

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

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Spring 2018

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 MgO and Mg.
- In problem 2, we will firstly deal with the vdW interactions in DFT. Then we will compare the total energy per atom of graphite and diamond to estimate the transition pressure between these two structures.
- In problem 3, we will compare the total energy of Cobalt in different magnetic and structural configurations.

Some helpful conversions:

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

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

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1 Band structure of MgO and Mg

In the first problem we will compute the band structure and the density of states of magnesium oxide (MgO) and magnesium (Mg).

1.1 Theory

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

1.1.1 Bands

Owing to the periodicity of the crystal structure, the solutions of the time-independent Schrödinger equation are labeled 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.

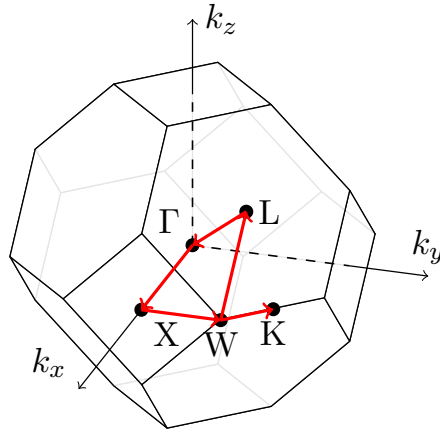


Figure 1: Brillouin zone of a FCC lattice with conventional names of most relevant high-symmetry points. The red line highlights the path in reciprocal space (connecting high-symmetry points) along which you are asked to compute the band structure of MgO.

1.2 Information on materials

1.2.1 MgO

As you have already discovered in Lab 2, magnesium oxide has a face-centered cubic (FCC) structure in its ground state, with 8 atoms in the conventional unit cell. The primitive cell of the lattice is characterized by a basis that includes two atoms (one Mg atom and one O atom). The FCC Bravais lattice is selected in QE with the flag `ibrav=2` (see https://www.quantum-espresso.org/Doc/INPUT_PW.html), which corresponds to the following choice for the lattice vectors:

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

The positions of the two atoms are $\mathbf{d}_1 = a (0, 0, 0)$ and $\mathbf{d}_2 = a/2 (1, 1, 1)$.

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.)

Fig. 1 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 MgO along the line W-L- Γ -X-W-K, shown in red in Fig. 1.

1.2.2 Mg

Magnesium is an alkaline earth metal characterized by a close-packed lattice. In a magnesium crystal the stacking of the hexagonally-packed atomic layers involves an in-plane shift that

repeats every other layer according to the sequence: ABABAB... The primitive cell of the so-called hexagonal close-packed (HCP) lattice is characterized by a basis that includes two atoms. Furthermore, it is fully defined by two parameters: a , which defines the distance between the metal atoms in the hexagonal planes, and c , which defines the separation between planes. 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 https://www.quantum-espresso.org/Doc/INPUT_PW.html):

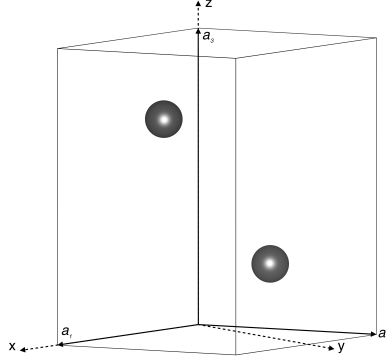


Figure 2: Magnesium structure. The primitive lattice vectors \mathbf{a}_i are reported according to the choice adopted in Quantum ESPRESSO.

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

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

The positions of the two atoms in the primitive cell are $\mathbf{d}_1 = a \left(\frac{1}{3}, \frac{2}{3}, 0 \right)$ and $\mathbf{d}_2 = a \left(\frac{2}{3}, \frac{1}{3}, \frac{c}{2a} \right)$.

