

# Lab 3: Advanced topics in first-principles electronic structure calculations

Report due: 18/05/2025

In this problem set, we will perform additional first-principles calculations that focus on aspects of DFT complementary to those presented in Lab 2. First of all, we will learn how to calculate the electronic band structure for MgO. In this case the non-self-consistent algorithm implemented in Quantum ESPRESSO will be used, also to compute the density of states (DOS) and PDOS (projected DOS). In the second exercise, we will investigate a material for which standard DFT functionals need to be augmented to include the physics of van der Waals interactions in order to reproduce the correct experimental structure. Finally, the third exercise will give a general overview on how to simulate magnetic systems (using cobalt as a test case), highlighting all the necessary calculation parameters.

# General information and advice

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In this, Lab we will learn how to use some more functionalities of the Quantum Espresso (QE) package, introduced in Lab 2. Please keep in mind the things learned and the Handout from Lab 2. The current investigation is composed of three parts:

- In exercise 1, we will compute and analyze the band structure and density of states of MgO.
- In exercise 2, the effect of van der Waals interactions on the structural relaxation of MoS<sub>2</sub> will be investigated.
- In exercise 3, we will compare the total energy of cobalt in different magnetic and structural configurations.

Some helpful conversions:

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

Note: Linux command to **uncompress/open a tar archive**: `$ tar zxvf file.tar.gz`

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# 1 Band structure and DOS of MgO (30 points)

Band structures are a fundamental concept in material science, allowing for a deeper understanding on how electrons behave in solids. In this exercise, you will be asked to compute the band structure of FCC MgO along high-symmetry lines within a non-self-consistent-field (NSCF) algorithm. Two additional quantities that can be easily obtained from an NSCF calculation and that you are asked to compute are the density of states (DOS) and projected density of states (PDOS).

## 1.1 Theory

In order to help you with the theoretical discussion of the results of this exercise, let's quickly review the theory of the band structure and density of states (DOS).

### 1.1.1 Band Structure

Owing to the periodicity of the crystal structure, the solutions of the time-independent Schrödinger equation can be 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:

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

The goal of the first exercise is 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.

MgO is a face-centered cubic (fcc) lattice with a basis of two atoms per unit cell. The underlying Bravais lattice can be selected in Quantum ESPRESSO with the flag `ibrav=2`, which corresponds to the following choice for the primitive lattice vectors:

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

The positions of Mg and O are at  $(0, 0, 0)$  and  $a(1/2, 1/2, 1/2)$ , respectively. The corresponding reciprocal lattice is a body-centered cubic (BCC) lattice with primitive vectors

$$\mathbf{b}_1 = 2\pi/a (-1, -1, 1) , \quad \mathbf{b}_2 = 2\pi/a (1, 1, 1) , \quad \mathbf{b}_3 = 2\pi/a (-1, 1, -1) . \quad (3)$$

(As an exercise, derive these expressions by solving  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$  as explained during the lectures.)

The first Brillouin zone for this lattice and its conventional high-symmetry points are shown in Fig. 1. For this exercise you are asked to compute the band structure of MgO along the path W-L- $\Gamma$ -X-W-K, as indicated in Fig. 1. The coordinates of the high-symmetry points required to

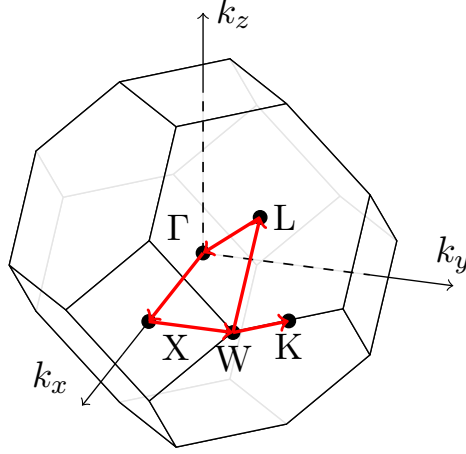


Figure 1: Brillouin zone of an FCC lattice with conventional names for the most relevant high-symmetry points. The red line highlights the path in reciprocal space (connecting high-symmetry points) along which you are asked to compute the band structure of MgO.

build this path are as follows:<sup>1</sup>

$$\Gamma = (0, 0, 0), \quad X = \frac{2\pi}{a}(1, 0, 0), \quad L = \frac{2\pi}{a} \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right), \quad (4)$$

$$W = \frac{2\pi}{a} \left( 1, \frac{1}{2}, 0 \right), \quad K = \frac{2\pi}{a} \left( \frac{3}{4}, \frac{3}{4}, 0 \right). \quad (5)$$

### 1.1.2 Density of states (DOS)

The density of states (DOS), indicated as a function  $D(E)$ , 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  $E_\alpha$ , with  $\alpha$  a complete set of quantum numbers, then a formal expression for the DOS is

$$D(E) = \sum_{\alpha} \delta(E - E_{\alpha}), \quad (6)$$

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

$$D(E) = 2 \frac{V}{(2\pi)^3} \sum_n \int_{\text{B.Z.}} \delta(E - E_n(\mathbf{k})) d\mathbf{k}. \quad (7)$$

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 this algorithm is implemented in the Quantum ESPRESSO package.

