized two charts will automatically be displayed, `<seedname> Band Structure Alpha.xcd` and `<seedname> Band Structure Beta.xcd`.

Access methods

Menu	<i>Modules CASTEP Analysis Band structure</i>
Toolbar	 <i>Analysis Band structure</i>

Core level spectroscopy selection

The following options are available when [Core level spectroscopy](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the core level spectroscopy information will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Note: Core level spectra can only be calculated for single atoms. One atom should be selected in the active 3D Atomistic document before carrying out a core level spectroscopy analysis.

Tip: If you included a core hole in your calculation, you can select the relevant atom using the Atom Selection dialog.

Spectrum: Specify the type of spectrum that will be calculated. If there is a core hole in the shell a * symbol is included in the spectrum name, for example 1s*[K1]. Available options (with and without core holes) are:

- 1s[K1]
- 2s[L1]
- 2p[L23]
- 3s[M1]
- 3p[M23]
- 3d[M45]
- 4s[N1]
- 4p[N23]
- 4d[N45]
- 5s[O1]
- 5p[O23]

Type: Specify the type of spectrum that will be calculated. Available options are:

- [Absorption](#) - the predicted absorption spectrum
- [Emission](#) - the predicted emission spectrum

More...: Opens the [CASTEP EELS Analysis Options dialog](#).

Calculation: Specify the polarization of the incident radiation for the core level spectroscopy calculation.

Polarization: Specify the direction of the polarization of the incident radiation in fractional (lattice) coordinates. Not available when [Unpolarized](#) is selected for *Calculation*.


Atom Selection...: Opens the Atom Selection dialog.

View: Displays the selected core level spectrum.

A chart document is created using the information contained in the active grid document.

Note: If the requested spectrum is not available, a warning message will be returned explaining the reasons.

Access methods

Menu	<i>Modules CASTEP Analysis Core level spectroscopy</i>
Toolbar	 <i>Analysis Core level spectroscopy</i>

CASTEP EELS Analysis Options dialog

The CASTEP EELS Analysis Options dialog allows you to specify the parameters controlling the core level spectroscopy broadening options.

Spectrum: Reports the spectrum specified on the CASTEP Analysis dialog when [Core level spectroscopy](#) is selected.

Instrumental smearing: Specify the Gaussian broadening from the instrument to be used.
Default = 0.2 eV.

Lifetime effects: When checked, lifetime broadening effects will be taken into account.

Core level broadening: Specify the broadening to be used at the core level. Default values for lifetime broadening are tabulated based on the compilation by Fuggle and Inglesfield ([1992](#)).

Reset broadening to default: Resets the *Core level broadening* to its default value.

Include spin-orbit splitting: When checked, spin-orbit splitting for the core level is added to the spectrum.


Spin-orbit splitting: Specify the value of the core level spin-orbit splitting to be used. Default values for spin-orbit splitting are taken from atomic spectroscopic data (see the WebElements Periodic Table: <http://www.webelements.com>). These values represent the difference between reported binding energies for core electrons of the given species, for example the difference between $2p_{1/2}$ and $2p_{3/2}$ gives the $L_{2,3}$ splitting.

Reset spin-orbit splitting to default: Resets the *Spin-orbit splitting* to its default value.

Normalize spectrum: When checked, the resulting spectrum will be normalized to 1 at maximum.

Help: Displays the Help topic in a browser.


Access methods

Menu	<i>Modules CASTEP Analysis Core level spectroscopy More...</i>
Toolbar	 <i>Analysis Core level spectroscopy More...</i>

Density of states selection

The following options are available when [Density of states](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the density of states information will be taken.

When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Energy units: Specify the energy units to be used for the density of states graph. Available options are:

- eV
- Ha

Full DOS: When selected, indicates that the total density of states will be displayed.

Partial: When selected, indicates that the partial density of states (PDOS) will be displayed.