The first Brillouin zone for this lattice together with the conventional names for some high-symmetry points is reported in Fig. 3. For this exercise you are asked to compute the band structure of magnesium along the line K- Γ -M-K-H-A-L-H, shown in red in Fig. 3. The high-symmetry points are defined by the following **crystal** coordinates

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

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

1.3 QE Calculations

Let us now move to the practical calculations with QE. MgO will be used as an example in the input files shown here. The same procedure can be applied to the other material, Mg.

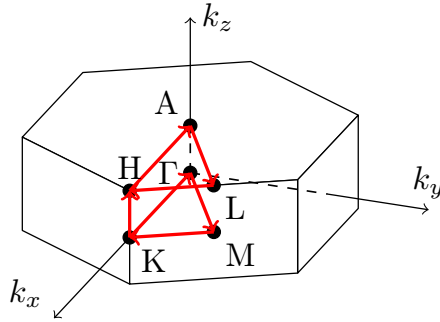


Figure 3: Brillouin zone of a HCP lattice with conventional names of most relevant high-symmetry points. The red line highlights the path in reciprocal space (connecting high-symmetry points) along which you are asked to compute the band structure of magnesium.

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 in the class material. 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 `Mg0.scf.in` should be similar to the following:

```
&control
  calculation = 'scf'
  restart_mode = 'from_scratch'
  prefix = 'Mg0'
  tstress = .true.
  tprnfor = .true.
  pseudo_dir = '../PP/'
  outdir = '../temp/'
/
&system
 ibrav = 2
  celldm(1) = 8.0374557182
  nat = 2
  ntyp = 2
```

```
ecutwfc = 45.0
ecutrho = 360.0
/
&electrons
  diagonalization = 'david'
  mixing_mode = 'plain'
  mixing_beta = 0.7
  conv_thr = 1.0d-8
/
ATOMIC_SPECIES
  Mg 24.305 Mg.pbe.uspp.UPF
  O 15.9994 O.pbe.uspp.UPF
ATOMIC_POSITIONS {alat}
  Mg 0.00 0.00 0.00
  O 0.50 0.50 0.50
K_POINTS {automatic}
  4 4 4 0 0 0
```

At this point we have the ground-state density of MgO 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 `MgO.band.in`):

```
&control
  calculation = 'bands'
  prefix = 'Mg0'
  pseudo_dir = '../PP/'
  outdir = '../temp/'
/
&system
 ibrav = 2
  cellldm(1) = 8.0374557182
  nat = 2
  ntyp = 2
  ecutwfc = 45.0
  ecutrho = 360.0
  nbnd = 16
/
```

```
&electrons
/
ATOMIC_SPECIES
  Mg  24.305  Mg.pbe.uspp.UPF
  O   15.9994  O.pbe.uspp.UPF
ATOMIC_POSITIONS {alat}
  Mg  0.00  0.00  0.00
  O   0.50  0.50  0.50
K_POINTS {crystal_b}
... <- Fill this in
```

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 MgO. For magnesium, 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 MgO). 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: https://www.quantum-espresso.org/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 `MgO.bands.in`):

```
&bands
  prefix = 'MgO'
  outdir = '../temp'
  filband = 'MgO.bands'
/
```

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

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

At this point bands are reported in the output file `MgO.bands`, 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 `MgO.bands` 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 `MgO_bands_4plot.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 `MgO.nscf.in`):

```
&control
  calculation = 'nscf'
  prefix = 'MgO'
  pseudo_dir = '../PP/'
  outdir = '../temp/'
/
&system
  ibrav = 2
  celldm(1) = 8.0374557182
  nat = 2
  ntyp = 2
  ecutwfc = 45.0
  ecutrho = 360.0
  occupations='tetrahedra'
/
&electrons
/
ATOMIC_SPECIES
  Mg 24.305 Mg.pbe.uspp.UPF
  O 15.9994 O.pbe.uspp.UPF
ATOMIC_POSITIONS {alat}
  Mg 0.00 0.00 0.00
  O 0.50 0.50 0.50
K_POINTS {automatic}
  8 8 8 0 0 0
```

Notice that we are using a denser mesh of **k**-points in this case ($8 \times 8 \times 8$).

