Atomistic and quantum simulations of materials: First-principles calculations of the electronic properties of materials

Simon DECONIHOUT

EPFL

In this work, different structural properties of materials are studied using Density Functional Theory (DFT) [1]. The numerical calculations are done with the software Quantum ESPRESSO [2]. The first part will focus on the bands structure and density of states determination of an Zinc oxide (ZnO) crystal, an interesting semiconductor used in electronic devices or as a sensor[3]. It will then be studied another interesting material: Hexagonal Boron Nitride, whose layers have the particularity of being weakly coupled via Van der Waals interactions [4]. Both cases with and without this interactions for the bands structure and DOS, will be computed and compared. Finally, the stimulation of magnetic system using nickel will be studied.

2   Zinc oxide band structure and DOS calculation

2.1   Zinc oxide (Zn0)

This first part will focus on the study of the Zinc oxide, a semiconductor widely used in the industry. This material is a hexagonal lattice with a basis of 4 atoms per unit cell. The atoms that compose the ZnO are the Zinc Zn and the Oxygen O. The Zinc is a metal of atomic number 30 whereas the oxygen is a non-metal of atomic number 8. The lattice parameter used for the next calculation are $a = 3.25$Å, and $c = 5.20$Å, which correspond to the theorical value for such material [5].

2.2   self-consistent-field (SCF) calculation for ZnO

Using PWscf[2],a self-consistent-field (SCF), calculation for ZnO will be performed. In order to get a sufficiently dense k-points grid, the cutoffs, ecutwfc and ecutrho, will be assigned values using the [6]. Thus the Ecutoff recommended will be, for the Zn ecutwfc 40Ry and ecutrho 320Ry.
As for the O, the Ecutoff will be, ==ecutwfc 50Ry, ecutrho 400Ry. (As== one could have already notice, the ecutrho is 8 times the ecutwfc, it is in respect with the theory for ultrasoft pseudopotential).
In order to ensure a good convergence of the k-points, the highest values of the cutoff (ecutwfc 50Ry, ecutrho 400Ry), will be uses for the case of the ZnO.
Using the values above for the cutoff and the lattice parameter, the total energy per atom in

the bulk found after a SCF calculation is $E = -3.418 \cdot 10^3$ eV, and the highest occupied level by a state (or the Fermi energy) is $\varepsilon_F = 8.557$eV.

2.3 Bands structure:

Using the data acquired with the SCF calculation, it is now possible to plot the band structure for the Zn0 Fig.1.
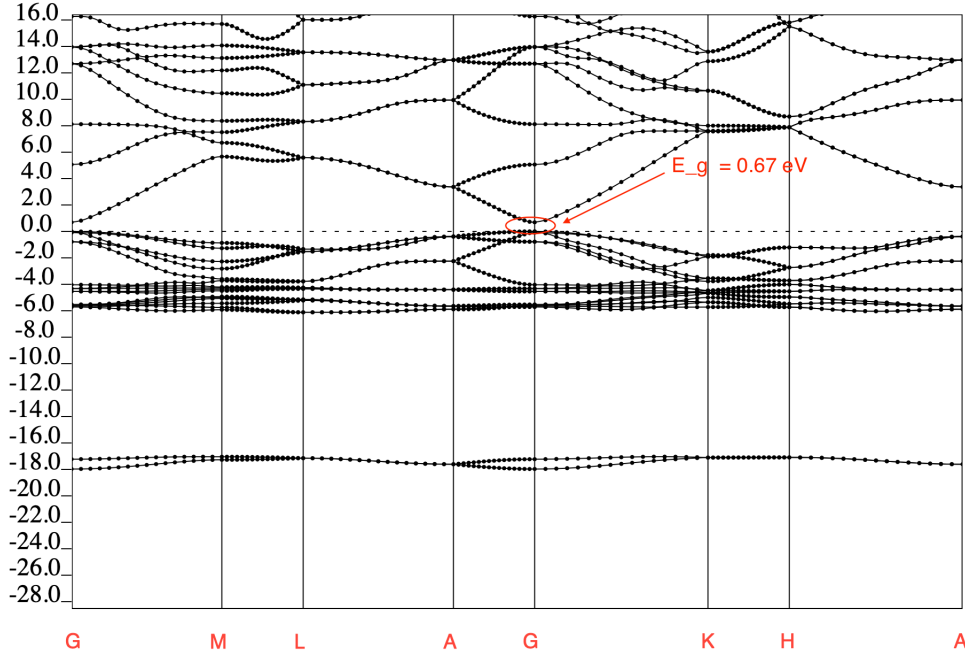

Figure 1: Bands structure and Energy gap E_{gap} (in eV) of the Zn0.

