

## Chem 253

### Tutorial for Materials Studio

This tutorial is designed to introduce Materials Studio 7.0, which is a program used for modeling and simulating materials for predicting and rationalizing structure properties relationships. The program allows users to import, edit or even create from scratch crystals or molecules. Then it is possible to perform a wide variety of calculations such as predicting the powder diffraction pattern, geometry optimization, sorption of porous materials and even DFT using the modules included in the program.

If you run into difficulties using this software, the 'Help' resource is especially useful, and includes both practical examples and theory behind the modules and modeling.

Notable modules include **CASTEP** for first-principles quantum mechanical calculations, **Forcite** for geometry optimization, **Discover** for molecular dynamics calculations and **Reflex** for powder diffraction pattern simulation and refinement.

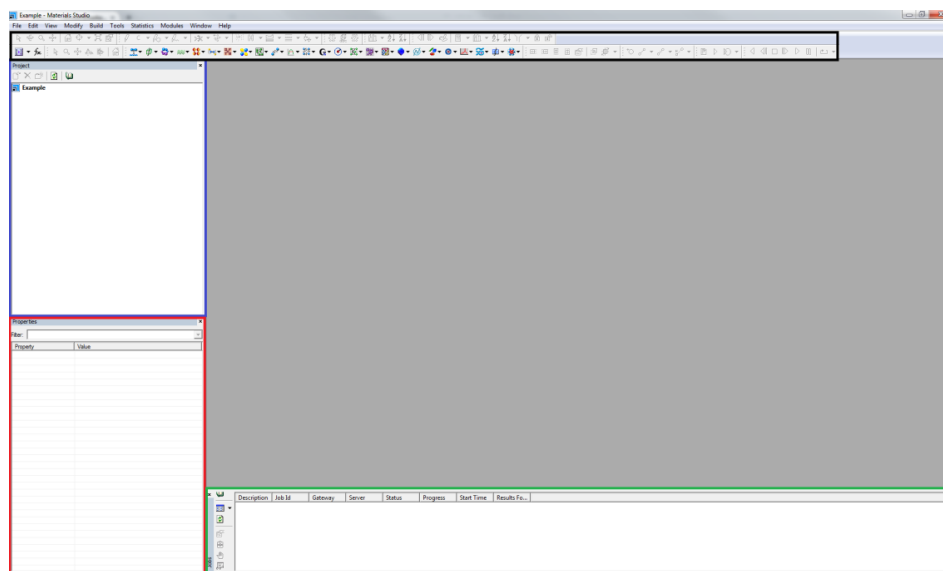
For up-to-date details on the login process, check:

[http://glab.cchem.berkeley.edu/glab/faqs/windows\\_share.html](http://glab.cchem.berkeley.edu/glab/faqs/windows_share.html)

To begin, login to a linux workstation in the MGCF (credentials will be provided to you during your tutorial session). Double-click on the Win7 environment icon and start the VM. Login as guest (no password). Click on the desktop icon **Materials Studio 7.0** to open the program, select 'Create a new project'. Name it whatever you wish.

#### 1. Interface Guide

Under **View -> Explorers**, there are three windows that may be displayed (see image below). First is the **Project Explorer** which displays the file and folders in the current project. Next is the **Properties Explorer**, which contains information on any selected atoms or bonds in the structure. Finally, the **Job Explorer** lists any ongoing module calculations and their % completeness. Note the toolbars may be arranged in a different configuration than described in the guide as they are customizable.



The toolbar, highlighted in black, at the top of the image provide the user with a variety of ways to interact with the structures. Note these toolbars are customizable and may be displayed or hidden under **View -> Toolbars**. The most useful are described. From left to right, the first toolbar (**3D Viewer**), the first arrow icon is for selection; the second icon for rotation; magnifier icon for zoom; the fourth icon for translation; house icon for reset; the sixth icon for recentering; the seventh icon for fit the viewer; the eighth icon for display style.

For the next toolbar (**Sketch**): the first icon is for sketching an atom; second icon for sketching a ring; third icon for sketching a fragment; fourth icon for Measure/Change; fifth icon for creating a centroid; sixth icon for cleaning up the structure geometry; H icon for adjusting hydrogen atoms (auto-update hydrogen); eighth icon for modifying the element; ninth icon for modifying the bond type; tenth icon for modifying hybridization.

The second row includes shortcuts to the modules that may otherwise be accessed under **Modules** at the top of the screen.

## 2. Exercises

These exercises are designed to provide an introduction to common and useful features available in Materials Studio. This includes the creation or import of structures, manipulating them and performing calculations using the modules.

**Exercise 1:** Create a structure from known coordinates and space group, geometry optimize and calculate the powder diffraction pattern.