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

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

where the input file is

```
&dos
  prefix      = 'MgO'
  outdir      = '../temp'

  emin        = -20.0
  emax        = 40.0
  deltae      = 0.1

  fildos      = 'MgO.dos.dat'
/
```

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 Optimize the Mg lattice parameters

In your class material you will find a script that will generate and run a set of Mg structures with different a and c parameters, i.e. `run Mg.loop.sh`. In addition to the usual `celldm(1)` parameter (a , in a.u.), the hexagonal case requires a value for `celldm(3)`. This parameter defines the $\frac{c}{a}$ ratio and is therefore unit-less. Also remember that the primitive cell of an HCP lattice includes two atoms (you will need to set `nat = 2`). The script will loop in the a and c/a list of parameters you have to define. To fix one of the parameters, simply put only one item in the list. The script 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 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
```

Hints for point D

Be careful when you compute the energy-versus-volume curve for magnesium. 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). To find the minimum 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 `file.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 `file.dat` file and type:

```
$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 .....
```

2 The graphite-diamond transition under pressure

In this problem, we will start discussing the issue of van der Waals interactions in a layered material like graphite. Then, we will compare energy of the carbon atoms in the graphite and diamond structures in order to evaluate the transition pressure between the two phases.

2.1 Theoretical reminders

2.1.1 The van der Waals interaction

In the first part of Exercise 1 you are 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)].

2.1.2 Structural transition under pressure

In the second part of this exercise, we will compare energy of the carbon atoms in graphite and in diamond in order to evaluate the transition pressure between the two structures. The phase transition between the graphite and diamond structures occurs at a given pressure (and we assume the temperature to be $T = 0$ K). At the transition point the Gibbs free energy (that coincides with the Enthalpy at zero temperature) of the two structures must be the same:

$$G_{\text{graph}} = G_{\text{diam}} \quad \implies \quad E_{\text{graph}}(V_{\text{graph}}) + V_{\text{graph}}P = E_{\text{diam}}(V_{\text{diam}}) + V_{\text{diam}}P . \quad (11)$$

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. Note that the energy and volume appearing in the equation above are extensive quantities, therefore they must be normalized per atom in order to be compared (we are comparing the Gibbs free energy per atom).

2.2 Information on materials

2.2.1 Diamond

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` (please check at https://www.quantum-espresso.org/Doc/INPUT_PW.html), as already used for MgO. However, 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. 4).

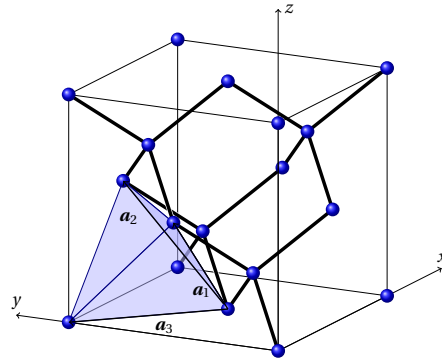


Figure 4: Diamond structure. The primitive lattice vectors \mathbf{a}_i are reported according to the choice adopted in Quantum ESPRESSO.

2.2.2 Graphite

Graphite is the most stable form of carbon under standard conditions, and its structure, represented in Fig. 5, consists 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`, (please check at https://www.quantum-espresso.org/Doc/INPUT_PW.html), already used for Mg.

2.3 QE calculations

The same guidelines discussed in the exercises 1 apply also here, have a look at the almost ready to use input file and scripts that we provided and set the paths where needed.

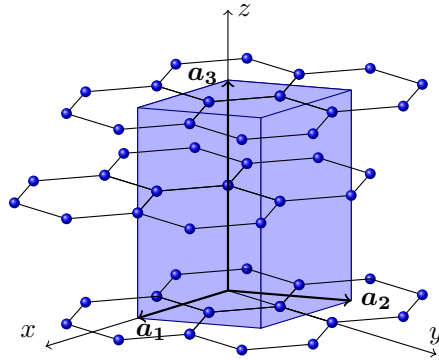


Figure 5: Graphite structure. The primitive lattice vectors \mathbf{a}_i are reported according to the choice adopted in Quantum ESPRESSO.

2.3.1 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. The scripts work in a similar way as the one you have used to optimize the magnesium lattice parameters.

2.3.2 Structural transition under pressure

At first we will calculate the total energy of diamond for different volumes. For this point you can use the results from the geometry optimization of diamond since in this case there is a one-to-one correspondence between variation of the volume and variation of the (unique) lattice parameter. You need to save in a file the various values of the energy versus the volume. You can vary the volume in the range $[-5\%, +5\%]$ of the equilibrium value.

