

Excercise sheet 4

Exercise 1: Band alignment between monolayer boron nitride and antimonene

Here, you will calculate the electronic structure of monolayer BN and antimonene from the previous two exercises and estimate the relative band alignment

- (a) Use the structure of monolayer antimonene from Exercise sheet 1 and optimize the geometry. Then calculate the electronic bandstructure of antimonene within the PBE approximation. Use a path from M point (0.5 0.0 0.0) to Gamma point (0.0 0.0 0.0) to K point (1/3 1/3 0.0) back to the M point (0.5 0.0 0.0). These are the high-symmetry points of hexagonal monolayer materials. You can use the provided input files as reference.

Plot the electronic structure.

- (b) Do the same for the monolayer BN structure that was calculated within the PBE approximation on Exercise sheet 2. Note that the BN structure I provided for Exercise sheet 2 had a 60° angle between the in-plane lattice vectors, which changes the coordinates of the K point in units of the reciprocal lattice vectors to (1/3 -1/3 0.0)¹.
- (c) Now, we are interested in the band alignment between monolayers of BN and antimonene, under the approximation that they are not in contact. Following the lecture, this means that we have to extract the vacuum levels and work functions of the individual materials and shift the bandstructures such that the vacuum levels of both materials are aligned.

Far away from the surface, the electrostatic potential energy approaches the vacuum level. Use the input file `pp.in_pot` to extract the electrostatic potentials (remember to adjust prefix and outdir according to the material) from the DFT results. These potentials can then be averaged within the x-y plane, giving a line plot along the z-axis, i.e. into the vacuum. This can be achieved by using the `average.x` program. The necessary input file is provided in the .zip file. For each of the calculations, this yields an output file `avg.dat`, which contains the desired plane-averaged electrostatic potential and another 'macroscopically averaged potential' along the z axis.

Plot the averaged potentials and derive the value of the vacuum level for each material. Note that the potential energy in `avg.dat` is given in units of Rydberg.

Then shift the bandstructures plotted in (a) and (b) in such a way that the vacuum level would be at 0 eV. The shifted value of the Fermi energy is now the negative of the work function and the absolute band energies between the materials can be compared.

In what which material would the valence band maximum be, in which material the conduction band minimum? Use your results to estimate the conduction and valence band offsets between the two materials.

¹ Sorry about that

Exercise 2: Magnetism in two-dimensional Mn_2C .

Here, we will study magnetism in Mn_2C , which was recently (Nanoscale 8, 12939 (2016)) proposed as a novel two-dimensional antiferromagnetic metal. The structure of Mn_2C is shown in the figure, once from the top and once from the side. It takes on a hexagonal structure with three atoms per unit cell and is structurally equivalent to MoS_2 and similar recently extremely popular 2D transition-metal dichalcogenides. The primitive cell and a larger, rectangular, unit cell are shown in the figure. A good guess at the atomic positions of the primitive cell is also included in the .zip file.

Warning: The calculations in this exercise are a bit heavier than those from previous exercises and also use a lot of storage space to store the wavefunctions. In order to not use too much space in the home folder on the HPC, you should run the calculations in your “scratch” folder on the HPC.

For easy access, create a link from your home directory to the scratch folder by issuing the command

```
In -s $FASTTMP scratch
```

This should create a link which you can use to go to the scratch folder in WinSCP (or similar). Using the command terminal (Putty etc), you can switch to this folder either by

```
cd $FASTTMP
```

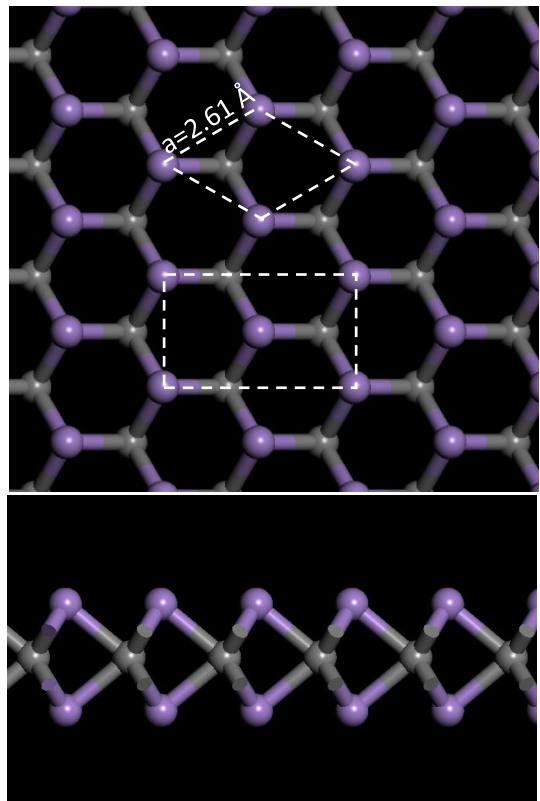
or by

```
cd ~/scratch
```

While it is known that Mn_2C is antiferromagnetic, different antiferromagnetic spin alignments are possible, as we have several Mn atoms per unit cell. In a previous study, the antiferromagnetic spin alignment AFM-2 from the figure below has been identified as the most stable one. We will compare this spin alignment with results for ferromagnetic and nonmagnetic Mn_2C .

