

Laboratory 3 Handout: Advanced topics in first-principles electronic structure calculations

—
Spring 2016

In this lab we continue our use of the Quantum-Espresso(QE) package, introduced in the Lab 2. Please keep in mind the handout from Lab 2.

- In problem 1, we will compute the band structure and the density of states of different carbon allotropes.
- In problem 2, we will compare the total energy of iron in different magnetic and structural configurations and then estimate the transition pressure from a BCC to a HCP structure.

Some helpful conversions:

$$\begin{aligned}1 \text{ bohr} &= 0.529177249 \text{ \AA} \\1 \text{ ryd} &= 13.6056981 \text{ eV} \\1 \text{ eV} &= 1.60217733 \times 10^{-19} \text{ Joules}\end{aligned}$$

how to decompress on deneb: `$ tar zxvf file.tar.gz`

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1 Band structure of carbon's allotropes

In this first problem we will compute band structures and density of states of three carbon allotropes, diamond (already discussed in the previous Lab), graphene and graphite. We will also discuss the issue of van der Waals interactions in a layered material like graphite.

1.1 Theory

Here you can find a few theoretical reminders about the concepts discussed in this lab: bands, density of states, and van der Waals interactions.

1.1.1 Bands

Owing to the periodicity of the crystal structure, the solutions of the time-independent Schrödinger equation are labelled by two quantities: a wave vector \mathbf{k} (known as *crystal momentum*) inside the so-called first Brillouin zone and an index n that counts the different solutions at a given \mathbf{k} . Thus the Schrödinger equation can be written in this form:

$$H\psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) . \quad (1)$$

Our interest will be to find the energy bands $E_n(\mathbf{k})$ for a set of \mathbf{k} -values that lie along a given path within the the first Brillouin zone.

1.1.2 Density of state (DOS)

The density of states (DOS) $D(E)$ is defined as the number of states of the system between energy E and $E + dE$, with dE infinitesimal. If the eigenenergies of the system are E_α , with α a complete set of quantum numbers, then a formal expression for the DOS is

$$D(E) = \sum_{\alpha} \delta(E - E_{\alpha}) , \quad (2)$$

where $\delta(x)$ is the Dirac delta function. In our case, assuming for simplicity that we have spin degeneracy, this translates into:

$$D(E) = 2 \frac{V}{(2\pi)^3} \sum_n \int_{\text{B.Z.}} \delta(E - E_n(\mathbf{k})) d\mathbf{k} . \quad (3)$$

Thus, once the energy bands are known over a sufficiently dense mesh of \mathbf{k} -points, the DOS can be easily computed as an integral over the Brillouin zone. Of course one needs to use some numerical method to treat the delta function and perform the integral efficiently when we have only a limited number of \mathbf{k} -points. This method is called the tetrahedra method (P.E. Blöchl, PRB **49**, 16223 (1994)). Without going into the details, it suffices to know that it is implemented into QE.

1.1.3 Van Der Waals interaction

In the last part of Exercise 1 you're asked to relax the graphite structure, and to study the different geometries obtained with and without van der Waals interaction. In spite of its remarkable successes, Density Functional Theory has its shortcomings. Among them, the treatment of non-local correlations, and dispersion interaction in general, seems to be one of the most important open issues to be addressed. Commonly named van der Waals forces, dispersion interaction is an ever present binding mechanism in weakly bonded materials, from biological systems to rare-gas molecules. Arising from the interactions of charge fluctuations among separated chunks of matter, van der Waals forces are on the edge between classical physics and quantum effects. Dipoles generated by instantaneous charge fluctuations, due to quantum mechanical zero-point energy vibrations or thermal fluctuations, interact as classical electromagnetic dipoles with a typical $\frac{1}{R^6}$ long range decay. This is an inherently non-local effect that cannot be accounted for by local (LDA) or semi-local (GGA) approximations, and new theoretical techniques are necessary.

