

## EXERCISE 2

# BULK CRYSTALS: BAND STRUCTURES AND DENSITY OF STATES

Here we will focus on a crystalline material, FCC Al.

### Convergence with **k**-point sampling

In bulk systems the electronic states can be characterized by a continuous quantum vector **k**, the so-called Bloch vector or crystalline quasi-momentum of the electrons. The physical quantities (like the energy, charge density, etc) can be expressed as integrals over **k**-space (usually over the so-called Brillouin zone). However, these integrals are in practice computed using a discrete grid:

$$F = \frac{1}{\Omega} \int_{BZ} f(\vec{k}) d\vec{k} \approx \frac{1}{N_k} \sum_k f(\vec{k})$$

In any calculation in a crystal, you should check the convergence of the physical properties (typically the energy) with the sampling of **k**-points. This means that you should use as many **k**-points as necessary to converge the physical properties within the desired tolerance.

The most popular scheme to generate this integration mesh is the Monkhorst-Pack algorithm. This is also used in SIESTA. The integration grid in the Brillouin zone is specified using the block *kgrid\_Monkhorst\_Pack*

For metals there are electronic bands that are not completely filled and therefore for an accurate description of the total energy, forces and all properties of the materials it is necessary to use a better sampling in reciprocal space (Bloch vectors) than for insulators. In the input file *Al\_bulk.fdf* a 4x4x4 grid is used. This might be insufficient for a good description of aluminum.

Explore the convergence of total energy and the equilibrium lattice parameter, with respect to the fineness of the **k**-sampling.

### Density of states

To plot the DOS you have to use the utility program *eig2dos.x*. This program reads the information contain in the file *Al.EIG* which contains all the eigenvalues for each **k**-point. In order to run the program *eig2dos.f* you have to add some extra information to the first line of the input file, namely, a broadening for each states in eV (a value of the order of 0.1 eV is usually reasonable), the number

of energy points where the DOS will be calculated and the Emin and Emax of the energy window where the DOS will be calculated. (Read the comments in the header of file *eig2dos.f* for more details) Once you have add this info to the file *Al.EIG* you just need to execute

```
eig2dos.x < Al.EIG > dos
```

and plot the *dos* file using the *gnuplot* program.

Check how does the DOS change when you change the number of **k**-points in the sampling of the Brillouin zone.

## **Band structure**

The file *Al\_bulk.fdf* will also produce a file *Al.bands* containing the band structure along the several lines in the Brillouin zone as specified using the block *BandLines*. To plot the band structure you need to use the utility program *gnubands.x*

```
gnubands.x < Al.bands > out.bands
```

and you can plot *out.bands* using *gnuplot*. A SZ basis set is specified in the file *Al\_bulk.fdf*, but it might be quite interesting to see how the band structure changes when more complete basis sets are used (DZ,DZP).