<sup>1</sup>You can check the high-symmetry path of any material at <https://www.materialscloud.org/seekpath>. Note that the given coordinates of the high-symmetry points will be given in the crystal basis rather than Cartesian coordinates (see difference between tpiba and crystal, from the Quantum ESPRESSO user guide in the K\_POINTS section).

## 1.2 Quantum ESPRESSO Calculations

All the necessary input files and scripts to run the calculations for this exercise are provided. Before using any of these input files:

- have a **good** look at them!
- make sure you filled up everything that was left **TO BE COMPLETED**.
- in input files, check the paths to the temporary ("tmp") and pseudopotentials ("PP") directories. Make sure they exist in the path or change the path accordingly.

### 1.2.1 Self-Consistent-Field (SCF)

**Note:** For Exercises 1 & 3, each calculation folder will contain a `run_local.sh` **bash** script. Simply run this script with **bash** providing the input file as a parameter, e.g.:

```
bash run_local.sh scf.in
```

As an essential first step, we must compute the ground-state electronic density of the system. In order to do this, we'll execute a self-consistent-field (SCF) calculation.

The **UPF files** that define the pseudo potentials needed used in this exercise will be provided as part of the Lab3 material. You should always make sure the `pseudo_dir` input of the `control` namespace points to the directory that contains the pseudo potentials. These pseudo potentials were chosen from the "Standard solid-state pseudo potentials (SSSP) library". The **Materials Cloud** website provides access to this library, and important information on how it was designed, and how it should be used. In particular, it should be noted that for each element of the periodic table there is a suggested value for the kinetic energy cutoff for both the wave functions as well as the charge density.

Below you can see the input file template for performing the self-consistent field calculation for MgO (found in `exercise_1/MgO/scf.in`):

```
&control
  calculation = 'scf'
  restart_mode = 'from_scratch'
  prefix = 'MgO'
  pseudo_dir = '< TO COMPLETE >'
  outdir = '../tmp'
/
&system
  ibrav = 2
```

```

    celldm(1) = 8.0374557182
    nat = 2
    ntyp = 2
    ecutwfc = < TO COMPLETE >
    ecutrho = < TO COMPLETE >
/
&electrons
    diagonalization = 'david'
    mixing_mode = 'plain'
    mixing_beta = 0.7
    conv_thr = 1.0d-8
/
ATOMIC_SPECIES
    Mg 24.0350 Mg.pbe-n-kjpaw_psl.0.3.0.UPF
    O 15.9994 O.pbe-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS (alat)
Mg 0.000000000 0.000000000 0.000000000
O 0.500000000 0.500000000 0.500000000
K_POINTS {automatic}
8 8 8 0 0 0

```

### Task

For this first step, find the recommended cutoffs for both the wave functions (`ecutwfc`) and charge density (`ecutrho`) on the [Materials Cloud SSSP efficiency](#) website, and complete the template above to run the SCF calculation.

### Task

Test this recommendation by increasing `ecutwfc` and/or `ecutrho`. Are you convinced that the recommended values are sufficiently converged?

## 1.2.2 Band structure calculation

Once the SCF in the previous section has been completed, Quantum ESPRESSO has stored the ground-state density of MgO and the self-consistent Kohn-Sham (KS) potential, which can be used to restart for subsequent calculations.

### Task

Before starting the next run, you need to take note of the energy of the highest occupied level resulting from this calculation. This value can be obtained by looking at the following line in the output "`highest occupied level (ev):`" by means, for example, of the `grep` command. We'll use this for plotting the electronic structure later.

On top of this SCF run, we can now perform a non-self-consistent-field (NSCF) calculation of the bands, by setting `calculation='bands'` in the control section. In an NSCF-type calculation, the charge density obtained from the SCF calculation is used to construct the Hamiltonian, which is subsequently diagonalized in order to find its eigenvalues  $E_n(\mathbf{k})$ . This is still a non-trivial task (as we're dealing with a high-dimensional Hamiltonian matrix), but at least we no longer ask for self-consistency in the KS potential. The input used for SCF must be modified in order to perform an NSCF-type calculation for computing the bands (see `exercise_1/MgO/pwbands.in`).

Here it is of paramount importance that `outdir` and `prefix` are the same as in the SCF calculation since the KS potential is read from files already stored in these directories. Next, in the `&system` namelist we need to add an input variable: `nbnd`, to specify 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 (Note: this is so because each band can host up to two electrons per unit cell, where the factor two comes from spin degeneracy, and this gives an equal number of filled/valence and empty/conduction bands). This setup should be fine in the case of MgO.