Non-local correlation is a critical issue especially in graphite, where the inter-layer binding forces are of the van der Waals type. Without the ability to correctly account for these forces the optimal structures predicted by GGA calculations in graphite will be far away from the real experimental values, and this affects all the electronic structure properties we can hope to obtain.

Nevertheless, in recent years a new advancement has been proposed to handle non-local correlation interactions in Density Functional Theory, with minimal computational effort, through an additional term in the exchange and correlation functional called *non-local correlation*. Quantum ESPRESSO implements several flavors of this new functionals, and in this exercise you'll learn how to use the vdW-DF one [M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2006)].

1.2 Information on materials

1.2.1 Diamond

As already discussed during the previous Lab, the diamond structure is a face-centered cubic (FCC) lattice with a basis of two atoms per unit cell. The underlying Bravais lattice can be selected in QE with the flag `ibrav=2`, which corresponds to the following choice for the primitive lattice vectors (please check at http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html):

$$\mathbf{a}_1 = a/2 (-1, 0, 1) , \quad \mathbf{a}_2 = a/2 (0, 1, 1) , \quad \mathbf{a}_3 = a/2 (-1, 1, 0) . \quad (4)$$

The positions of the two carbon atoms are $\mathbf{d}_1 = a (0, 0, 0)$ and $\mathbf{d}_2 = a/4 (1, 1, 1)$ (See Fig. 1). The corresponding reciprocal lattice is a body-centered cubic (BCC) lattice with primitive vectors

$$\mathbf{b}_1 = 2\pi/a (-1, -1, 1) , \quad \mathbf{b}_2 = 2\pi/a (1, 1, 1) , \quad \mathbf{b}_3 = 2\pi/a (-1, 1, -1) . \quad (5)$$

(Please, as an exercise, derive these expressions from Eq. (8) by solving $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ or by using the formulas seen during the lectures.)

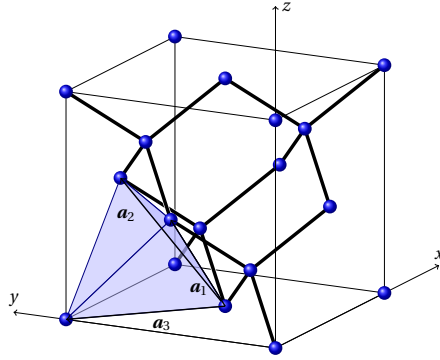


Figure 1: Diamond structure. The primitive lattice vectors \mathbf{a}_i are reported according to the choice adopted in Quantum ESPRESSO.

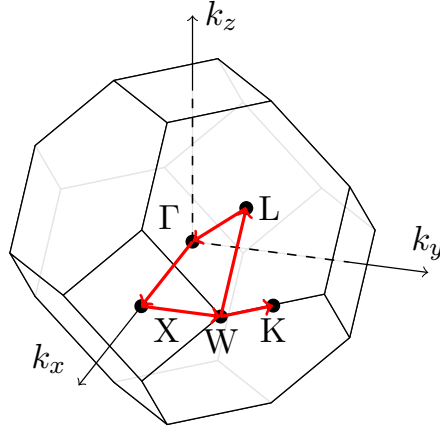


Figure 2: Brillouin zone of a fcc lattice with conventional names of most relevant high-symmetry points. The red line highlights the path in reciprocal space (connecting high-symmetry points) along which you are asked to compute the band structure of diamond.

Fig. 2 shows the first Brillouin zone for this lattice together with the conventional names for some high-symmetry points. Their coordinates are given by

$$\Gamma = (0, 0, 0), \quad X = \frac{2\pi}{a}(1, 0, 0), \quad L = \frac{2\pi}{a}\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right), \quad (6)$$

$$W = \frac{2\pi}{a}\left(1, \frac{1}{2}, 0\right), \quad K = \frac{2\pi}{a}\left(\frac{3}{4}, \frac{3}{4}, 0\right). \quad (7)$$

In this exercise you are asked to compute the band structure of diamond along the line W-L- Γ -X-W-K, shown in red in Fig. 2.