- (a) Let's start with the antiferromagnetic spin alignment. A magnetic order, where the spin-polarizations of all Mn atoms are antiferromagnetically aligned, requires a unit cell that is larger than the hexagonal primitive cell, due to periodic boundary conditions. The rectangular cell shown in the figure (and given in the input file `Mn2C.in` in the folder `Exercise2/a`), however, is sufficient for our purposes, as you can easily confirm yourself by drawing an antiferromagnetic spin alignment onto the Mn atoms in the unit cell and surrounding unit cells.

Examine the input file. In exercise 2 of exercise sheet 3, you already performed calculations for ferromagnetic iron. As in that previous exercise, we need to tell Quantum Espresso to do a collinear spin calculation by setting `nspin=2` in the `&system` block. We also need to give an initial guess for the spin polarization of the atoms, using the `starting_magnetization`



keyword. Here, `starting_magnetization(i)=n` defines the initial spin n of *all atoms of species i* ($i=1$ would be the species defined in the first line of the `ATOMIC_SPECIES` block). A good approach to choose n is using Hund's rule for the d electrons, giving $n=5$ for Mn. Positive n correspond to spin-up polarization, negative n to spin-down polarization. However, the definition of spin by the atomic species in QE poses a problem if we are interested in antiferromagnetic initial spin alignments, as in this case at least some Mn would have opposite spin alignments to the other Mn atoms². For this reason, we apply a little trick here (probably less a trick than the way the QE developers intend it to be done): We define a species Mn1 (the name is arbitrary) for atoms that are initial spin-up polarized and another species Mn2 for atoms that are initialized with a down spin. The same pseudopotential is used for both auxiliary species. Confirm that the initialization defined in Mn2C.in indeed gives the antiferromagnetic alignment between all Mn atoms in the system that is called AFM1 in the figure.

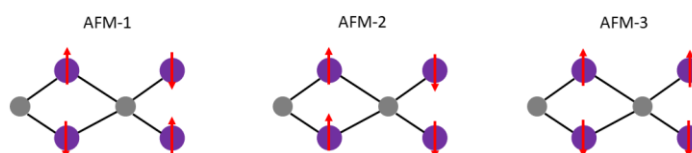
In the end, we are interested in total energy differences between different magnetic orders and these total energy differences could be quite small. We thus need to make sure that the obtained total energies are sufficiently accurate.

For this reason, do a geometry relaxation for the AFM-2 magnetic order. Observe, how the total magnetization and absolute magnetization of the system change throughout the SCF procedures. After the Kohn-Sham energy is converged for a given geometry, Quantum Espresso also reports on the magnetic momenta per atomic site. Notice that it is not only the Mn atoms that are magnetized, but a small amount of spin-polarization is also induced onto the carbon atoms.

You can visualize this using the `pp.x` code, using `plot_num=6`. Adjust a `pp.in` input file from one of the previous exercises or take the reference file `pp.in_spindens`. The resulting `.xsf` file can be plotted with XCrysDen (under Linux) or using VESTA.

If you want a challenge, you can repeat these calculations for the other two AFM orderings, AFM-1 and AFM-3, by taking the input file Mn2C.in used before and adjusting `starting_magnetization` accordingly (if you have difficulties doing this, compare with the reference input files in folder Exercise2/b). AFM-1 differs from AFM-2 in that in AFM-1 the pairs of Mn atoms with the same x - and y -positions have the same initial spin polarization, while in AFM-1, the atoms in a pair have opposite spin. In case of AFM-3, the spins are antiferromagnetically aligned within a pair, but the top and bottom layers of Mn atoms, when looked at the structure from the side, show a ferromagnetic alignment.

Optimize the geometries and derive the total energies. This can be a non-trivial task, because the convergence of the geometry is slow and the



² I should stress that this is only talking about the initial guess for the atomic spin polarization; the spin-polarization of each atom can (and probably does) change during the SCF minimization and even a ferromagnetic initial guess can change into an antiferromagnetic or non-magnetic final state. Careful though: if one does not define an initial spin-polarization, Quantum Espresso will always predict a non-magnetic ground state without spin-polarization.