Note: PDOS analysis formalism is not valid for high energy states in the conduction band: PDOS representation will usually decay to zero at about 20 eV above the Fermi level. This is related to the fact that expansion of essentially free electron states in terms of a limited number of atomic-like basis functions is impossible to carry out with any degree of accuracy. Only the valence band and lower part of the conduction band are meaningful in the PDOS plot.

The angular momenta to be included in the PDOS display can be controlled using the *s*, *p*, *d*, *f*, and *Sum* checkboxes.

Note: When the appropriate structure document is active and atoms are selected, the contribution to the density of states from the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.

Display DOS: Specify which spin components should be plotted in the density of states graph. For a spin-polarized calculation, the supported options are:

- **Total** - contributions from both spin-up and spin-down eigenstates are summed
- **Alpha** - contributions from spin-up eigenstates only
- **Beta** - contributions from spin-down eigenstates only
- **Alpha and Beta** - contributions from both spin-up and spin-down eigenstates are displayed in a butterfly plot
- **Spin** - difference between contributions from spin-up and spin-down eigenstates is displayed
- **Total and Spin**

When a non-spin-polarized CASTEP calculation is analyzed, only the **Total** option is available.

Note: If you have calculated DOS for a spin polarized system with a non-zero initial spin and the total spin is not optimized only the **Total** option is available. In this case, two charts will automatically be displayed, `<seedname> DOS Alpha.xcd` and `<seedname> DOS Beta.xcd`.

Function: Specify whether to plot the untreated DOS or the integrated density of states (the number of states).

Scissors: Specify the scissors operator to be used in plotting the density of states.


The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

Atom Selection...: Opens the Atom Selection dialog.

More...: Provides access to the [CASTEP DOS Analysis Options](#) dialog, which allows you to specify parameters controlling the density of states integration method.

View: Displays the density of states using the options specified.

Access methods

Menu	<i>Modules CASTEP Analysis Density of states</i>
Toolbar	 <i>Analysis Density of states</i>

CASTEP DOS Analysis Options dialog

The CASTEP DOS Analysis Options dialog allows you to specify the parameters controlling the density of states integration method.

Integration method: Select the method to be used for integrating the density of states results from the dropdown list. Supported methods are:

- **Smearing** - Gaussian broadening is applied to the eigenvalues obtained from the CASTEP calculation.
- **Interpolation** - eigenvalues (and partial weights for a partial density of states) from the CASTEP calculation are interpolated onto a finer k-point grid.

The **Interpolation** method provides an improved representation of the density of states. However, it can only be used when eigenvalues are available on a Monkhorst-Pack grid with 3 or more points in each direction. The k-point set for density of states calculations can be specified on the [CASTEP Density of States Options - Properties](#) tab on the [CASTEP Calculation dialog](#). If the **Interpolation** method cannot be used for the selected results, it will be absent from the dropdown list.

Smearing width: Specify the Gaussian broadening to be used.

Note: This option is enabled only if the **Smearing** integration method is selected.

Accuracy level: Specify the quality of the interpolation to be used. Available options are:

- **Coarse** - Interpolates onto a k-point grid of about 50×50×50
- **Medium** - Interpolates onto a k-point grid of about 100×100×100
- **Fine** - Interpolates onto a k-point grid of about 200×200×200

Instrument broadening: Specify an additional broadening to be applied to the interpolated density of states.

Note: The *Accuracy level* and *Instrument broadening* options are enabled only if the **Interpolation** integration method is selected.



Number of points per: Specify number of points per 1 eV or per 1 Ha energy range. Use high settings to generate charts that remain smooth after a zoom-in operation.

OK: Updates the settings with any changes and closes the dialog.

Cancel: Closes the dialog without updating any settings.

Help: Displays the Help topic in a browser.


Access methods

Menu	<i>Modules CASTEP Analysis Density of states More...</i>
Menu	<i>Modules CASTEP Analysis Band structure More...</i>
Toolbar	 <i>Analysis Density of states More...</i>
Toolbar	 <i>Analysis Band structure More...</i>

Elastic constants selection

The following options are available when [Elastic constants](#) is selected from the list of properties.