1.2.2 Graphite

Graphite is the most stable form of carbon under standard conditions, and its structure, represented in Fig. 5, consist in two different sheets of carbon atoms arranged in a honeycomb lattice. Two parameters are necessary to fully define this structure, the usual lattice constant a governing the atomic positions on the planes, and c , governing the sheets separation. The corresponding Bravais lattice can be selected in QE with the flag `ibrav=4`, which corresponds to the following choice for the primitive lattice vectors (please check at http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html):

$$\mathbf{a}_1 = a(1, 0, 0), \quad \mathbf{a}_2 = a\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}\right), \quad \mathbf{a}_3 = a\left(0, 0, \frac{c}{a}\right). \quad (8)$$

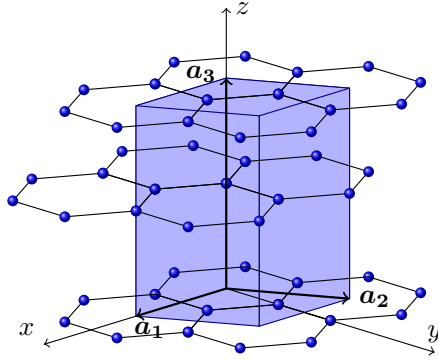


Figure 3: Graphite structure. The primitive lattice vectors \mathbf{a}_i are reported according to the choice adopted in Quantum ESPRESSO.

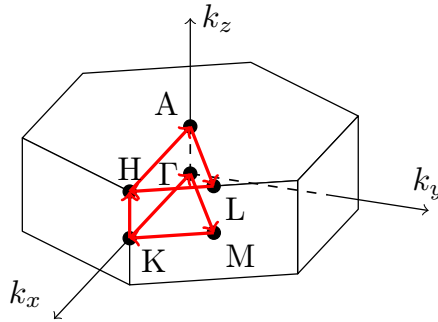


Figure 4: Brillouin zone of a hexagonal lattice with conventional names of most relevant high-symmetry points. The red line highlights the path in reciprocal space (connecting high-symmetry points) along which you are asked to compute the band structure of graphite.

(It is left as an exercise to compute the relative reciprocal lattice vectors.)

The first Brillouin zone for this lattice together with the conventional names for some high-symmetry points is reported in Fig. 4. For this exercise you are asked to compute the band structure of graphite along the line K- Γ -M-K-H-A-L-H, shown in red in Fig. 4. The high-symmetry points are defined by the following **crystal** coordinates

$$\Gamma = (0, 0, 0), \quad K = \left(\frac{1}{3}, \frac{1}{3}, 0\right), \quad M = \left(\frac{1}{2}, 0, 0\right), \quad (9)$$

$$A = \left(0, 0, \frac{1}{2}\right), \quad H = \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{2}\right), \quad L = \left(\frac{1}{2}, 0, \frac{1}{2}\right), \quad (10)$$

1.2.3 Graphene

Graphene, the last allotrope you are asked to analyze, is simply defined as a single sheet of graphite. In this case the crystal lattice is identical to the graphite's one, but to be able to compute a single graphite sheet in periodic boundaries conditions you need to pay attention. As we discussed before, in the unitary cell of graphite the c parameter defines exactly how much the two sheets are separated, and from this point of view graphene is nothing but graphite with sheets infinitely apart from each other. Since infinite is hardly supported by modern computers, a big enough c parameter will be sufficient.

