Practical 1 – Electronic ground state calculation

Learning Objectives

- Introduction to CASTEP input and output files.
- Perform first ground state electronic structure calculations on silicon (a simple covalent semiconductor), aluminium (a simple metal) and sodium chloride (a simple ionic material).

Introduction

The aim of this exercise is to familiarise you with CASTEP input and output files and running the code, some associated utilities and conversion programs. You will run some simple and small CASTEP calculations on canonical examples of covalent and ionic bonded materials - silicon and sodium chloride - and use the results to study the bonding from an electronic structure perspective.

While performing the exercises try to think about the reasons for each step, and about how to interpret the results. The point of the exercise is not merely to reach the end but to learn the path. The exercise below contains a number of questions. Please take note when a question is asked of you, and think about the answer. Feel free to discuss the answer with one of the demonstrators after you have thought about it for a while.

Enabling CASTEP and related utilities

We shall be using the UoY Physics Computer Lab machines for this session. Make sure the PC in front of you has been booted into linux. Logon using your standard UoY username and password and then open a terminal. Ask a demonstrator if you are unfamiliar with linux!

CASTEP has already been installed on this system. To enable access you should need to type some simple commands every time you open a new terminal (or add these commands to your **.bashrc** file to automate the process):

```
module load CASTEP
alias castep="castep.serial"
```

You should now have a functioning CASTEP installation!
NB The **module** system is commonly used on Linux facilities to manage different packages. Hence the name of the packages may change with time and different systems. If any of the module commands given above fail, you

can do **`module avail`** to get a list of the modules available on the current system.

Alternatively, you can try **`module spider CASTEP`** to find which module(s) are relevant and then use the **`module load`** command.

You will also need some visualization tools. The simplest is Jmol:

```
module load Jmol
```

and it also has the best native CASTEP support. If your system does not have Jmol, then it is simple to install and use yourself – just go to http://jmol.sourceforge.net/download/ and follow the instructions. It does not need any special permissions to install - you can easily put it in your own filespace.

Another popular alternative is VESTA

```
module load VESTA
```

which you may prefer. Both are good for visualizing structures, and Jmol can additionally visualize 3D fields such as charge density.

Where To Find Help

If you want more information about a particular CASTEP keyword, or you want to find if CASTEP has particular functionality, there are a few places you can look.

1 There is information on this website: **www.castep.org**

2 CASTEP has an in built help option to assist with using particular keywords. Information on using CASTEP can be seen by using:

```
castep --help
```

To get more information on a particular input file keyword (e.g. task) use:

```
castep --help task
```

If you don't know the keyword you need to use, then you can search on a particular keyword. This returns a list of keywords that you might be interested in, e.g. to look at all keywords which contain a reference to symmetry.

```
castep --search symmetry
```

Finally, to list all keywords, use:

```
castep --search all
```

Note that the long-form arguments **--help** and **--search** can optionally be replaced with **-h** and **-s**, respectively.

Example 1 - Silicon

1. Get the files required for this exercise (copy to local pc)

```
mkdir $HOME/work
cd $HOME/work
wget http://www-users.york.ac.uk/~mijp1/teaching/grad_FPMM/files/1.tar.gz
```

2. Unzip and untar them, then move into the new directory

```
gunzip 1.tar.gz
tar -xvf 1.tar
cd Si2
```

3. Examine the CASTEP input files **Si2.cell** and **Si2.param** using your favourite text editor (e.g. **nano**). The **Si_00.usp** file is a pseudopotential file, you do not need to understand it at the moment.

```
nano Si2.cell
nano Si2.param
```

4. It is useful to view the structure before submitting your calculation using CASTEP. Type **jmol.sh** to launch Jmol and then use File => Open and navigate to your **Si2.cell** file. Alternatively, you can drag and drop the **Si2.cell** file into the Jmol window, and Jmol will open it. It can be helpful to view multiple repeat units of your unit cell. The easiest way to do this in Jmol is to open a console window, click File => Console and type:

```
load "" { 2 2 2 }
```

To show a 2x2x2 supercell. Check the geometry of the input file is what you expect it to be before moving onto the next step.

5. Launch CASTEP to do your calculation

```
castep Si2
```

This should only take a few seconds and produce a readable output file **Si2.castep**. Examine this file and try to understand the meaning of the various parts. In particular check the section following the header, which lists all of the input parameters, both explicit and default. Note what default values of the major parameters CASTEP chose where you did not specify them explicitly. (There will be some whose meaning has not been explained. Don't worry about these.)

> *Q: Find the section of the file that monitors the SCF loop and the approach to convergence. How many SCF iterations did it need?*

6. Jmol can also be used to view the isodensity map. Open the castep file by dragging and dropping the **`Si2.castep`** file into the Jmol window.
Open the Jmol console (File => Console) and type the following commands:

```
load "" { 2 2 2 }
isosurface cutoff 14 "Si2.den_fmt" lattice { 2 2 2 }
```

- Note: depending on how Jmol is set up you may have to supply a full path to the file. NB Jmol uses forward slash for paths to files on windows and linux based machines.

This **`Si2.den_fmt`** file is a formatted file produced by CASTEP that contains the value of the electron density on a grid of points. This isosurface command in Jmol plots an isodensity surface over your atomic positions.

You can also plot a 2D slice of the charge density, e.g.

```
isosurface plane (atomno=1) (atomno=2) (atomno=3)
"Si2.den_fmt"
```

Answer the following questions:

1 Can you explain what you see as you vary the isosurface value?
2 Can you see any features that might be characteristic of a covalently-bonded crystal?
3 What happens to the electron density close to the Si nucleus?
4 Can you explain this in terms of type of calculation you have just done?

Example 2 – aluminium and sodium chloride

Repeat steps 1-6 above using input files for aluminium and sodium chloride that were also unpacked in the previous steps.

Now think about the following questions:

- *What similarities and differences do you find compared to silicon?*
- *Does this help explain the difference in bond chemistry between silicon, sodium chloride and aluminium?*
- *Does this help explain why there are many reasonable classical potential functions for NaCl to be found in the simulation literature, but that finding good potentials for silicon is a very tough challenge?*
- *What about aluminium? See the OpenKIM website https://openkim.org …*