Results file: Select the CASTEP results file from which the elastic constants information will be taken.

When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Calculate: Analyzes stress-strain relationship and calculates the tensors of the elastic constants and the compliances. These results are used to produce the bulk modulus, compressibility, averaged sound velocity, elastic Debye temperature, Young modulus, Poisson ratio, Lamé constants, Vickers hardness, and universal anisotropy index. All of these properties including polycrystalline averages using Voigt, Reuss, and Hill schemes, are written to a new text document, *seedname* Elastic Constants .txt, in the results folder.

Note: The empirical expression for Vickers hardness cannot be applied if the calculated shear modulus is negative (this can happen, for example, when the calculation settings are not sufficiently accurate). In such a case the summary report will not include the hardness.


Access methods

Menu	<i>Modules CASTEP Analysis Elastic constants</i>
Toolbar	 <i>Analysis Elastic constants</i>

Electron density selection

The following options are available when [Electron density](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the electron density information will be taken.

When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Density field: Select the type of density field to be imported. For a spin-polarized calculation, the supported options are:

- [Total density](#) - the total electron density
- [Spin density](#) - the difference between alpha- and beta-electron densities
- [Alpha density](#) - the density of spin-up electrons
- [Beta density](#) - the density of spin-down electrons

When a non-spin-polarized CASTEP calculation is analyzed, only the [Total density](#) option is available.


View isosurface on import: When checked, an isosurface will be created automatically when the density field is imported.

Save density to file: Creates a plain text file that contains either the charge density or, for spin-polarized calculations, the charge and spin density on a uniform grid in real space. The file has the extension .charg_frm.

Note: This file is hidden by default. Use the *Tools | Folder Options... | View | Show hidden files and folders* option in Windows Explorer to access the file.


Import: Imports the selected density field from the CASTEP results file into the current structure document.

Access methods

Menu	<i>Modules CASTEP Analysis Electron density</i>
Toolbar	 <i>Analysis Electron density</i>

Electron density difference selection

The following options are available when [Electron density difference](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the information required to visualize the electron density difference will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.


Use atomic densities: When checked, the electron density difference with respect to the sum of the atomic densities will be created. If unchecked, the density difference with respect to the sum of the densities of sets of atoms will be created.

View isosurface on import: When checked, an isosurface will be created automatically when the electron density difference field is imported.

Import: Imports the selected electron density difference field from the CASTEP results file into the current structure document.


Note: Analysis based on atomic densities requires the presence of a binary file with the extension `.chdiff`; analysis based on sets of atoms requires that for each set of input files, `seed_Subset*. *`, there are binary files with the extension `.check` present.

Access methods

Menu	<i>Modules CASTEP Analysis Electron density difference</i>
Toolbar	 <i>Analysis Electron density difference</i>

Electron localization function selection


The following options are available when [Electron localization function](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the ELF information will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

View isosurface on import: When checked, an isosurface will be created automatically when the ELF field is imported.

Import: Imports the ELF field from the CASTEP results file into the current structure document.


Access methods

Menu	<i>Modules CASTEP Analysis Electron localization function</i>
Toolbar	 <i>Analysis Electron localization function</i>

Energy evolution selection

The following options are available when [Energy evolution](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the energy evolution information will be taken.


When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

View: Generates chart documents as described in the [Displaying trajectory and chart data](#) topic.

These charts are the same as would be generated by selecting *Update graphs* in the [CASTEP Job Control Options](#) dialog. Charts generated using [Energy evolution](#) can be generated whether or not you chose *Update graphs* in the original calculation.


Note: Each time you select *Update graphs* the existing chart documents are rewritten, and any changes or annotations you have made to the charts will be lost.

Access methods

Menu	<i>Modules CASTEP Analysis Energy evolution</i>
Toolbar	 <i>Analysis Energy evolution</i>

Fermi surface selection

The following options are available when [Fermi surface](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the band structure data will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Filter: Choose how to filter the available Fermi surfaces, options are:


- **All** - all Fermi surfaces are available.