SCF procedure is prone to be caught in the wrong (or at least a non-desired) energy minimum. Make, again, sure that the forces and lattice stress are small. Note that Quantum Espresso always uses the ground state density from the previous geometry as a starting guess for the SCF procedure after the geometry was updated. For this reason, always do another geometry optimization run with the desired initial spin-alignment and see whether this causes changes in the geometry.

- (b) Let's now compare the results from (a) with calculations for a fully ferromagnetic initial spin alignment and a non-magnetic calculation (i.e. without spin-polarization). Do a geometry optimization and compare the total energies with those from (a). Can you make your life easier by using a different unit cell for these calculations? How big is the energy difference between the antiferro-, ferro- and nonmagnetic states? Which magnetic structure is the most stable?

Remember that the total energy is extensive and that you need to scale it so that you compare systems of the same size.

- (c) The Mn atoms obviously contain d electrons. We learned in the lecture that PBEsol (and similarly LDA or other GGAs) are not very good in terms of localized magnetic states. For this reason, let's compare the magnetization of the AFM-2 structure obtained in (a) with a calculation adding additional Coulomb repulsion effects using a Hubbard correction (i.e. the Hubbard U method.) As the reference input file in the folder Exercise2/d shows, such a calculation is invoked by simply adding the keyword `lda_plus_u=.true.`. We also have to define the value of the Hubbard U for each species, using the `Hubbard_U` keyword. Here, the value corresponds to the Coulomb repulsion (in eV) that is added to d and f localized orbitals³. We will use $U=5$ eV, which is often a good value, and the lattice constants and atomic positions from (a). How does addition of a U correction term affect the magnetization of the atoms?

If you are interested, you can also calculate the electronic band structure and compare it with one calculated without Hubbard U .

- (d) Finally, we will look at the effect of noncollinear spin and spin-orbit-coupling on the results. For this, two input files are prepared. First examine the input files `Mn2C_noncollinear.in`. We now go beyond the collinear spin approximation, which means that we replace `nspin=2` by `noncollin=.true.`. The latter keyword automatically sets `nspin=4`, which thus does not need to be defined. We can (and probably should) still give an initial guess for the magnetic structure. Use the most stable magnetic structure from (a)-(c) here. Now run the calculation.

In the output file, you will see that Quantum Espresso now reports the initial spin polarization of the atoms in polar coordinates. During the SCF procedure, not only the magnitude and sign of the magnetization will be allowed to change, but also the polar angles, and thus the orientation. Compare the results and the time spent per SCF step between this noncollinear calculation and the corresponding collinear calculation for this structure. What (if any) effect did inclusion of noncollinear spin have on the magnetizations, the total energy and the time spent per SCF step?

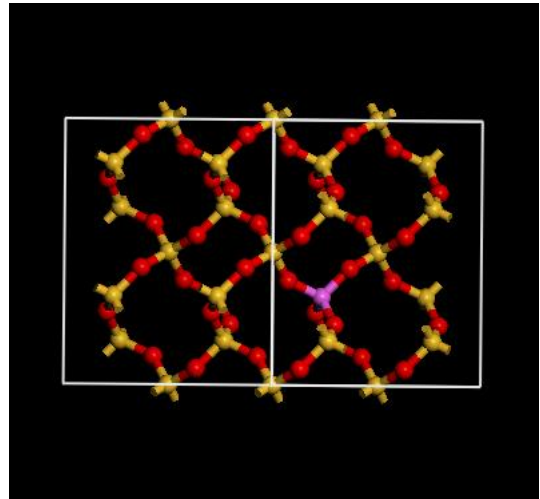
³ Other codes allow to set different U for d and f electrons in, for instance, materials with lanthanide atoms. Or even, as an empirical tool for the correction of underestimated electronic bands gaps, for s and p orbitals. One would need to hack the source code in order to do this in Quantum Espresso.

Now we will include spin-orbit coupling effects as well, which were missing the previous calculation. This is invoked by adding `lspinorb=.true.` to the `&system` block (see the reference input file `Mn2C_spinorb.in`), still with the settings for a noncollinear spin calculation. Rerun the calculation. What effect has additional inclusion of spin-orbit coupling effects on the time for and SCF step and the total energy and magnetizations?

Extra-Exercise: Aluminum-doped SiO₂

Here, we will look into the topic of defects and impurities in semiconductors, specifically the case of Aluminum-doped α -SiO₂. α -SiO₂ has a hexagonal structure with 9 atoms per unit cell. In the figure on the right side, a 2x2x2 supercell (i.e. 72 atoms) was doped by replacing a silicon atom by an aluminum atom.

Typically, we want to simulate such systems in the limit of dilute doping or defect concentration in order to increase comparability with experiments (where the doping or defect concentrations are much smaller than those in DFT calculations). However, this would require massive system sizes of several tens of thousands of atoms, which are infeasible in most cases.