The elpasolite-cryolite structure of double perovskites has the formula  $A_2BB'O_6$ , with Fm-3m space group. This is a face-centered array with all of the tetrahedral and octahedral holes filled. An example of this type of structure is  $Sr_2CuWO_6$ . The coordinates are as follows:

A ( $\frac{1}{4}$ ,  $\frac{1}{4}$ ,  $\frac{1}{4}$ )

B (0, 0, 0)

B' ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ )

O (x, 0, 0);  $x \sim \frac{1}{4}$

1. What are the oxidation states of each of the species present in  $Sr_2CuWO_6$ ?
2. Left-click the blank page icon at the top left corner. Select **New -> 3D Atomistic**. Rename this file to Double Perovskites.
3. Click **Build -> Crystals -> Build Crystal...** Input the information on the space group and select **Build**. The unit cell lengths are unimportant at this stage, so the default of 10 Å is fine.
4. Click **Build -> Add Atoms**. Create  $Sr_2CuWO_6$  with the correct oxidation states using the coordinates listed above. Note the space group generates all symmetry-equivalent atom positions within the unit cell.

Since the ions are located too far away from one another to be bonding within this unit cell, the next step is to geometry optimize the cell.

5. Run **Modules -> Forcite -> Calculation**. From here, the Task is *Geometry Optimization, Fine quality*, and under More..., tick the *Optimize Cell* option. Click *Run*, and when completed this will create a new folder with a second 3D Atomistic file along with other files detailing the calculation performed. Check the Termination Status is 'Normal' and that the refinement has converged. Rename the output 3D Atomistic to 'Double Perovskites GO', for Geometry Optimized.

6. What are the new unit cell parameters? What is the coordination number of copper (6), tungsten (6) and strontium (8)? Look up the ionic radii of Sr, Cu, W and O for the appropriate coordination number and oxidation state. What do you predict the unit cell length to be assuming the bonding is entirely ionic in character? Considering copper as the face-centered array, what species lies in the tetrahedral hole, and which lies in the octahedral hole?

7. Now calculate the powder diffraction pattern. First make sure the geometry-optimized 3D Atomistic file is selected. Then click **Modules -> Reflex -> Powder Diffraction**. Change the 2-theta min and max to be 10 and 80° respectively. This module can also be used to account for experimental parameters such as the source wavelength, FWHM of peaks, crystal size and preferred orientation to better represent

experimental data. For now the remaining default values are acceptable. Click **Calculate**. A new window should open with the diffraction pattern.

8. Select the window, type **Ctrl-A, Ctrl-C** and open up Excel. Paste the data into Excel, which should give you 4 columns. The first is the 2-theta angle in the specified step size. Next is the intensity corresponding to the 2-theta angle. The last two columns are to define where peaks are expected to appear from indexing. Save this file and keep it for later use.

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### Exercise 2: Editing existing structures.

1. Right-click the geometry-optimized structure you made in exercise 1. Click **Open containing folder**, copy the 3D atomistic file and navigate to the base directory within the Materials Studio project by double-clicking on the Materials Studio icon in the Project Navigator. Here, create a new folder entitled 'AgCl structure', and paste the file into this folder. Rename it to 'AgCl'. Refresh the project window in MS, and the changes made should appear.

2. Open the AgCl 3D atomistic document. Delete the strontium and oxygen atoms by selecting one of them (by symmetry all will be deleted).

3. Check the Properties Window is open by verifying there is a check mark next to next to Property Explorer under **View -> Explorers**. Next, select the copper atom, and under Properties in the lower left-hand side window, change the ElementSymbol box to silver. Also convert tungsten to chloride by the same method. Check the oxidation states are the expected values.

4. Optimize the structure's geometry using Forcite as in exercise 1. Confirm the geometry optimization was successful. What structure type is this?

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### Exercise 3

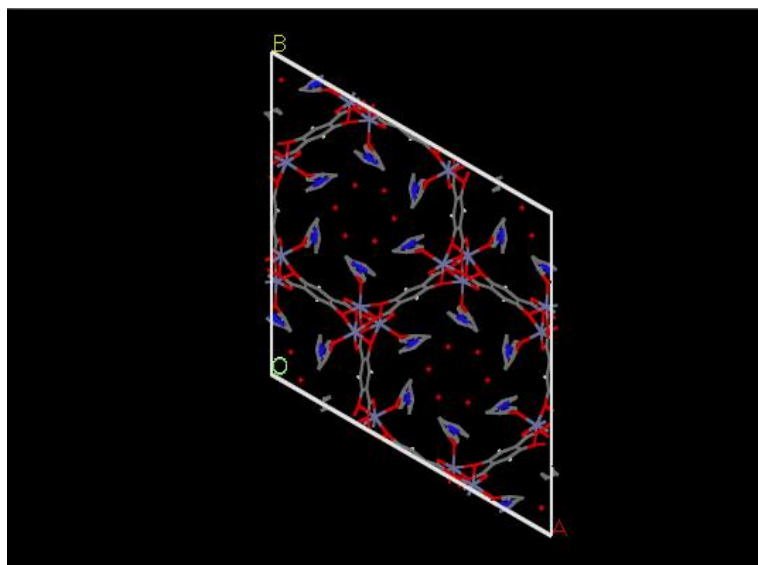
Copy the geometry-optimized  $\text{Sr}_2\text{CuWO}_6$  structure into a new folder named 'CaF<sub>2</sub>'. Create the CaF<sub>2</sub> fluorite structure by deleting, repositioning and reassigning the elements as necessary. Then perform a geometry optimization calculation and calculate the powder diffraction pattern as in previous exercises. What is the unit cell length? How does this compare with the known atomic radii of Ca<sup>2+</sup> and F<sup>-</sup>?