Show only bands crossing Fermi level: When checked only the bands which traverse the Fermi level will be listed in the table below.

- *Band* - the index of the band in this row
- *Spin* - the spin for this band
- *From* - lowest value of the energy for the band (in eV)
- *To* - highest value of the energy for the band (in eV)


Import: Imports the selected Fermi surface from the CASTEP results file into the current structure document.

Access methods

Menu	<i>Modules CASTEP Analysis Fermi surface</i>
Toolbar	 <i>Analysis Fermi surface</i>

IR spectrum selection

The following options are available when [IR spectrum](#) is selected from the list of properties.


Results file: Select the CASTEP results file from which the Hessian (dynamical matrix) and ATP tensor (Born charges) information will be taken. When more than one set of results are available, use the  button to browse the current directory and appropriate subdirectories for results files.

Import Hessian from CASTEP output: Imports the Hessian and ATP tensor data, if present, from the selected CASTEP results file into the current structure document.

Note: This button is enabled only if the currently active document contains a structure for which CASTEP results for the dynamical matrix at the Γ -point are available.

Once a Hessian has been imported, vibrational mode frequencies and, if ATP tensors were calculated, absorption intensities can be displayed in the form of a list of values or graphically as a vibrational spectrum using the Vibrational Analysis tool.


Access methods

Menu	<i>Modules CASTEP Analysis IR spectrum</i>
Toolbar	 <i>Analysis IR spectrum</i>

NMR selection

The following options are available when [NMR](#) is selected from the list of properties.

Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Results file: Select the CASTEP results file from which the NMR information will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.


Assign isotropic chemical shielding to structure: Adds the *NMRShielding* property to the atoms for which NMR shielding data are available.

Assign electric field gradients to structure: Adds the *EFGQuadrupolarCoupling* and *EFGAsymmetry* properties to the atoms for which electric field gradient data are available.

Once added, all three of these properties are accessible in the Properties Explorer and can be used for labeling.

Show J-coupling constants: Generates and opens a study table reporting the calculated J-coupling constants. This option is only available when the [Results file selector](#) is set to use a *seedname_*NMRJC.castep file.


Access methods

Menu	<i>Modules CASTEP Analysis NMR</i>
Toolbar	 <i>Analysis NMR</i>

Optical properties selection

The following options are available when [Optical properties](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the optical properties information will be taken.

When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Calculation: Specify the type of optical properties calculation to be performed. Available options are:

- [Polarized](#) - optical properties are calculated for plane polarized light with the specified polarization direction.
- [Unpolarized](#) - optical properties are averaged over polarization directions perpendicular to the specified incident direction.
- [Polycrystalline](#) - optical properties are averaged over all polarization directions, thereby imitating an experiment on a polycrystalline sample.

Smearing: Specify the Gaussian broadening to be used for calculating the dielectric function.

Scissors: Specify the scissors operator to be used for calculating the dielectric function.

The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

Polarization: Specify the polarization of the incident radiation for the optical properties calculation. The direction is specified in fractional (lattice) coordinates.

Note: This option is enabled only if a [Polarized](#) calculation is selected.

Incidence: Specify the incident direction of radiation the for optical properties calculation. The direction is specified in fractional (lattice) coordinates.

Note: This option is enabled only if an [Unpolarized](#) calculation is selected.

Function: Specify which optical property should be displayed as a function of frequency when the *View* button is pressed. Available options are:

- [Reflectivity](#)
- [Absorption](#)
- [Refractive Index](#) - both the real part, n , and imaginary part, k , of the complex optical constant are displayed.
- [Dielectric Function](#) - both the real and imaginary parts are displayed.
- [Conductivity](#) - both the real and imaginary parts are displayed.
- [Loss Function](#)

Units: Specify the frequency units used for the display of optical properties.