### Task

Figure out a good value to choose for `nbnd`, based on the number of electrons reported in the previous SCF calculation. Is this the number of electrons you would expect for this system? Consider the number of electrons of a Mg atom and an O atom, and discuss any agreement or disagreement.

The last thing we need to specify with respect to the previous SCF calculation is the set of  $\mathbf{k}$ -points. We will compare our results with the ones reported in a paper [J Comput Electron (2016) 15 1521–1530] included as part of the Lab3 material. For ease of comparison of our band structure plot with theirs, we will choose the very same path (W-L- $\Gamma$ -X-W-K). The path is specified in the K\_POINTS card in various ways. Using the card option `tpiba_b`, indicates that we will use Cartesian coordinates of the points in reciprocal space, and in units of  $2\pi/a$  (where  $a$  is defined by the value of `cellldm(1)`). More specifically, the input for the K\_POINTS will look like

```
K_POINTS  tpiba_b
6
1.000 0.500 0.000  n1 !W
0.500 0.500 0.500  n2 !L
...
```

where the values of `n1, n2, ...` correspond to the number of  $\mathbf{k}$ -points along the path segment connecting the current high-symmetry point to the next one.



### Task

Enter the correct symmetry points in the input file to reconstruct the (W-L- $\Gamma$ -X-W-K) path. Think about how many k-points to calculate along each segment of the path. Would you assign to each segment the same number of points to have a balanced representation of the bands?

Once you have finished providing all the inputs, run the calculation using:

```
$ bash run_local.sh pwbands.in
```

The final step to obtain the band structure is to run the Quantum ESPRESSO executable `bands.x`, e.g. by the command

```
$ bash run_local.sh bands.in
```

where the input file has the following content (see `exercise_1/MgO/bands.in`):

```
&bands
  prefix = 'MgO'
  outdir = '../tmp'
  filband = 'MgO-bands.dat'
/
```

where `filband` is the name of the file in which bands are written.

At this point bands are reported in the output file `MgO-bands.dat`, but in a rather unfriendly way for plotting. In order to overcome this problem, another QE executable comes to our rescue: `plotband.x`. Run it *interactively* from the folder where the file `MgO-bands.dat` is, and by replying to the questions that will be prompted. In particular you will be asked to provide the name of the file where bands have been stored as raw data (`MgO-bands.dat`). For the subsequent question, about the range of energies for the plot of the bands, choose a similar range to the one used in the cited reference [see **Figure 2** of J Comput Electron (2016) **15** 1521–1530]. Next, the name of the file (xmgrace/gnuplot) in which you want to write out the bands (different from the previous one, of course!) and the name of the postscript file that will be generated (e.g., `MgO-bands.ps`). The program then asks for the value of `Efermi`. In this case, it corresponds to the energy of the highest occupied level found earlier during this exercise. For the final question (`deltaE`, reference E (for tics) ), the suggested value for `deltaE` is 2.0, whereas for the reference Energy, we use the same value as for `Efermi`.

### Task

A qualitative comparison should be made of the plotted bands with the analogous plot from the reference publication [see **Figure 2(a)** of J Comput Electron (2016) **15** 1521–1530]. In particular, estimate the value of the *band gap* from your results and compare it with the analogous estimate from the graph in the cited publication.

### Task

The experimentally measured band gap of MgO is 7.90 eV at zero temperature. Comment about possible discrepancies with experiment, and the quality of the DFT functional used in the current exercise.

### Task

Does your result suggest that this material should appear colorless?

## 1.2.3 DOS

To obtain the DOS, we start by performing a fresh NSCF calculation with the proper calculation setting, with an input file similar to the following (see also `exercise_1/MgO/nscf.in`):

```
&control
  calculation = 'nscf'
  prefix='MgO'
  pseudo_dir = '< TO COMPLETE >'
/
&system
  ibrav = 2
  celldm(1) = 8.0374557182
  nat = 2
  ntyp = 2
  ecutwfc = < TO COMPLETE >
  ecutrho = < TO COMPLETE >
  occupations='tetrahedra'
  nbnd = < TO COMPLETE >
/
&electrons
/
ATOMIC_SPECIES
  Mg  24.0350  Mg.pbe-n-kjpaw_ps1.0.3.0.UPF
  O   15.9994  O.pbe-n-kjpaw_ps1.0.1.UPF
ATOMIC_POSITIONS (alat)
Mg      0.000000000  0.000000000  0.000000000
O       0.500000000  0.500000000  0.500000000
K_POINTS {automatic}
16 16 16 0 0 0
```

It is worth noting that we are using a denser mesh of **k**-points compared to the SCF calculation, and that we do not select a **k**-point path as in the calculation of the bands, rather we use a regular mesh. Moreover, note the new keyword `occupations='tetrahedra'` in the `&system` namelist.