For graphene you are asked to compute bands along the K- Γ -M-K path, where the points' coordinates are identical to the ones of graphite. Pay attention that graphene has a peculiar electronic distribution, where the Fermi surface is collapsed on a single point, a condition

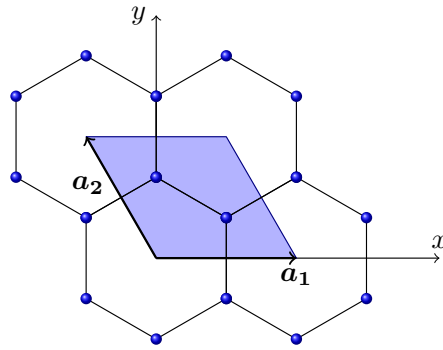


Figure 5: Graphene structure. The primitive lattice vectors \mathbf{a}_i are reported according to the choice adopted in Quantum ESPRESSO.

that requires a very high density of \mathbf{k} -points to correctly integrate the Brillouin zone. In the class material you will find SCF input files with already set a dense \mathbf{k} -point mesh, but if you're interested you can reduce that mesh and study the behavior of the pseudo energy gap that arises. Do you see anything strange?

1.3 QE Calculations

Let us now move to the practical calculations with QE. Diamond will be used as an example in the input files shown here. The procedure is similar for the other two carbonaceous structures remaining, graphite and graphene. These two allotropes represent some of the most studied materials in the recent years exactly for their peculiar electronic properties, that you are asked to compute.

Since you already learned how to obtain the equilibrium lattice constant, energy cut-off and \mathbf{k} -point grid sufficient for convergence, these parameters are now already given to you. We provide all the necessary input files and scripts. They are almost ready to be used, but before running them:

- have a look at them!
- make sure you filled up everything that was left blank.
- in input files, check the paths to the temporary ("tmp") and pseudopotentials ("PP") directories. Make sure they exist or change the paths.
- in scripts, check the path to QE executables ("QEDIR") and results directories. Make sure they exist or change the paths.

1.3.1 Self-Consistent-Field (SCF)

As an essential first step, we must first compute the ground-state electronic density of the system. We need to perform a self-consistent-field (SCF) calculation, like in the previous lab.

The input file `diamond.scf.in` should be similar to the following:

```
&control
  calculation = 'scf'
  restart_mode='from_scratch',
```

```
    prefix='diamond',
    pseudo_dir = .....,
    outdir= .....
/
&system
    ibrav= 2,
    celldm(1) = 6.74
    nat= 2,
    ntyp= 1,
    ecutwfc = 40
    ecutrho = 320
/
&electrons
    mixing_mode = 'plain'
    mixing_beta = 0.7
    conv_thr = 1.0d-8
/
ATOMIC_SPECIES
  C 12.0107 C.pbe-rrkjus.UPF
ATOMIC_POSITIONS
  C 0.0 0.0 0.0
  C 0.25 0.25 0.25
K_POINTS automatic
  8 8 8 1 1 1
```

At this point we have the ground-state density of diamond and the self-consistent Kohn-Sham potential.

1.3.2 Band structures

On top of the SCF run, we can now perform a non-self-consistent-field (NSCF) calculation to compute the bands. In a NSCF calculations, we use the information coming from the SCF calculation to construct the Hamiltonian and then we simply need to diagonalize it in order to find its eigenvalues $E_n(\mathbf{k})$. This is still a non-trivial task (since the dimension of the Hamiltonian is very large), but at least we no longer need to reach self-consistency. The control namelist must be modified in the following way in order to compute the bands (see `diamond.band.in`):

```
&control
  calculation = 'bands'
  prefix      = 'diamond'
  pseudo_dir  = '.....'
  outdir      = '.....'
/
&system
  nat=2, ntyp=1,
```

```
ibrav=2, celldm(1)=6.74027528
ecutwfc = 40.0
ecutrho = 320.0
nbnd =8
/
&electrons
  diagonalization = 'cg'
  conv_thr = 1.0e-8
/
```

```
ATOMIC_SPECIES
  C 12.0107 C.pbe-rrkjus.UPF
```

```
ATOMIC_POSITIONS (alat)
  C   0.0   0.0   0.0
  C   0.25  0.25  0.25
```

```
K_POINTS tpiba_b    <--- Units
....
```

<--- You have to fill this part

where it is very important that `outdir` and `prefix` are the same as in the SCF calculation since the potential is read from file in that directory.