More...: Provides access to the [Optics Analysis Options dialog](#), which allows you to specify any Drude contribution to the optical properties.

Calculate: Calculates the dielectric function from the optical matrix elements and eigenvalues in the CASTEP results file.


A grid document is produced containing the calculated dielectric function.

View: Displays the selected optical property as a function of frequency.

Note: This button is enabled only if the current document is a grid document containing a dielectric function.

A chart document is created using the dielectric function information contained in the active grid document.

Access methods

Menu	<i>Modules CASTEP Analysis Optical properties</i>
Toolbar	 <i>Analysis Optical properties</i>

Optics Analysis Options dialog

The CASTEP Optics Analysis Options dialog allows you to specify the Drude contribution to the optical properties.

Plasma frequency: Specify the value of the plasma frequency which is used in the Drude term.

Tip: A value of zero, no Drude correction, should be used for insulators and semiconductors. For metals, a typical value range is 2-10 eV.

Drude damping: Specify the lifetime broadening for the Drude contribution.


Tip: Typical values range from 0.02 eV to 0.08 eV.

OK: Updates the settings with any changes and closes the dialog.

Cancel: Closes the dialog without updating any settings.


Help: Displays the Help topic in a browser.

Access methods

Menu	<i>Modules CASTEP Analysis Optical properties More...</i>
Toolbar	 <i>Analysis Optical properties More...</i>

Orbitals selection

The following options are available when **Orbitals** is selected from the list of properties.

Results file: Select the CASTEP results file from which the orbitals information will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Filter: Choose which orbitals are displayed in the table:

- **Alpha** - displays data only for alpha-spin orbitals (spin up)
- **Beta** - displays data only for beta-spin orbitals (spin down)

Note: For non-spin-polarized calculations, this option is not available.

The orbital analysis table, below the *Filter* dropdown list, lists the eigenvalues and other information about each orbital. The list starts with the lowest energy orbital. Other information contained in the table includes:

- *N* - number of the orbital, with 1 corresponding to the lowest energy orbital
- *s* - spin, + for alpha, and - for beta.

Note: In a non-spin-polarized calculation, all orbitals are labeled +.

- *From* - lowest value of the energy of the Nth band at any k-point (in eV)
- *To* - highest value of the energy of the Nth band at any k-point (in eV)


Scissors: Specify the scissors operator to be used in displaying the orbital eigenvalues.

The scissors operator is only applied for insulating systems, which have a clear separation between valence band and conduction band states. It is ignored for metallic systems.

View isosurface on import: When checked, an isosurface will be created automatically when the orbital field is imported. The units for the isovalues are $e/\text{\AA}^3$.

Import: Imports the selected orbital field from the CASTEP results file into the current structure document.


Access methods

Menu	Modules CASTEP Analysis Orbitals
Toolbar	 Analysis Orbitals

Phonon dispersion selection

The following options are available when **Phonon dispersion** is selected from the list of properties.

Results file: Select the CASTEP results file from which the phonon dispersion information will be taken.

When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Units: Specify the frequency units to be used for the phonon dispersion graph. Available options are:

- THz
- meV
- cm^{-1}

Graph style: Specify the style to be used for the band structure graph. Available options are:

- Points
- Line

Show DOS: When checked, indicates that a phonon density of states from the specified results file will be displayed, together with the phonon dispersion graph.

Display DOS: Specify the type of the phonon density of states that will be displayed. Available options are:

- Full
- Partial


Note: When atoms are selected in the active structure document, the contribution to the phonon density of states from only the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.

More...: Provides access to the [CASTEP Phonon DOS Analysis Options](#) dialog which allows you to specify parameters that control the density of states integration method and DOS normalization scheme.

Note: The *DOS display* and *More* options are enabled only if *Show DOS* is checked.


View: Displays the phonon dispersion using the options specified.