This instructs Quantum ESPRESSO to prepare the output for the subsequent DOS calculation using the tetrahedron method. Complete the input file above in line with the parameters used for the band structure calculations, and run the NSCF:

```
$ bash local.sh nscf.in
```

Once the NSCF calculation is finished we can compute the DOS:

```
$ bash local.sh dos.in
```

with the input

```
&dos
  prefix = 'MgO'
  outdir = '../tmp'
  fildos = 'MgO-dos.dat'
  Emin = 0.0
  Emax = 32.0
  DeltaE = 0.1
/
```

Here `fildos` is the file onto which the DOS data will be written. `Emin`, `Emax`, identify the energy interval in which the DOS is computed, whereas `deltaE` sets the size of the energy discretization bin. The output file specified in `fildos` contains three different columns: the discrete values of energies  $E$  considered, the corresponding values of the DOS function  $D(E)$ , and the integral of the DOS up to that energy, respectively.

### Task

Use your favorite tool for plotting data in order to get a graphical representation of the function  $D(E)$ . Compare the obtained DOS with the band structure. Is everything as you would expect? Comment on the salient features of the DOS, especially close to the band extrema.

From the output of the NSCF calculation, you can also read the computed *Fermi energy* (e.g. using the `grep` command). By looking at the DOS plot around this Fermi energy, you can get a confirmation of your previous estimate for the band gap.

Finally, we can produce the so-called projected density of states (PDOS). The projected (a.k.a. partial) density of states represents the relative contribution of a particular atom/orbital to the total DOS. It is a useful tool to reconcile the plane-wave representation of the electronic structure of solids with the “atomic orbital” picture familiar in chemistry. With the data available from the NSCF calculation, the QE executable `projwfc.x` helps us to compute such PDOS:

```
$ bash run_local.sh projwfc.in
```

where the input is the following:

```
&projwfc
  prefix = 'MgO'
  outdir = '../tmp'
  filpdos = 'MgO-pdos.dat'
  lwrite_overlaps = .true.
/
```

With the filename specified above for the keyword `filpdos`, the code will produce new files. In particular, you should notice three new files referencing the magnesium atom and its valence orbitals (with names `MgO-pdos.dat.pdos_atm#1(Mg)_wfc#1(s)`, and similarly for the other *s* and the *p* wave functions), as well as two files referencing the oxygen atom and its *s* and *p* wave functions. With the help of yet another Quantum ESPRESSO executable, `sumpdos.x`, we can extract information from the above files, running the following series of commands<sup>2</sup>:

```
sumpdos.x MgO-pdos.dat.pdos_atm#*(Mg\)*\(s\) > atom_Mg_s.dat
sumpdos.x MgO-pdos.dat.pdos_atm#*(Mg\)*\(p\) > atom_Mg_p.dat
sumpdos.x MgO-pdos.dat.pdos_atm#*(Mg\)* > atom_Mg_tot.dat
sumpdos.x MgO-pdos.dat.pdos_atm#*(O\)*\(s\) > atom_O_s.dat
sumpdos.x MgO-pdos.dat.pdos_atm#*(O\)*\(p\) > atom_O_p.dat
sumpdos.x MgO-pdos.dat.pdos_atm#*(O\)* > atom_O_tot.dat
```

Using your favorite tool for plotting data, it is possible to render the information contained in the files `atom_*` in a graphical format. Through such graphical representations, you should be able to **characterize the type of atom (Mg or O) and atomic orbital (*s* or *p*) that contribute near the Fermi energy of the system**. A similar analysis can be found in the cited publication [see **Figure 4(a)** of J Comput Electron (2016) **15** 1521–1530].

### Task

Plot the results for the PDOS of the *s* and *p* orbitals of the Mg and O atoms near the valence band maximum. Can you reconcile the results from the (P)DOS with the electronic configuration given to the Mg and O atoms in the periodic table, and the familiar notion of ionic bond?

---

<sup>2</sup>Note the use of the backslash character needed to escape characters (parentheses in this case) that have a special meaning in the shell.

## 2 Layered materials and van der Waals interactions (40 points)

Layered materials are characterized by strong chemical bonds between atoms belonging to the same layer while neighboring layers are held together by weak van der Waals (vdW) interactions. A prototypical example is graphite, but many other materials present a similar layered structure. In this exercise, we will focus in particular on molybdenum disulfide ( $\text{MoS}_2$ ). The description of such systems within Density Functional Theory (DFT) is non-trivial due to dispersion interactions, commonly named van der Waals forces that are 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 correlations are critical to be included, especially in layered materials, 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 will be far away from the real experimental values, and this affects all the electronic structure properties we will obtain.