Then, in the system namelist we need to add a variable: `nbnd`, that is the **number of bands** we want to compute. Since we want to compute both valence and conduction bands, a good estimate is in general given by the number of electrons we have in the unit cell (remember that each band can host up to two electrons per unit cell, where the two comes from spin degeneracy, so that half of them should be full and half empty). This should work for diamond. For graphite and graphene, however, you may have to increase this number (doubling it is a safe guess).

The last thing we need to specify with respect to the previous SCF calculation is the set of **k**-points. We want to compute the bands along a certain path (W-L- Γ -X-W-K for diamond). This can be specified in the `K_POINTS` card in two ways: using cartesian (`tpiba_b`) or crystal (`crystal_b`) coordinates (see here for more details: http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html). Pay attention to put a reasonable number of **k**-points along each segment of the path! Should each segment have the same number of points?

The next step is to run the QE executable `bands.x` giving as an input a file with the following content (see `diamond.bands.in`):

```
&bands
  prefix='diamond',
  outdir='....'
  filband='diamond.dat'
/
```


where `filband` is the name of the file in which bands are written. If you save this input file as `diamond.bands.in`, you then need to run

```
theos@theosvm:$ bands.x < diamond.bands.in > diamond.bands.out
```

At this point bands are reported in the output file `diamond.dat`, but in a rather unfriendly way for plotting.

In order to overcome this problem another executable exists: `plotband.x`. Run it interactively and reply to the questions that you will be prompted. In particular you will be asked to provide the name of the file where bands are written (for instance `diamonds.dat` if you use the input file above), the range of energies where you want to plot the bands, and the name of the file in which you want to write out the bands (different from the previous one, of course. For instance `diamond_bands4plot.dat`). Press `ENTER` or `CTRL+C` when you are asked to provide a name for the ps file for the band plot. Use instead `xmgrace` to plot the bands by yourself.

Before interpreting the band structure results, make sure you know the energy of the highest occupied level or Fermi level. This information can be found in the the output of the NSCF calculation.

1.3.3 DOS

We simply need to perform an other NSCF calculation with a flag that activates this method. The input file should be similar to the following (see `diamond.nscf.in`):

```
&control
  calculation='nscf'
  pseudo_dir = .....,
  outdir= .....,
  prefix='diamond'
/
&system
  ibrav= 2, celldm(1) = .....,
  nat= 2, ntyp= 1,
  ecutwfc = 40, ecutrho = 320,
  nbnd = .....,
  occupations='tetrahedra',
/
&electrons
/
ATOMIC_SPECIES
  C 12.0107 C.pbe-rrkjus.UPF
ATOMIC_POSITIONS
  C 0.0 0.0 0.0
  C 0.25 0.25 0.25
K_POINTS automatic
  16 16 12 1 1 1
```

Notice that we are using a denser mesh of **k**-points in this case ($12 \times 12 \times 12$).

Once the NSCF calculation is finished we can use the QE executable `dos.x` to compute the DOS:

```
theos@theosvm:$ dos.x < diamond.dos.in > diamond.dos.out
```

where the input file is

```
&dos
  outdir= .....
  prefix='diamond'
  fildos= .....
  Emin=-6.0, Emax=17.0, DeltaE=0.1
/
```

Here `fildos` is the file in which the DOS will be written. `Emin`, `Emax`, and `deltaE` are the limits of the energy range in which DOS is computed and the step with which energy is discretized. The output file specified in `fildos` contains on three different columns the discrete values of energy considered, the DOS at that energy, and the integral of the DOS up to that energy.