Access methods

Menu	<i>Modules CASTEP Analysis Phonon dispersion</i>
Toolbar	 <i>Analysis Phonon dispersion</i>

Phonon density of states selection

The following options are available when [Phonon density of states](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the phonon density of states information will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Display DOS: Specify the type of the phonon density of states that will be displayed. Available options are:

- Full
- Partial

Note: When atoms are selected in the active structure document, the contribution to the phonon density of states from only the selected atoms will be plotted. Otherwise, the contribution from all atoms is considered.


Units: Specify the frequency units to be used for the phonon dispersion graph. Available options are:

- THz
- meV
- cm^{-1}

More...: Provides access to the [CASTEP Phonon DOS Analysis Options](#) dialog which allows you to specify parameters that control the density of states integration method.

View: Displays the phonon density of states using the options specified.

Access methods

Menu	<i>Modules CASTEP Analysis Phonon density of states</i>
Toolbar	 <i>Analysis Phonon density of states</i>

CASTEP Phonon DOS Analysis Options dialog

The CASTEP Phonon DOS Analysis Options dialog allows you to specify the parameters that control the phonon density of states integration method.

Integration method: Select the method to be used for integrating the density of states results from the dropdown list. Supported methods are:

- **Smearing** - Gaussian broadening is applied to the eigenvalues obtained from the CASTEP calculation.
- **Interpolation** - eigenvalues (and partial weights for a partial density of states) from the CASTEP calculation are interpolated onto a finer k-point grid.

The **Interpolation** method provides an improved representation of the density of states. However, it can only be used when eigenvalues are available on a $3 \times 3 \times 3$ or larger Monkhorst-Pack grid. If the **Interpolation** method cannot be used for the selected results, it will be absent from the dropdown list.

Smearing width: Specify the Gaussian broadening to be used.

Note: This option is enabled only if the **Smearing Integration method** is selected.

Accuracy level: Specify the quality of the interpolation to be used. Available options are:

- **Coarse** - Interpolates onto a k-point grid of about $50 \times 50 \times 50$.
- **Medium** - Interpolates onto a k-point grid of about $100 \times 100 \times 100$.
- **Fine** - Interpolates onto a k-point grid of about $200 \times 200 \times 200$.

Instrument broadening: Specify an additional broadening to be applied to the interpolated density of states.

Note: The **Accuracy level** and **Instrument broadening** options are enabled only if the **Interpolation** integration method is selected.

Normalization: Select the required normalization scheme from the dropdown list. Available options are:


- **1** - the integral of the generated density of states is 1.
- **3N** - the integral of the generated density of states is the total number of vibrational degrees of freedom.

OK: Updates the settings with any changes and closes the dialog.

Cancel: Closes the dialog without updating any settings.

Help: Displays the Help topic in a browser.


Access methods

Menu	<i>Modules CASTEP Analysis Phonon Density of states More...</i>
Toolbar	 <i>Analysis Phonon Density of states More...</i>

Population analysis selection

The following options are available when **Population analysis** is selected from the list of properties.

Results file: Select the CASTEP results file from which the population analysis information will be taken.

When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Assign charges to structure: Imports the selected charges into the active structure document and assigns them to each atom. You can see the charges by labeling the atoms according to their charge. Select the type of charges that you wish to import from the dropdown list, available options are:


- Mulliken
- Hirshfeld

Assign spins to structure: Imports the selected spins into the active structure document and assigns them to each atom. You can see the spins by labeling the atoms according to their spin. Select the type of spins that you wish to import from the dropdown list, available options are:

- Mulliken
- Hirshfeld


Assign Mulliken bond orders to structure: Imports Mulliken bond orders into the active structure document and assigns them to each bond.

Access methods

Menu	<i>Modules CASTEP Analysis Population analysis</i>
Toolbar	 <i>Analysis Population analysis</i>

Potentials selection

The following options are available when [Potentials](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the potentials information will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Note: If nonlocal exchange was used for the calculation of local potentials, they are poorly defined and are not available for analysis.

Note: The local potential cannot be analyzed for calculations with spin-orbit interaction taken into account.