In recent years advancements have been proposed to handle non-local correlation interactions in DFT with minimal computational effort, through an additional term in the exchange and correlation functional called *non-local correlation*. Quantum ESPRESSO implements several flavors of these new functionals, and in this exercise you will learn how to use the vdW-DF and vdW-DF2-c09 ones [M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2006), K. Lee *et al.*, Phys. Rev. B **82**, 081101 (2010) and V.R. Cooper, Phys. Rev. B **81**, 161104(R) (2010)].

The calculations in this exercise are probably heavier than in previous exercises in this course (especially if you use the virtual machine). Therefore, make sure to give yourself enough time to set up, test, run, and rerun the calculations!

### 2.1 Molybdenum disulfide

In this exercise, you are asked to optimize the cell parameters of  $\text{MoS}_2$  using the vdW-DF2-c09 functional and compare your results with experiments and with what you can obtain with functionals that do not take vdW interactions into account. The crystal structure of  $\text{MoS}_2$  is presented in the left panel of Fig. 2, where you can see that each layer is made of a plane of Mo atoms sandwiched between planes containing S atoms. In each plane, the atoms are arranged in a hexagonal Bravais lattice, which in the case of S is rotated by 60 degrees with respect to the Mo-plane. When seen from above, this gives a honeycomb structure to a single layer of  $\text{MoS}_2$  (see the right panel in Fig. 2). Two parameters are necessary to fully define the unit cell: the

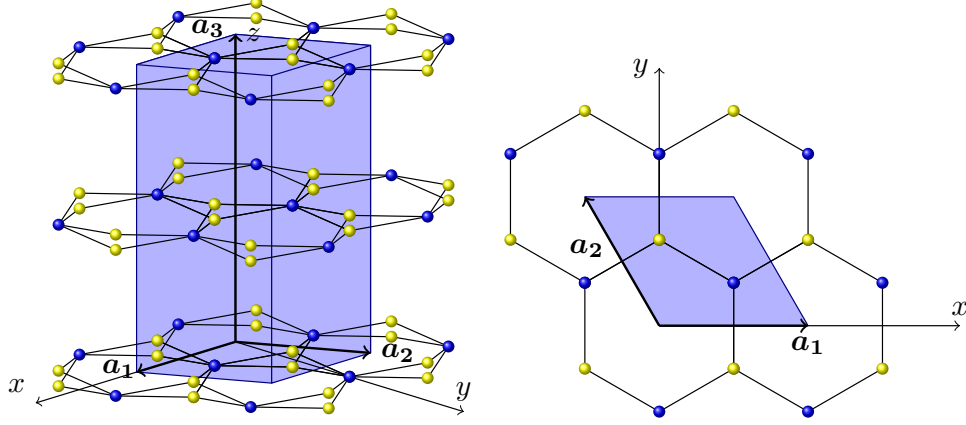


Figure 2: Crystal structure of bulk (left) and monolayer (right) molybdenum disulfide. The primitive lattice vectors  $\mathbf{a}_i$  are reported according to the choice adopted in Quantum ESPRESSO. The vertical displacement of S atoms from the plane of Mo atoms is not to scale to emphasize the honeycomb structure of each layer.

usual lattice constant  $a$  governing the atomic displacement in the planes, and  $c$ , governing the interlayer separation. The corresponding hexagonal 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](http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html)):

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

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

## 2.2 Geometry optimization of MoS<sub>2</sub>

You have to **optimize two parameters to define the structure**, one defining the in-plane structure within each layer, the other defining the separation between the layers. For layered materials like MoS<sub>2</sub>, those **two parameters are weakly coupled and thus can be optimized separately**.

The value of  $a$  can be specified by entering a value for `celldm(1)` (in a.u.) in the system namelist. Furthermore, 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. In your class material, you will find some example input files and scripts to help you. You will need to optimize both  $a$  and  $c$ . Since we are dealing with a layered material, for simplicity we can perform the optimization of the two parameters separately.

## Task

First optimize  $a$  by keeping  $c$  fixed (e.g., equal to the experimental value  $c_{\text{exp}} = 12.30 \text{ \AA}$ ; note that the unit cell includes two layers) by running several calculations for different values of  $a$  and finding when the energy is minimal. You might want to consider a range of values around the experimental one ( $a_{\text{exp}} = 3.16 \text{ \AA}$ ). Do the optimization with and without accounting for the van der Waals interactions. Compare the features of the resulting curves in the two cases. Fit the curves to find the optimized in-plane lattice parameter, and compare both cases.

Pay attention to the fact that if you want to keep  $c$  fixed, the parameter `cellldm(3)`, defined as  $c/a$ , will actually vary.