The energy gap found using the quantum espresso GGA approximations is $E_{gap} = (0.67 \pm 0.05)$ eV. Here due to the file format (ps), the energy gap has been deducted only by measuring the space in the Fig.1. This result is nevertheless in accordance with the first-principles DFT study[7], with a value $E_{gap} = 0.67$ eV for the calculation with a GGA approximations. In order to find a value closer to the experimental one $E_{gap,the} = 3.4$eV[5], it is necessary to use the Hubbard U semiempirical corrections[7, 8]. As it a semiconductor of type II-VI semiconductor group, it should appears transparent ($E_{gap} = 3.4$eV), nevertheless without the Hubbard correction, the result is not the same. Using the eq.1,

$$E = \frac{hc}{\lambda}, \tag{1}$$

where $h \simeq 6.63 \cdot 10^{-34}$J.s is the Planck constant, $c = 3.00 \cdot 10^8$m.s^{-1} the speed of light, and λ [m] the wavelength, it is possible to determine whether the material is transparent or opaque. Indeed as the E_{gap} in a material represent the energy that an electron needs to pass from the valence to the conduction band, then in function of the E_{gap} the light will pass through the material or not. With the theorical value for the energy gap the wavelength λ_{the} will be:

$$\lambda_{the} = \frac{hc}{E_{gap}} = 3.65 \cdot 10^{-7}\text{m},$$

which is just under the visible light spectrum $((3.80 - 7.50) \cdot 10^{-7}\text{m}[9])$. Thus as said before, the ZnO is transparent. Nevertheless the energy gap found above shows the opposite:

$$\lambda = \frac{hc}{E_{gap}} = 1.85 \cdot 10^{-6}\text{m},$$

thus, far above the wavelength for the visible light, so the ZnO should be opaque according to this formula.

2.4 DOS and PDOS

Density Of State (DOS) and Pseudo Density Of State (PDOS) are essentials tools to understand the properties of each atom in the material. In this work the DOS have been computed as the PDOS for the Zinc atoms and the Oxygen atoms.
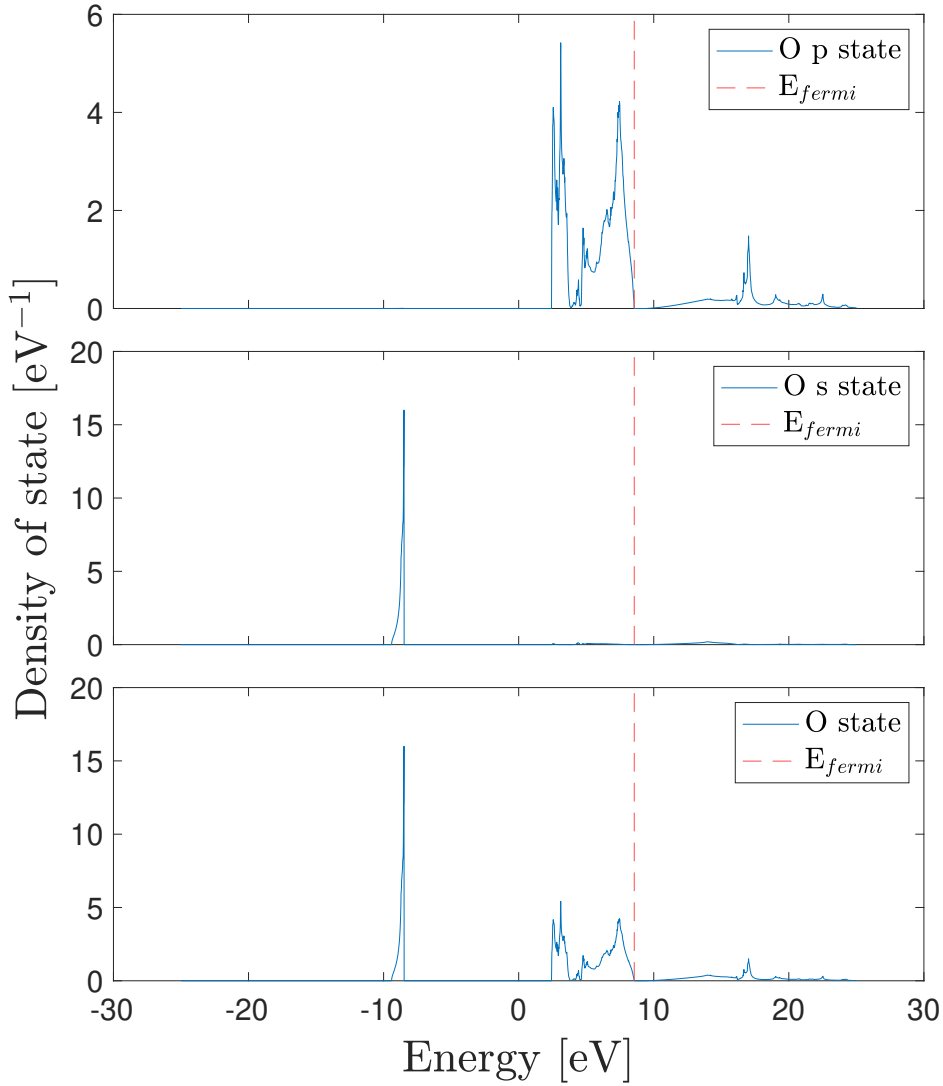