Then, we will repeat this procedure (with a different volume variation range) for graphite. In this case 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. Since graphite is a weakly bonded layered material the changes in energy produced by a variation of the c axis are smaller than those produced by a variation in a and thus the following procedure is adopted:

- A certain cell volume V is chosen in the range $[\bar{V} - \delta V, \bar{V} + \delta V]$, where \bar{V} is the equilibrium volume. Since we are interested in a high-pressure transition, you can consider an asymmetric volume interval (e.g. δV ranging from $-15\%\bar{V}$ to $+5\%\bar{V}$);
- Vary the cell parameter a in a range around the equilibrium value (say, $\pm 5\%$). For each value of a determine the value of $c(a, V)$ that returns the desired volume V and compute the energy of the system $E(a, c(a, V))$;
- For a given V , plotting $E(a, c(a, V))$ versus a gives a curve which can be used to determine the parameter values that minimize the energy at fixed volume V :

$$a_{\min}(V) = \operatorname{argmin}_a E(a, c(a, V)). \quad (12)$$

You can compute this value by finding the minimum of the parabola resulting from a quadratic fit of $E(a, c(a, V))$ versus a .

- For each volume V , save in a file the corresponding minimum energy versus volume, in the same way as you did for diamond.

You can use the program `ev.x` in the QE distribution to fit these values with the Birch-Murnaghan isothermal equation of state (`birch1` in `ev.x`). See the handout of the lab 2 for details, notice that you need to use '`noncubic`' as a lattice type in input to `ev.x` since you are providing volume versus energy data. Once you have the parameters from the fit, you can plot the corresponding curves E versus V for both diamond and graphite and apply the common tangent construction (mentioned in the class) to determine the transition pressure. Remember that energy is an extensive quantity!

Hint for the construction of the common tangent

The Birch-Murnaghan equation implemented in `ev.x` (`birch1`) has the following form:

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}, \quad (13)$$

and `ev.x` gives the parameters E_0 , V_0 , B_0 , B'_0 fitting your volume-energy data.

You can use the above function to make a plot and compute the derivatives (you can also use symbolic calculus) that are required for the common tangent construction. Note that you need to convert the parameters in output from `ev.x` in the proper units.

In order to solve the common tangent problem, you have to find the solution of the following non-linear system:

$$\begin{cases} \left. \frac{dE_{\text{graph}}}{dV} \right|_{V=V_{\text{graph}}} = \left. \frac{dE_{\text{diam}}}{dV} \right|_{V=V_{\text{diam}}} \\ \frac{E_{\text{diam}}(V_{\text{diam}}) - E_{\text{graph}}(V_{\text{graph}})}{V_{\text{diam}} - V_{\text{graph}}} = \left. \frac{dE_{\text{diam}}}{dV} \right|_{V=V_{\text{diam}}} \end{cases} \quad (14)$$

where the first equation accounts for the equality of the derivatives (we have used $P = -\frac{dE}{dV}$) and the second one for the equality of the free energies. As a solution of the problem you will find the pair of values $V_{\text{graph}}, V_{\text{diam}}$ that satisfies Eq. (14).

You may use the python packages **scipy** (in particular **fsolve** in **scipy.optimize**) and **sympy** for a fast solution of this problem. In this case, note that you have to give a meaningful interval where to look for the solution.

If you prefer, you can also solve the problem using Mathematica.

3 Phase Stability and Magnetism in Cobalt

In problem 2, we will compare energy of cobalt (Co) in the hexagonal close packed (HCP) and face-centered cubic (FCC) structure. At first we will calculate the total energy of a bulk HCP Co and FCC Co 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 non- magnetic ground states of HCP Co.

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 `Co_hcpafm` and `Co_hcpfm`. For the geometry optimization you should compare your results with the experimental lattice parameters $a = 2.50 \text{ \AA}$ and $c = 4.06 \text{ \AA}$ for HCP cobalt, while for the FCC structure $a = 3.54 \text{ \AA}$ [T. Nishizawa and K. Ishida, Bulletin of Alloy Phase Diagrams 4, 387 (1983)].

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

