Lab 4. Density of states and band structures

This lesson is related to Chapters 8.1-8.2 in Sholl and Steckel.

The electronic band structure is among the most important properties that can be calculated using DFT. It contains a lot of detailed information about the system, and it can be represented in a variety of different ways. We will in this lesson use three of the most common ways: Energy resolved in the density of states (DOS); atom and/or orbital projected in the local DOS (LDOS); and momentum resolved in band structures.

We use bulk Si for this, so you can go back to the files from Lesson 1. Alternatively, you could start by making a new directory and copy the input files from Lesson 1 there. You then have to run VASP once to get output.

The pymatgen library (http://pymatgen.org/) is a very convenient way of assessing and plotting the band structure of materials. In order to make this work, you need to install it to your local directory on abel:

```
  >  module purge
  >  module load Anaconda3
  >  pip install --user --upgrade pymatgen
  >  export PYTHONPATH=$HOME/.local/lib/python3.5/site-packages:$PYTHONPATH
  >  export PATH=$HOME/.local/bin:$PATH
```

You should copy the last two lines of these commands to your ~/.bashrc file; then you don't need to load these variables manually each time you log in. The "module load" lines have to be performed each time you log in and want to use the following commands.

1 The band gap

Before moving to the plots and detailed information, we start by looking at the perhaps most important parameter that can be extracted from the band structure: the band gap. This can be found in many of the output files, and we have previously used the OUTCAR file with the bandgap script. We will now use the vasprun.xml file to get some other information, using the bandgap.py script:

```
  >  bandgap.py vasprun.xml
  {'transition': '(0.000,0.000,0.000)-(0.200,0.000,0.000)', 'direct': False,
'energy': 0.5867999999999993}
```

We see that the calculated band gap for bulk Si is 0.5868 eV. The valence band maximum (VBM) is located at 5.836 eV – this is also by default taken by VASP to be the Fermi level. This corresponds to the highest occupied molecular orbital (HOMO) in molecular science. Similarly, the conduction band minimum is at 6.4228 eV. Another name of this is the lowest unoccupied molecular orbital (LUMO). It is

identified as an indirect band gap, going from Gamma (0,0,0) to the k-point (0.2,0,0). We will later see that the location of the CBM can be more accurately located when the band structure is plotted.

The experimental band gap of Si is 1.2 eV, which means that the DFT predicted value is far too low. This is a well-known problem in DFT calculations, and one of the main reasons to move beyond DFT. See chapter 10 in Sholl and Steckel for more about this topic.

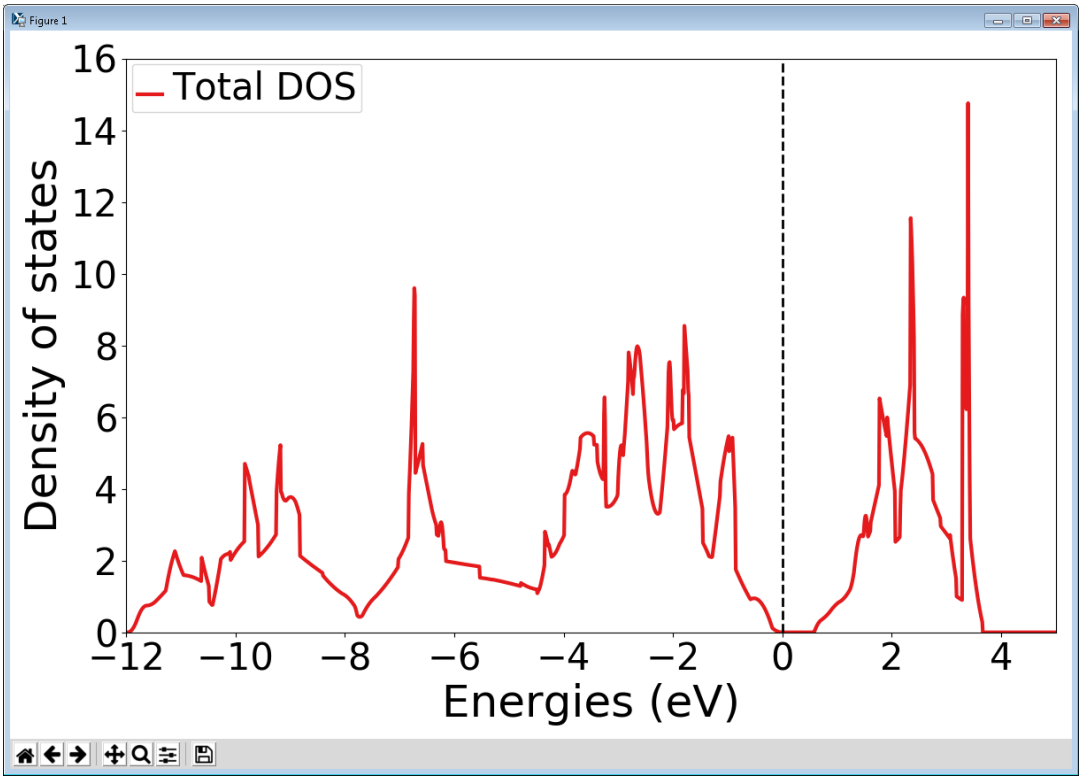
2 The density of states (DOS)

We would often like to know more about the electronic structure than the band gap. One important way of visualising it is using the density of states (DOS). This is the number of electronic states in a given energy interval. The DOS is contained in the file DOSCAR and in vasprun.xml, and can be plotted with the script plotdos.py:

```
> plotdos.py vasprun.xml
```

This will plot the DOS from the vasprun.xml in your current directory.