Figure 2: PDOS $[\text{eV}^{-1}]$ as the function of the energy $[\text{eV}]$, for the Oxygen (O) atoms in the ZnO
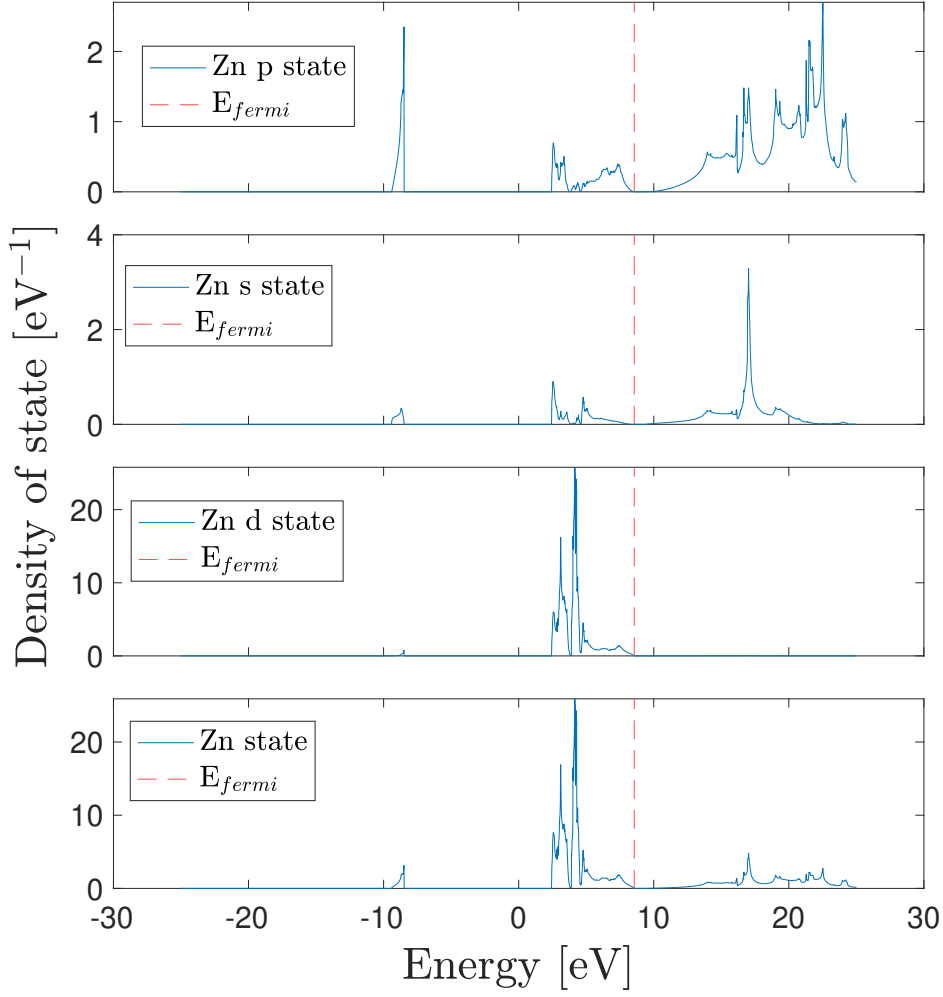
Figure 3: PDOS $[eV^{-1}]$ as the function of the energy [eV], for the Zinc (Zn) atoms in ZnO
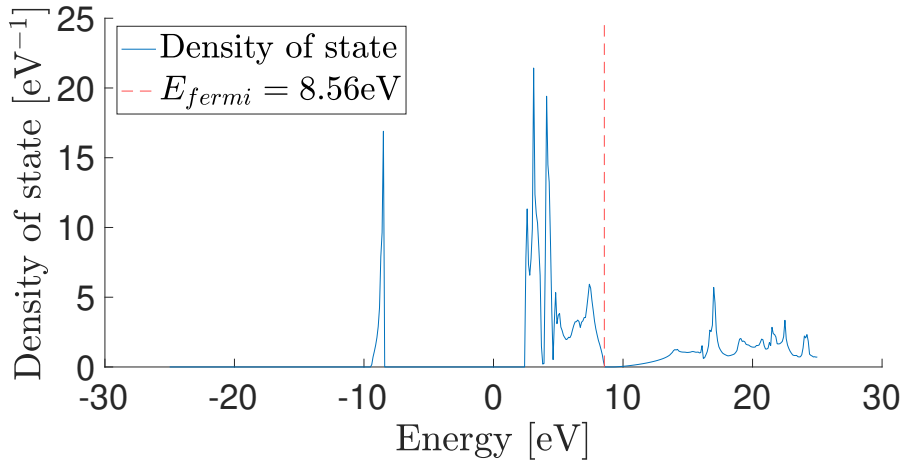