Potential field: Indicates the type of potential field to be imported. Currently only [SCF local potential](#) is available.

View isosurface on import: When checked, an isosurface will be created automatically when the potential field is imported.

Import: Imports the selected potential field from the CASTEP results file into the current structure document. If the structure is a slab with a region of vacuum, a Chart document named `<seedname> Potential Profile.xcd` is also displayed containing a plot of the potential averaged in the planes perpendicular to the surface normal. This chart document also contains the value of work function calculated as a difference between the potential level in a vacuum and the Fermi energy.

Note: When calculating a work function from a periodic slab model, you should ensure that the self-consistent dipole correction is activated on the [SCF tab](#) of the [CASTEP Electronic Options](#) dialog.

Access methods

Menu	<i>Modules CASTEP Analysis Potentials</i>
Toolbar	 <i>Analysis Potentials</i>

Reaction kinetics selection

Select the *Reaction kinetics* option on the CASTEP Analysis dialog to display the Reaction kinetics dialog.

Results file: Indicates the document containing the reaction ingredients. This field displays the name of the active document. You can change the active document by clicking on the desired document window or by double-clicking on the document name in the Project Explorer.

Note: Reaction kinetics calculation can be performed only if the collection document contains well-defined reaction ingredients: the reactant(s), the product(s), and the transition state. All the structures must have Hessians and total energy calculated. Reactant(s) and product(s) systems must be in the ground state - that is all the eigenfrequencies must be real and non-negative. The transition state must be a valid saddle point with one and only one imaginary frequency for which eigenvectors represent the reaction path.

From: To: Specify the temperature range for the output of the calculated rate coefficient.

Apply tunneling correction: When checked, indicates that the reaction rate coefficient will be calculated taking into account the tunneling correction.

Threshold correction: Specify the value to be added to the DFT reaction threshold. This correction compensates for the underestimation of reaction barriers at the DFT level of theory.


Note: Vibrational frequencies scaling: Specify the value of the scaling coefficient to be applied to calculated vibrational frequencies before evaluation of vibrational partition functions.

Note: In some reactions, the transition state may have optical isomers with degeneracy n . These require the prefactor of the Arrhenius rate to be corrected by a factor n . Materials Studio does not automatically include this prefactor, users are encouraged to add it to the results study table by hand.

Calculate: Calculate and display a [study table](#) containing rate coefficients for the forward and reverse reactions.


Note: The prefactor for the modified Arrhenius equation is calculated using $T_0 = 298.15$ K as reference temperature.

Access methods

Menu	<i>Modules CASTEP Analysis Reaction kinetics</i>
Toolbar	 <i>Analysis Reaction kinetics</i>

Raman spectrum selection

The following options are available when [Raman spectrum](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the Hessian (dynamical matrix) and ATP tensor (Born charges) information will be taken. When more than one set of results are available, use the  button to browse the current directory and appropriate subdirectories for results files.

Function: Specify whether to calculate the [Intensity](#) or the [Activity](#) of the vibrational mode.

Temperature: If the intensity of the vibrational mode is being calculated set the temperature in Kelvin.

Incident light: If the intensity of the vibrational mode is being calculated specify the wavelength of the incident light in nm. The default value of 514.5 nm corresponds to a standard Ar laser. Other popular wavelengths for laser Raman spectrometers include 632.8 nm (He-Ne), 785 nm (diode), and 1064 nm (Nd:YAG).

Smearing: Specify the type of broadening (Gaussian or Lorentzian) and width to be used. Default [Lorentzian](#) broadening with width = 20.0 cm⁻¹.

Units: Specify the units for the X axis of the spectrum, options are:

- [meV](#)
- [THz](#)
- [cm⁻¹](#)


Reverse wavenumber axis: When checked, indicates that the values on the X axis will decrease from right to left.

Reverse intensity axis: When checked, indicates that the values on the Y axis will decrease from bottom to top.

Once a Hessian has been imported, vibrational mode frequencies and, if ATP tensors were calculated, absorption intensities can be displayed in the form of a list of values or graphically as a vibrational spectrum using the Vibrational Analysis tool.