Switching on and off van der Waals interactions is achieved by adding or removing the property `input_dft` with value `VDW-DF2-C09`:

```
...
&system
  nat=6, ntyp=2,
  ibrav=4, cellldm(1)=....., cellldm(3)=.....,
  ecutwfc = 40.0
  ecutrho = 600.0
  input_dft = 'VDW-DF2-C09'
/
...
```

In addition, since for a given value of  $a$  and  $c$  the forces on the atoms are not zero by symmetry, you will need to relax the atoms to their equilibrium positions within the unit cell for each calculation. This means that you have to specify the calculation type as `'relax'`:

```
&control
  calculation = 'relax'
  restart_mode='from_scratch'
  .....
/
```

## Task

You can now use the optimized in-plane lattice parameter from the previous question. Study the ground-state energy as a function of the separation between the layers, with and without accounting for van der Waals interactions. Compare the features of the resulting curves in the two cases. Can you find a clear minimum in both cases? Can you see the effects of the van der Waals interactions? Fit the curves appropriately to find the optimized interlayer separation when possible. How do these values compare with each other and with experimental results?

If you do not find a clear minimum when not using van Waals corrections, check the behavior of the total energy for very large inter-layer distances. Note that in the input file we provided, the **positions of the atoms in the unit cell are given in crystal coordinates**. This means that the positions are expanded by the primitive vectors (see Quantum ESPRESSO input webpage for more details). As a consequence, when we increase  $c$ , the unit cell elongates in the  $z$  direction, and the atom positions also change along  $z$  preserving the relative alignment between atoms. That is, not only the distance between the two layers is increasing but also the  $z$  displacements of the atoms within a given layer. As we are using QE `relax` calculation mode, the tendency is that the atoms of each layer fall back to their equilibrium position such that effectively we only change the distance between layers. This should work well for lattice constants around the equilibrium values, but for very large  $c$  it might not be the case. If you want to consider very large  $c$  values, start from the relaxed coordinates of a converged calculation with similar  $c$  value or adapt the  $z$  coordinates of atoms appropriately.

### 2.2.1 Giving you a hand

In the folder for exercise, you will find a folder called “geometry\_optimization”. There, you will find two folders, one for the pure PBE calculations and another when including vdW. The scripts inside of these folders will help you with automating the calculations to obtain the optimal lattice constants  $a$  and  $c$ : the `run_pbe_loop.sh` for the calculations with PBE (GGA) functional, and the other `run_vdw_loop.sh` will run QE with PBE (GGA) AND the vdW-DF correction. Compare these two scripts to see how they differ. For example, to correctly use the new functionals with vdW interactions, as you can see in the script, it is necessary to activate a flag in the system card called `input_dft`, as shown here:

```
...
&system
  ibrav= 4,
  celldm(1) = 4.7999062695
  celldm(3) = 2.59763779527
  nat= 6,
  ntyp= 2,
  ecutwfc = 40
  ecutrho = 600
  input_dft = `VDW-DF2-C09'
/
...
```

Modify the scripts to prepare the calculations. Go through them reading the comments. For example, make sure that paths in the variables `PSEUDODIR`, and `OUTDIR` are correct. If you are running the calculations on the EPFL SCITAS supercomputers (Helvetios), make sure that the lines with the expressions `module ...` are un-commented; or comment them out if you are running in the virtual machine.



The two scripts will loop in the  $a$  and  $c$  list of parameters you have to define. To fix one of the parameters, simply put only one item in the list. The scripts will generate the corresponding input and outputs, plus two files where you will find the results. Modify the script to write exactly what you want in the result files. In the scripts, modify the `OPTIMIZE` variable that serves as a label (for your reference) about the calculation you are running. For example, you can use “optA” if you optimizing the constant  $a$  or “optC” for the calculations optimizing  $c$ .

Then, run the scripts. To run the script on the SCITAS supercomputer (Helvetios) use the command:

```
sbatch run_XXX_loop.sh
```

In the virtual machine, just run `bash run_XXX_loop.sh` or `./run_XXX_loop.sh`. If you have a problem executing the script in the virtual machine, try to change the file permission with the command `chmod +x run_XXX_loop.sh`

## 2.3 Band structure of bulk MoS<sub>2</sub>

### Task

By using the lattice constants previously obtained (with van der Waals), compute the band structure of MoS<sub>2</sub>. Where is (in momentum space) the top of the valence band? Where is the bottom of the conduction band? How many inequivalent global minima are present in the lowest conduction band? Is the band gap direct or indirect? How large is it?