We will now have a look at the electronic structure and energetics introduced by the aluminum impurity. The approach is more general and also applies for other defect-related calculations, for example for the case of a vacancy (i.e. a silicon or oxygen atom missing in the lattice) or similar defects.

As this project uses larger systems, it is computationally more complex and needs to be run on the HPC. Also, as it requires a number of small calculations, it was split into two parts, with the second part being on exercise sheet 5. Further, to remove the need for long relaxation run, the .zip file contains the atomic positions of doped SiO₂ optimized with the PBEsol functional. If you are interested, you can also take the unrelaxed geometry (also provided in the zip file) and run a geometry optimization.

These calculations should also be run in the scratch folder, because the `TMP_DIR` can become huge.

- (a) Use the relaxed structure in the input file and minimize the total energy of the system. To break the spin symmetry of the system, the spin for oxygen atoms is initialized with +1.

What total magnetization does the calculation converge to? Extract and plot the spin density of the system using the `pp.x` utility. You will see that the spin is mostly localized on the four oxygen atoms bonded to the Al impurity center. Using VESTA or XCrysDen, you can also conveniently study the bond length between the atoms. PBEsol predicts that the four Al-O bond lengths are the same by symmetry. However, this is actually an incorrect result: Due to reasons seen in (b), a 'real' Al-doped crystal will try to lower the total energy by breaking the symmetry of the four oxygen atoms surrounding the Al atom. This is the so-called Jahn-Teller effect. Here, one oxygen atom will move further away from the Al center and will carry almost all the spin-polarization of the system. This localized spin gives rise to a prominent electron

paramagnetic resonance (EPR) signal and has been studied experimentally. Due to the over-delocalization from LDAs and GGAs, this Jahn-Teller effect is not well reproduced with these functionals. Hybrid functionals, however, work much better, of course at an increased cost (Phys. Rev. B 85, 014117 (2012)).

- (b) Let us now look at the effect of the dopant on the electronic structure. Most conveniently, one looks at changes in the DOS, as the bandstructure for such a supercell contains many bands and is not necessarily easily accessible.

Use the SCF run from (a) as a starting point and run a non-selfconsistent calculation so that you can extract the spin-resolved DOS. Use a 4x4x4 k-point grid and 224 bands, so that you also include the conduction band edge.

Plot the spin-resolved DOS and the total DOS and compare it with a DOS calculation for the unit cell, with a 8x8x8 k-point grid (this grid has the same sampling density as the 4x4x4 grid for the supercell) and 27 bands. The relaxed unit cell geometry of SiO₂ is included in the folder Exercise3/b.

Compare the DOS of the doped and of pristine SiO₂. Notice that the total DOS look relatively similar for the two systems, but that doping includes additional states in the band gap at about 4 eV below the valence band maximum that are absent for pristine SiO₂. Also, an additional occupied state appears just above the valence band maximum and is crossed by the Fermi energy. It is this additional state.

- (c) Often, one is also interested in the formation energy of a defect or impurity, i.e. the energy that is necessary to incorporate the defect into the system compared to the pristine, defect- or impurity-free, material.

If the total charge of the material is 0, this is described by the following equation:

$$E_{tot}^{SiO_2} + \mu_{Al} + \Delta E = E_{tot}^{SiO_2:Al} + \mu_{Si}$$

$E_{tot}^{SiO_2}$ and $E_{tot}^{SiO_2:Al}$ are the total energies of pristine SiO₂ and SiO₂ with an Al impurity. μ_{Si} and μ_{Al} are chemical potentials of Al and Si. One can think of the chemical potentials as adjustable factors that could, for example, correspond to the binding energies of Al and Si atoms in precursor materials used in CVD or similar growth techniques. Here, we will use the binding energies of single Al and Si in metal Al and bulk silicon for the chemical potentials.

The desired formation energy is then given by

$$\Delta E = E_{tot}^{SiO_2:Al} - E_{tot}^{SiO_2} + \mu_{Si} - \mu_{Al}$$

Calculate or extract the total energies of SiO₂ and SiO₂:Al from (a) and (b). For pristine SiO₂, you can take the total energy of the unit cell and multiply it such that it corresponds to the total energy of a 72-atom-supercell of SiO₂ and is thus comparable to the total energy for SiO₂:Al.

Then calculate the total energies of bulk Al and silicon using the provided input files and calculate the formation energy. Make sure that the chemical potentials you use for the calculation are the total energy *per atom*.

The absolute value of the total energy is not very meaningful by itself, because it depends on the values of the chemical potentials used. It becomes meaningful, however, in comparison with other defects or charge states, as we will see in the continuation of this exercise on Exercise sheet 5.