```
1  &control
2      calculation = 'scf'
3      restart_mode='from_scratch'
4      prefix='...'
5      tstress = .true.
6      tprnfor = .true.
7      outdir = '../temp/'
8      pseudo_dir = '../PP/'
9  /
10 &system
11     ibrav= 4
12     celldm(1) = ...
13     celldm(3) = ...
14     nat= 2
15     ntyp= 1
16     ecutwfc = 55
17     ecutrho = 440
18     occupations = 'smearing'
19     degauss = 0.01
20     smearing = 'm-v'
21     nspin = 2
22     starting_magnetization(1) = 0.7
23 /
24 &electrons
25     mixing_beta = 0.7
26     conv_thr = 1.0d-8
27 /
28 ATOMIC_SPECIES
29 Co 58.933194 Co.pbe-n-rrkjus_psl.1.0.0.UPF
```

```
30  ATOMIC_POSITIONS crystal
31  Co  0.333333 0.666667 0.25
32  Co  0.666667 0.333333 0.75
33  K_POINTS automatic
34    12 12 6 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 https://www.quantum-espresso.org/Doc/INPUT_PW.html.

- line 4

```
prefix='Co_hcp-fm'
```

Just to keep your files in order, you will want to change that to reflect what you are calculating – HCP, FCC, ferro-magnetic (fm), anti-ferromagnetic (afm), etc.

- lines 11-14

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

The `ibrav` is the Bravais lattice, this input is an integer, for FCC use `ibrav=2` 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 FCC you need only 1 atom but for an HCP lattice you will need to have 2.

- line 16-17

```
ecutwfc = 55
ecutrho = 440
```

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.

- lines 18-20

```
occupations='smearing',
smearing='m-v',
degauss=0.01,
```

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=0.01`). 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.

- line 21

```
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`.

- line 22

```
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 (Co) 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.*, Co1, Co2, etc.)

- lines 30-32

```
ATOMIC_POSITIONS (crystal)
```

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

For the HCP case you need to define two atomic positions

```
ATOMIC_POSITIONS (crystal)
  Co   0.333333  0.666667  0.25
  Co   0.333333  0.666667  0.75
```

while for the FCC case, only one will be needed.

```
ATOMIC_POSITIONS crystal
  Co   0.0 0.0 0.0
```

- lines 33-34

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

Remember that **k**-point sampling is related to the inverse of the cell parameters. That is, for FCC, 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 .

Hint for point (A and B)

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

Hint for point (C)

Inside the subfolder `Co_hcp-afm` you will find a prototype of the script that you have to use to compute the energy of the anti-ferromagnetic configuration (`Co_hcp-afm_deneb.sh`). As already mentioned in the comment to line 22 above, the trick is to define two *types* of cobalt: up (CoU) and down (CoD).

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

```
$gnuplot
gnuplot> plot 'co.dos' using 1:2 with lines, 'co.dos' using 1:(-$3) with lines
```

with the density of states of the non magnetic one

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