You can follow the same steps as in the first exercise. In this case, the first Brillouin zone together with the conventional names for some high-symmetry points is reported in Fig. 3. For this point you are asked to compute the band structure of bulk MoS<sub>2</sub> along the line K- $\Gamma$ -M-K, shown in red in Fig. 3. The high-symmetry points are defined by the following **crystal** (scaled) coordinates (note the difference with the previous exercise where coordinates were given in cartesian space in units of  $2\pi/a$ ):

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

Since you want to study the energy gap of the system, both valence and (low-lying) conduction bands have to be computed. We suggest you to compute `nbnd=34` bands. In order to understand how many bands are occupied remember that with the pseudopotentials we are using, each S atom contributes 6 valence electrons, while Mo atoms have 14 valence electrons (also the  $4s$  and  $4p$  states are considered as valence electrons in these calculations).

When plotting the band structure, focus in an energy range of about 20 eV around the Fermi energy (this is informed as the highest occupied state in the scf calculations of Quantum ESPRESSO).

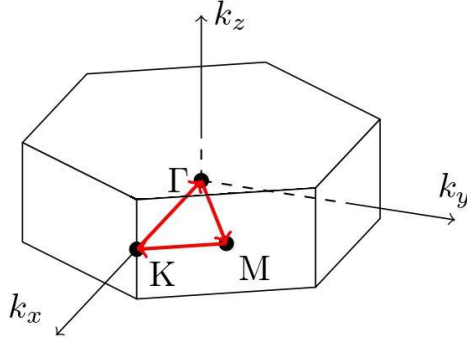


Figure 3: Brillouin zone of a hexagonal lattice with conventional names of the relevant high-symmetry points. The red line highlights the path in reciprocal space (connecting the high-symmetry points) along which you are asked to compute the band structure.

## 2.4 Single layer of MoS<sub>2</sub>

### Task

We now want to study a single layer of MoS<sub>2</sub>. In order to simulate the electronic properties of a two-dimensional single layer of MoS<sub>2</sub>, it is sufficient to account for a sufficiently large distance between layers. Determine an appropriate inter-layer distance to simulate a single layer of MoS<sub>2</sub>. Compute the band structure of monolayer MoS<sub>2</sub>. How does it change in comparison with the band structure of bulk MoS<sub>2</sub>?

The crystal structure can be easily obtained from the one of bulk MoS<sub>2</sub> by isolating a single layer. In order to study a single layer in periodic boundary conditions you will need a sufficient amount of vacuum between spurious periodic replicas in the third vertical direction. This can be done by properly choosing a large  $c$  parameter.

### Question

How large should  $c$  be to avoid interactions between periodic replicas of the layer?

Note that here it is more convenient to give the atomic positions in Cartesian coordinates instead of crystal coordinates as we did instead before. In Cartesian coordinates, we can easily increase the unit-cell size along the  $z$  axis without affecting the  $z$  displacement of the atoms within the layer. Now, you are asked to compute bands along the K- $\Gamma$ -M-K path, where the coordinates of the points are identical to the ones of the bulk. Remember to choose properly the number of bands to be computed, since in this case you have half the number of atoms (and of electrons) with respect to the bulk case.

### 3 Phase Stability and Magnetism in Cobalt (30 points)

**Note:** For Exercises 1 & 3, each calculation folder will contain a `run_local.sh` **bash** script. Simply bash this script while providing the input file, e.g.:

```
bash run_local.sh scf.in
```

The goal of this exercise is to find the correct geometric and magnetic ground state of Cobalt. The Perdew-Burke-Ernzerhof (PBE) GGA exchange-correlation functional will be used throughout. The suggested energy cutoffs and **k**-point meshes will be provided in the template input files. First we will calculate the total energy of a bulk HCP and FCC Co assuming we know the right ground state magnetic order of the two structures is ferromagnetic. 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.

#### 3.1 Comparing ferromagnetic FCC and HCP Cobalt

Energies should be computed using the experimental lattice parameters:  $a = 3.54 \text{ \AA}$  for the FCC cobalt and  $a = 2.50 \text{ \AA}$  and  $c = 4.06 \text{ \AA}$  for HCP structure [T. Nishizawa and K. Ishida, *Bulletin of Alloy Phase Diagrams* **4**, 387 (1983)]. Templates for the inputs that need to be run can be found inside the subfolders of `lab3/exercise_3`. The input files include settings that are specific for calculations on metals or magnetic structures. Let's have a look at some important input parameters<sup>3</sup>:

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

To keep your files in order, and avoid mixing results from different calculations without noticing, it is good practice to adapt the prefix to what you are calculating – HCP, FCC, ferro-magnetic (fm), anti-ferromagnetic (afm), etc. This has already been done in the various input files.

```
ibrav
celldm(1)
celldm(3)
nat
```

The **ibrav** is the Bravais lattice, which is an integer that defines the unit cell of the structure. `celldm()` allow you to define the lattice parameters. 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.

---

<sup>3</sup>The full description of all parameters in the input file can be found at [https://www.quantum-espresso.org/Doc/INPUT\\_PW.html](https://www.quantum-espresso.org/Doc/INPUT_PW.html)

### Task

Based on the description of the `ibrav` input, determine the correct `ibrav` for the FCC and HCP structures.