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**Exercise 4**

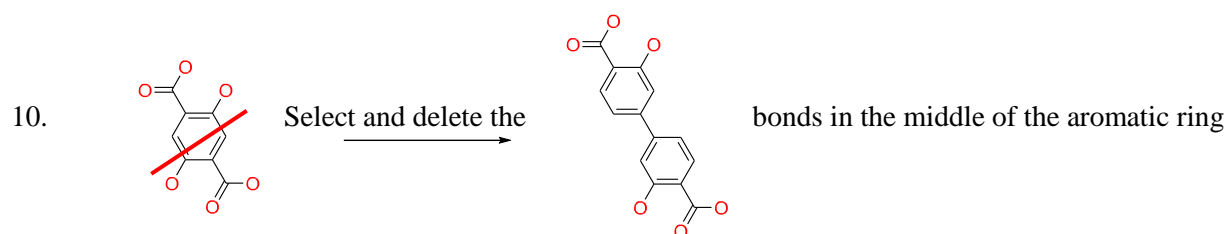
1. Navigate to the Cambridge Structural Database (CSD) at [www.ccdc.cam.ac.uk/](http://www.ccdc.cam.ac.uk/). If you prefer you may load Conquest in the Linux environment. If you do this, you can use the folder that is shared between the Linux and Windows environment under Documents/<username>-kvshare.
2. Click **Get Structures**, and enter the CSD refcode FIJDOS, corresponding to MOF-74. If you are not logged into the UC system you will also be required to input your name and institution to obtain structures from the CSD.
3. Select Download -> Download current entry and save the structure in your working folder
4. Click on the desktop icon **Materials Studio 7.0** to open the program.
5. Create a new project
6. Select **File -> Import**, and open the .cif file you just saved.
7. This creates a new 3D Atomistic file within your MS project, displaying the structure you downloaded.
8. Select **Build -> Bonds -> Calculate**, adjusting the tolerance under **Connectivity Options** as necessary to ensure all covalent bonds are present. The 'From' slider dictates the minimum bond length, and the 'To' slider controls the maximum length between two atoms to be considered a bond.

The structure should now look something like this:



9. Select and delete the oxygen atoms in the pore, and the terminal DMF ligand.

In the next few steps, we will replace the linker on the left with the linker on the right (see below). Sketch the new linker as follows:



(across the red line on the left-hand structure).

11. Create space to draw the expanded linker by selecting all the atoms except the carboxylate on the linker. Hold down Shift+Alt, right-click and drag the mouse.
12. Select **Sketch** from the toolbar, click on the linker and draw one more C atom. Complete the linker by sketching the remaining C atoms.
13. Select the bonds in the newly formed aromatic ring, and change the bond type to **Aromatic** in the **Properties** tab in the bottom right.
14. Click the 'H' icon on the toolbar to auto-update the hydrogen atoms in the structure.
15. Confirm the connectivity and bond types are correct. Now perform the geometry optimization using Forcite as with previous exercises. Be sure to optimize the cell parameters.
16. You may change the representation of the crystal by right-clicking on the 3D Atomistic document, selecting **Display Style**. The default is the Line representation. Converting to CPK will display more realistic atom separations and is useful in visualizing what the crystal structure and void space is really like. Under **Lattice** you can also change the range of atoms displayed by editing the unit cell range.
17. Under **Display Options** the background and perspective can be edited, and is very useful in making figures of structures.

**Exercise 5:** Create the fcu (face-centered cubic) net using the Reticular Chemistry Structure Resource.

1. Navigate to [rcsr.anu.edu.au/](http://rcsr.anu.edu.au/) and click Nets.
2. In the Symbol box, type fcu.

This lists the space group and topological information on the net fcu. You can use this information to create a new 3D Atomistic structure based on this topology.

3. In a new project, select **New -> 3D Atomistic**. Rename this file to fcu.
4. Click **Build -> Crystals -> Build Crystal...** Input the information on the space group and select **Build**. The unit cell lengths are unimportant at this stage, so the default of 10 Å is fine.
5. Click **Build -> Add Atoms**. Select Ag<sup>+</sup> as the element to add, and place it at the coordinates of the vertex in fcu (x,y,z = 0,0,0). Note the space group generates all symmetry-equivalent atom positions within the unit cell.
6. Add Cl<sup>-</sup> displaced halfway along the unit cell. (x,y,z = 0.5,0,0). This is the rock salt structure, adopted by the salt AgCl.
7. Since the ions are located too far away from one another to be bonding within this unit cell, the next step is to geometry optimize the cell. For each ion, set the correct charge.
8. Run **Modules -> Forcite -> Calculation**. From here, the Task is *Geometry Optimization, Fine quality*, and under More..., tick the *Optimize Cell* option. Click *Run*, and when completed this will create a new folder with a second 3D Atomistic file along with other files detailing the calculation performed. Check the Termination Status is 'Normal' and that the refinement has converged.