1.3.4 Van Der Waals

In your class material you will find two scripts that will generate and run a set of graphites with different *a* and *c* parameters; one, `run_graphite_pbe_loop.sh`, only with the PBE (GGA) functional, while the other `run_graphite_vdw_loop.sh` will run QE with revPBE (GGA) and the vdW-DF correction. To correctly use this new functionals, as you can see in the script, it's only necessary to activate a flag in the system card called `input_dft`, as shown here.

```
...
&system
  nat=4, ntyp=1,
  ibrav=4, celldm(1)=$A, celldm(3)=$CoA
  ecutwfc = 40.0
  ecutrho = 320.0
  input_dft = 'VDW-DF'
/
...
```

The two scripts will loop in the *a* and *c* list of parameters you have to define. To fix one of the parameter, simply put only one item in the list. The scripts will generate the corresponding input and outputs, plus two files where you'll find the results. Modify the script to write exactly what you want in the result files. You can also loop on the two parameters at the same time and visualize the results in the form of a surface plot. For a very fast visualization of the mesh you can use gnuplot with the following command, here `file.dat` is the tabulated file generated by the scripts.

```
gnuplot> splot 'file.dat' using 1:2:3
```

2 Study of Iron BCC and HCP structures

In problem 2, we will compare energy of iron (Fe) in the body centered cubic (BCC) and hexagonal close packed (HCP) structures at different pressures, in order to evaluate the transition pressure between the two phases [for details see “Possible thermal and chemical stabilization of body-centered-cubic iron in the Earth’s core”, L. Vocadlo *et al.*, Nature **424**, 536 (2003); Xianwei Sha and R.E. Cohen, Phys. Rev. B **73**,104303 (2006); M. Friak and M. Sob, Phys. Rev. B **77**, 174117 (2008)].

At first we will calculate the total energy of a bulk BCC Fe and HCP Fe assuming to know already the right ground state magnetic order of the two structures.

In the second part we will explore in more details the effect of magnetism calculating and comparing the ferro-, anti-ferro- and para- magnetic ground states of BCC Fe.

For the first point you can use a script similar to the one seen in Lab 2 or for the first exercise. Templates can be found inside the subfolders `Fe_BCC` and `Fe_HCP`. For the geometry optimization you should compare your results with the experimental lattice constant $a = 2.86 \text{ \AA}$ for BCC iron [Z.S. Basinski *et al.*, Proc. R. Soc. Lond. A **229**, 459 (1995)], while for the HCP structure $a = 2.45 \text{ \AA}$ and $c/a = 1.60$ [F.M. Wang and R. Ingalls Phys. Rev. B **57**, 5647 (1998)].

Please notice that the input file should include some additional parts since now we are studying a metal. For instance, for Fe in HCP phase the input file should read:

```

1  &control
2      calculation = 'scf'
3      restart_mode='from_scratch'
4      prefix= 'Fe_HCP'
5      tstress = .true.
6      tprnfor = .true.
7      outdir = .....
8      pseudo_dir = .....
9  /
10 &system
11     ibrav= ....
12     celldm(1) = ....
13     celldm(3) = ....
14     nat= ....
15     ntyp= 1
16     ecutwfc = 55
17     ecutrho = 240
18     nspin = 2
19     starting_magnetization(1) = 0.7
20     occupations = 'smearing'
21     smearing = 'm-v'
22     degauss = 0.03
23 /
24 &electrons

```

```
25     mixing_beta = 0.7
26     conv_thr = 1.0d-8
27 /
28 ATOMIC_SPECIES
29 Fe 55.845 Fe.pbe-n-rrkjus_psl.0.2.4.UPF
30 ATOMIC_POSITIONS crystal
31 ... ..
32 K_POINTS automatic
33 ... .. 0 0 0
```

The following describes some new input parameters (not seen in Lab 2 or in the first exercise) as well as the parameters we are concerned with varying in Lab 3. As mentioned several times, the full description of all parameters in the input file can be found at http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html.

- line 4

```
prefix='Fe_HCP'
```

Just to keep your files in order, you will want to change that to reflect what you are calculating – BCC, HCP, etc.

- lines 11-14

```
ibrav= ...
celldm(1)= ...,
celldm(3)=...,
nat= ...,
```

The `ibrav` is the Bravais lattice, this input is an integer, for BCC use `ibrav=3` and for hexagonal `ibrav = 4`. For both cases you need to enter a value for `celldm(1)` (in a.u.). Furthermore for the hexagonal case you must enter a value for `celldm(3)`, this value is defined as $\frac{c}{a}$ and is therefore unit-less, where a is `celldm(1)` and c is the length of the cell in the third dimension. As for `nat`, the number of atoms, this will also depend on the Bravais lattice, for BCC you need only 1 atom but for an HCP lattice you will need to have 2.