View: Displays the selected Raman spectrum.

Access methods

Menu	<i>Modules CASTEP Analysis Raman spectrum</i>
Toolbar	 <i>Analysis Raman spectrum</i>

STM profile selection

The following options are available when [STM profile](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the information required to model the STM profile will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Note: STM analysis is only available if [orbitals](#) were requested.


Note: When more than one set of results is available, it is preferable to use output files for DOS calculation, especially when STM images of empty bands are required.

STM bias: Specify the value of the bias for STM modeling. Positive bias corresponds to the imaging of empty (conduction) states, negative bias to the imaging of occupied (valence) states.

View isosurface on import: When checked, an isosurface will be created automatically when the STM profile field is imported.


Import: Imports the selected STM profile field from the CASTEP results file into the current structure document.

Access methods

Menu	<i>Modules CASTEP Analysis STM profile</i>
Toolbar	 <i>Analysis STM profile</i>

Structure selection

The following options are available when [Structure](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the structure information will be taken. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.


Update structure from CASTEP output: Restores atomic coordinates and cell parameters from the CASTEP results file.

Note: This button is enabled only if the current document contains a structure for which CASTEP results are available.

Create trajectory: Creates a trajectory (.xtD) file from the results of a CASTEP [Geometry Optimization](#), [Dynamics](#) or [TS Search](#) task.


Note: This button is enabled only if the current document contains a structure for which CASTEP trajectory results are available.

Access methods

Menu	<i>Modules CASTEP Analysis Structure</i>
Toolbar	 <i>Analysis Structure</i>

Thermodynamic properties selection

The following options are available when [Thermodynamic properties](#) is selected from the list of properties.

Results file: Select the CASTEP results file from which the information about phonon frequencies will be taken in order to evaluate thermodynamic properties. When more than one set of results is available, use the  button to browse the current directory and appropriate subdirectories for results files.

Note: Thermodynamic calculations can be performed only if the system is in the ground state, that is, geometry optimization is fully converged. This means that all the phonon eigenfrequencies must be real and non-negative.

From: To: Specify the temperature range for the output of the calculated thermodynamic properties.

Tip: The lower limit should be no less than be 5 K to avoid numerical noise due to inadequate Brillouin zone sampling at low temperatures. The upper limit should not be significantly greater than the Debye temperature because of the limited accuracy of the quasiharmonic approximation at high temperatures.

Plot Debye temperature: When checked, indicates that a separate chart with the temperature dependence of the Debye temperature will be displayed.


Assign temperature factors to structure: Adds temperature factor information to the structure.

View: Displays the thermodynamics properties using the options specified.

Note: Thermodynamic calculations performed only at the Γ -point give very poor results, as no acoustic degrees of freedom can be taken into account.

Note: Heat capacity is measured in calories per unit cell per Kelvin. The unit cell can contain several formula units.

Access methods

Menu	<i>Modules CASTEP Analysis Thermodynamic properties</i>
Toolbar	 <i>Analysis Thermodynamic properties</i>

Results file selector

The Results file selector dialog allows you to browse CASTEP results ([.castep](#)) files in the current directory and appropriate subdirectories and select the file you wish to use as the source of data for analysis of the chosen property.

Choose results file: Select the results file you wish to use as the source of data for analysis of the chosen property.

All CASTEP results files that are relevant to the current document and that contain results for the chosen property will be displayed.

OK: Updates the file selection on the [CASTEP Analysis](#) dialog and closes this dialog.

Cancel: Closes the dialog without updating the selection.

Help: Displays the Help topic in a browser.

CASTEP keywords

A wide range of input keywords and data blocks are recognized by CASTEP, including some that are not accessible from the CASTEP setup dialogs.

Tip: For information on CASTEP keywords, refer to the Materials Studio Online Help.

CASTEP References

A list of papers published using CASTEP can be found at the Materials Studio website:

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