A window like this one should appear:



This has been produced by pymatgen, more information about this can be found here: http://pymatgen.org/. For now, it is important to know that you can zoom into the plot using the buttons in the lower left corner.

At the same time, the file TDOS.png has been created; which can be used for reports etc. You can look at png files with the xv command (actually the display function of imagemagick):

```
> module load imagemagick
> xv TDOS.png
```

Check that you are able to read out the same band gap in this plot as was given by the bandgap script.

If you want to do more advanced processing with the plot, you can simply copy and modify the plotdos.py script; it is located at ~olem/fm4111/bin/. You may e.g. want to change the default boundaries of the plot, which are defined in the following line:

```
plotter.show(xlim=[-12, 5], ylim=[0, 16])
```

The local script can be run like this:

```
>  python plotdos.py vasprun.xml
```

3 The local density of states (LDOS)

It is often very interesting to know the nature of certain states; to which extent they belong to a particular element, their orbital angular momentum (s, p, d, etc.), and so on. This can be obtained by plotting the projected (or local) density of states, this is often called LDOS.

We have a script that is dedicated to plotting the LDOS from VASP calculations:plotldos.py. It is used in the same way as the plotdos.py script, using a vasprun.xml file as argument.

```
>  plotldos.py vasprun.xml
```

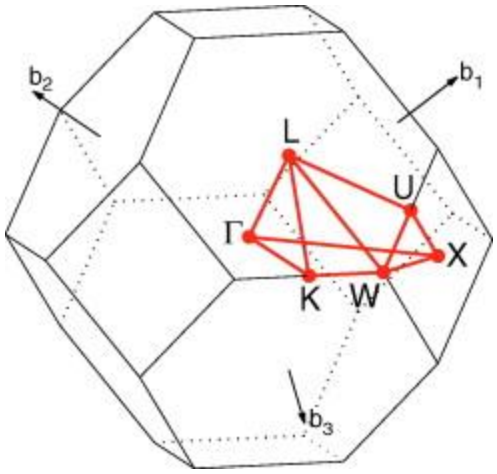
The plot is also saved as the file LDOS.png.

You can change the features of this plot in the same way as with plotdos.py; just copy the file plotldos.py from ~olem/fm4111/bin/ and change features in that file.

Here the s, p, and d orbital projections are plotted. It is possible to read out a lot of information from this.

4 Plotting the band structure

The electronic band structure can be plotted as a function of the wave vector **k**. This gives perhaps the most detailed information about the band structure, but it is also most tricky to calculate. Ideally, one would like to know the electron energies in the entire Brillouin zone (BZ). For the fcc lattice, the BZ looks like this:



In practice, however, it is more convenient to pick out special points and directions in the BZ. Some of these are marked in the figure above. For Si, it is usual to choose the points *L*, Γ, *X*, *W*, and *K* for such a plot.

This gives us a problem. Even if these directions are representative for the band structure of Si, they do not necessarily provide a good sampling of **k** points for the numerical calculations. The way we solve this is to perform the calculation in two steps:

1. Calculate the electronic density in the standard way, self-consistently. For this, you need to ensure that you have specified the primitive unit cell in POSCAR. This is available in the directory ~olem/fm4111/datalab/band_structure/. Remember to create a new KPOINTS file with the makekpoints script (using the appropriate density of k points identified above), since the unit cell size now has changed.
2. Use the calculated density (from the CHGCAR file) to calculate the band structure, without changing the density.

Step 1 should be straightforward. For step 2, you should create a new directory and copy all input files as well as the CHGCAR file. You have to specify in the INCAR file that you want to perform a non-self-consistent calculation; this is done by adding the following line with the ICHARG keyword to the INCAR file (only use space, not tab):

```
ICHARG = 11
```

You also have to change the line in INCAR specifying the smearing; change it to:

```
ISMEAR = 0
```

In addition you should specify which points you are going to use in the band structure calculations. Here you can use the line mode of the KPOINTS file as follows (you should copy this to the new KPOINTS file. It is also available from ~olem/fm4111/datalab/band_structure/):

```
k-points along high symmetry lines
 20     0  ! # of points per line
Line-mode
reciprocal
  0.500  0.250  0.750  W
  0.500  0.500  0.500  L

  0.500  0.500  0.500  L
  0.000  0.000  0.000  \Gamma

  0.000  0.000  0.000  \Gamma
  0.500  0.000  0.500  X

  0.500  0.000  0.500  X
  0.500  0.250  0.750  W

  0.500  0.250  0.750  W
  0.375  0.375  0.750  K
```

Typical high-symmetry ("special") k-points of a given lattice can be found in this paper: https://doi.org/10.1016/j.commatsci.2010.05.010. More information about special k-points of all space groups can be found at the Bilbao Crystallographic Server: http://www.cryst.ehu.es/cryst/get_kvec.html. Bulk Si has the space group number 227 (*Fd*-3*m*).

You can now run the VASP job with this KPOINTS file. The band structure will be available several places, but we will read it from the vasprun.xml file. A script called bandplot.py can do this for you automatically:

```
>  bandplot.py vasprun.xml
```

This is also available at ~olem/fm4111/bin/. It can be copied to the same directory where you just ran VASP if you want to change it and run it locally. The band structure will also be saved as bandstruct.png.

5 Report

Include all the relevant plots in a report. Try to extract some useful information from them. Also include discussions on how the results compare to experiments and other DFT calculations that can be found on the internet.