- line 16-17

```
ecutwfc = 55
ecutrho = 240
```

In QE it is possible to set up two different energy cut-offs for the plane wave expansion of wave-functions (`ecutwfc`) and density (`ecutrho`). This is very useful when using pseudopotentials.

- line 18

```
nspin=2,
```

Now we have some new inputs. First of all, `nspin` defines the spin-polarization of the system. In previous calculations this was set to 1 (the default) for a non-spin-polarized calculation – i.e., bands are occupied with 2 electrons each and there is no separate calculation for spin-up and -down electrons. However, if we are to treat magnetic systems we need to take spin-polarization into account, this is turned on by `nspin=2`. Since the ground-state of HCP iron is non-magnetic you can put `nspin=1`, while for BCC iron `nspin=2` is necessary in order to describe its ferromagnetic ground state.

- line 19

```
starting_magnetization(1) = 0.7,
```

Because we want to search for a magnetic ground state, we put the system in an initial magnetic state with `starting_magnetization(1)`. Here the integer 1 refers the atom *type* and the value 0.7 is the value of magnetization for that atomic type (and can range for -1 to $+1$). Since we have defined only one type (Fe) we can only find either a ferromagnetic or a non-magnetic state. You can imagine that other types of magnetism will require different definitions of both `starting_magnetization(1)` and atom types (one beauty of computation is that you can give many different *types* of the same atom – e.g., Fe1, Fe2, etc.)

- lines 20-22

```
occupations='smearing',  
smearing='m-v',  
degauss=0.03,
```

Because we are concerned here with a metallic system, we run into some issues with Brillouin zone integration. More specifically, in a metal bands are occupied up to the Fermi energy and because of this discontinuity, Brillouin zone integration with our rather sparse **k**-point grids will lead to large discrepancies in energy with regard to **k**-point sampling (think about if the band crossed the Fermi level at a **k**-point that we have sampled, versus somewhere in between sampled points). To cope with this problem (without going to enormous –read expensive– **k**-point grids) we introduce a fictitious temperature (or smearing). This results in fractional occupation of some of the states above the Fermi-energy and in effect make for a smoother function for the integration. To that end we use a few more parameters: First the temperature is turned on (with `occupations='smearing'`), then we decide on a type of smearing (in this case `smearing='m-v'`, *i.e.* the “Marzari-Vanderbilt” type¹), and finally we need to define a parameter that determines the ‘amount’ of smoothing (`degauss=0.03`).

¹You can get a description of the other types at the usual `INPUT_PW` url

This value is in Ryd units and is the spread of the smearing function. `degauss` should always be tested; small enough not to introduce unphysical effects, but large enough to decrease **k**-point sampling. However, in the interest of time we will not do so for this Lab.

- lines 30-31

```
ATOMIC_POSITIONS (crystal)
```

For the BCC case you need only define one atomic position

```
ATOMIC_POSITIONS (crystal)
Fe    0.0000000000  0.0000000000  0.0000000000
```

while for the HCP case, two will be needed.

```
ATOMIC_POSITIONS crystal
Fe    0.3333333333  0.6666666667  0.25
Fe    0.6666666667  0.3333333333  0.75
```

- lines 32-33

```
K_POINTS automatic
... .. 0 0 0
```

Remember that **k**-point sampling is related to the inverse of the cell parameters. That is, for BCC, sampling should be over a $12 \times 12 \times 12$ grid, while for the HCP case the sampling should be $12 \times 12 \times 6$, to reflect (as closely as possible) the difference in c versus a .