### Task

For both cases you need to enter a value for `celldm(1)` (**Important:** in a.u.). For the hexagonal case you must enter a value for `celldm(3)`, this value is defined as  $\frac{c}{a}$  and is therefore unitless, where  $a$  is `celldm(1)` and  $c$  is the length of the cell in the third dimension.

```
ecutwfc = 45
ecutrho = 360
```

As you should know by now, in Quantum ESPRESSO it is possible to set up two different energy cutoffs for the plane wave expansion of wave-functions (`ecutwfc`) and density (`ecutrho`). Once again we take the values recommended by the [Materials Cloud](#) website.

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

As 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 enormously dense – 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 results in a smoother function for the integration. To that end we use a few more parameters: First the smearing 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” type, and finally we need to define a parameter that determines the ‘amount’ of smoothing (`degauss=0.01`). This value is in Rydberg 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<sup>4</sup>. However, in the interest of time we will not do so for this Lab.

```
nspin
```

This defines the spin-polarization of the system. By default it is set to 1 (non-spin-polarized calculation – i.e., bands are occupied with 2 electrons each and there is no separate calculation

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<sup>4</sup>See the [following paper](#) for more details on the topic.

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 using `nspin=2`.

```
starting_magnetization(1)
```

Since we want to search for a magnetic ground state, we have to put the system in an initial magnetic state using `starting_magnetization(1)`. Here the integer 1 refers the atom type and the value is the value of magnetization for that atomic type, i.e. (acceptable range:  $-1$  to  $+1$ ). Since we have defined only one type (Co) for the FCC structure, we can only find either a ferromagnetic or a non-magnetic state.

### Task

To define the magnetic configuration, we still need to set the value of the `starting_magnetization` input. For ferromagnetic FCC (in directory `Co_fcc-fm`), start with the largest absolute value possible, and search for `magnetization` in the output file using `grep`. Do you think we can reduce the value further? Find a value that you think will get you the correct ferromagnetic ground state, and use it to set the magnetization for the other magnetic configurations.

### Task

Have a look at the k-points meshes defined in the `K_POINTS` card. Compare the mesh for the FCC and HCP structure; do the provided values make sense? Why? Are the K-meshes for HCP and FCC the same apart from folding, or do they have approximately the same density but not the same grid? How does this reflect on the convergence of your energy difference results?

Now that we understand all the input parameters, we can calculate the energies of the FCC and HCP structures.

### Task

Using `PWscf`, compute the energies for both HCP and FCC Co at the experimental lattice parameters by completing the input files in the `Co_fcc-fm` and `Co_hcp-fm` directories. Assume a ferromagnetic ordering for the two structures. Comment on the relative stability of the two phases. **Hint:** In comparing energies of different configurations, remember that the total energy is an extensive quantity!

## 3.2 Magnetic configurations in HCP Cobalt

Inside the folder `Co_hcp-afm` you will find a template of the input file that you have to use to compute the energy of the anti-ferromagnetic configuration. As before, we want to search for a magnetic ground state, hence we need to put the system in an initial magnetic state (keyword

`starting_magnetization(n)`, where the integer  $n$  refers the atom *type* and the assigned value can range between  $-1$  to  $+1$ ). If only one atom type (Co) is defined, the algorithm will necessarily converge towards either a ferromagnetic or a non-magnetic state. Other magnetic patterns require therefore a different definition of both the types of atoms and their starting magnetization. In the example of Co HCP, the anti-ferromagnetic configuration will be reached by defining two atom types occupying a different lattice site: Note the trick used in defining two *types* of cobalt atoms: (CoU) and (CoD) with associated spin-up and spin-down starting magnetization, respectively:

```
ATOMIC_SPECIES
  CoU  58.933194  Co.pbe-n-rrkjus_psl.1.1.0.0.UPF
  CoD  58.933194  Co.pbe-n-rrkjus_psl.1.1.0.0.UPF
ATOMIC_POSITIONS (crystal)
  CoU   0.333333  0.666667  0.25
  CoD   0.333333  0.666667  0.75
```

Now, a starting magnetization of equal magnitude but opposite sign can be assigned to the these two atom types:

```
starting_magnetization(1) = ...
starting_magnetization(2) = ...
```

### Task

Perform a stability analysis for HCP cobalt in the ferromagnetic, antiferromagnetic, and nonmagnetic states, comparing their energies (per atom).

### Task

For the FM and NM states, perform a non-self consistent calculation on a finer grid and compute the density of states. Do you see differences, and can you explain them? Try reverting the HCP FM starting magnetization and see how the DOS is affected. Do the changes make sense? Finally, is the material metallic in the FM, NM states, or both?