Hints for points (A and B)

Be careful when you compute the energy-versus-volume curve for the HCP structure. Several combinations of a and c/a can give the same volume and you need to consider the one that minimizes the energy of the system. To accomplish this, for each volume you may want to compute the total energy as a function of the ratio c/a (while fixing a according to the volume considered). Since, contrary to graphite, HCP Fe is not a weakly bonded layered material the changes in energy produced by a variation of the c axis are of the same order of magnitude of those produced by a variation in a and thus cannot be decoupled a priori. To find the minima you can construct a 3D plot with for example c/a vs a (or the volume) on the x and y axis and the energy on the z axis and then fit the point with a proper function. A way to do this is using gnuplot, construct a file 'data.dat' with c/a on the 1st column, a (or the volume) on the 2nd and the energy on the 3th and then open a terminal, move to the folder of the 'data.dat' file and type:

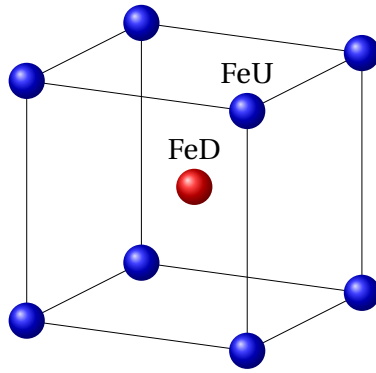


Figure 6: Conventional cubic unit cell for BCC iron required to simulate the antiferromagnetic state. The two atoms in the unit cell are assigned different atomic species (FeU or FeD) according to the spin orientation.

```
$gnuplot
gnuplot> splot 'data.dat' u 1:2:3
gnuplot> f(x,y) = .....
gnuplot> fit f(x,y) 'data.dat' u 1:2:3:(1) via .....
```

Remember that the phase transition between the BCC and HCP structures occurs at a given pressure (and we assume the temperature to be $T = 0$ K). Moreover, at the transition point the Gibbs free energy (that coincides with the Enthalpy at zero temperature) of the two structures must be the same:

$$G_{\text{BCC}} = G_{\text{HCP}} \quad \Rightarrow \quad E_{\text{BCC}}(V_{\text{BCC}}) + V_{\text{BCC}}P = E_{\text{HCP}}(V_{\text{HCP}}) + V_{\text{HCP}}P. \quad (11)$$

By expressing the pressure as $P = -dE/dV$, we notice that then the transition pressure can be obtained according to the Maxwell construction of the common tangent.

Hint for point (C)

Inside the subfolder **Fe_AFM** you will find a prototype of the script that you have to use to compute the energy of the anti-ferromagnetic configuration (**Fe_AFM_deneb.sh**). As already mentioned in the comment to line 19 above, the trick is to use a conventional cubic unit cell and to define two *types* of iron: up (FeU) and down (FeD) (see Fig. 6). Pay attention to the **k**-point grid you should use in order to compare meaningfully with the results for non-magnetic and ferromagnetic iron.

In comparing energies of different configurations, remember to first optimize the structure and do NOT forget that energy is an extensive quantity!

Compare the density of states corresponding to the two spin states in ferromagnetic iron,

```
$gnuplot
gnuplot> plot 'fe.dos' using 1:2 with lines, 'fe.dos' using 1:(-$3) with lines
with the density of states of the non magnetic one
```

```
$gnuplot
gnuplot> plot 'fe.dos' using 1:2 with lines
```

For a deeper analysis compare the results given by the projwfc.x code which in the files `'prefix".pdos_atm#N(X)_wfc#M(L)'` provides the DOS projected on atomic orbital X, having angular momentum L, for atom number N.

```
$gnuplot
gnuplot> plot './fe.pdos_atm#1(Fe)_wfc#2(d)' u 1:2 w l lt 1, \
            './fe.pdos_atm#1(Fe)_wfc#2(d)' u 1:($3) w l lt 3, \
            './fe.pdos_atm#1(Fe)_wfc#1(s)' u 1:2 w l lt 2, \
            './fe.pdos_atm#1(Fe)_wfc#1(s)' u 1:($3) w l lt 4 \
```