Figure 4: Density of state $[eV^{-1}]$ as the function of the energy [eV], in the ZnO

The Figs.2, 3 and 4 gives access to complete information on the states in ZnO, as expected, no state can appears near the fermi energy $\varepsilon_f = 8.56eV$ and the band gap of the state interdiction

can also be computed using this way, giving the result of $E_{gap} = 0.67$eV, in accordance with Fig.1.

3 Structural optimization of h-BN

3.1 Hexagonal Boron Nitride (h-BN)

Hexagonal Boron Nitride is a typical layered material in which the layers weakly interact with each other via van der Waals interactions.

As in the h-BN lattice, the in-plane parameter a and the inter-plane parameter c are weakly corelated, it is possible to determine one without influence from the second. Then it will first be computed the a parameter and then the c parameter.

3.1.1 In-plane lattice parameter

Without Van der Waals interactions: First, it is important, in order to have a comparison, to write the lattice parameters from experiences[10]. These values are taken for a temperature of 10K, first for the in plane parameter: $a = 2.50579 \simeq 2.51$Å (as always the precision of the lattice parameter in this work is in order 10^{-2}Å). Then for the interlayer parameter the experimental value is $c = 6.6026 \simeq 6.60$Å.

The in plane lattice parameter a calculated without Van der Waals interactions (see Fig.5) is $a = 2.51$Å for an energy of $E - 216.583$eV/atom. It is clear that the SCF calculation, even without the Van der Waals interactions, with pseudo-potenials allows a precision calculation of this parameter, as it is the same value found experimentally.
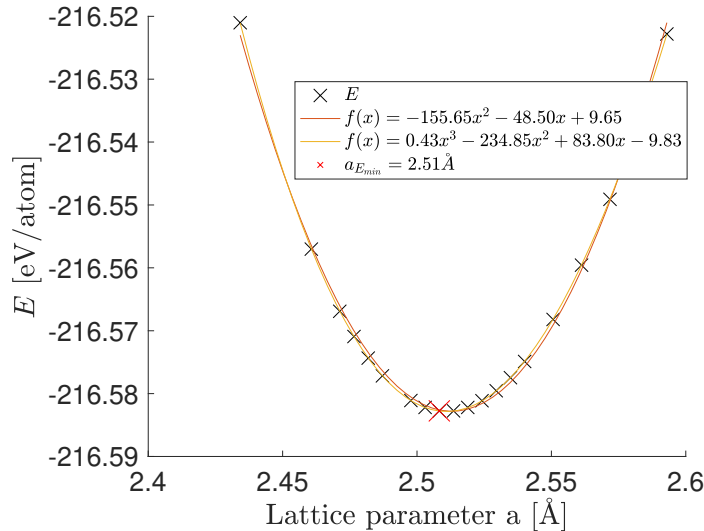

Figure 5: Energy E [eV/atom] as a function of the in-plane lattice parameter a [Å], without taking account of the WdV interactions

With Van der Waals interaction: Then lets add the effects of the Van der Waals interactions between the layers(see Fig.6), the values found for the in plane parameter does not

change: $a = 2.51$Å this time for an energy $E = -215.8674$eV which is a bit higher than without Van der Waals interactions. It was expected that the Van der Waals interactions, as it only acts between the different layers, would not change the value of a. Furthermore it is again expected to have a value for the energy slightly different as for the second cases the VdW interactions increases the values for the energy.
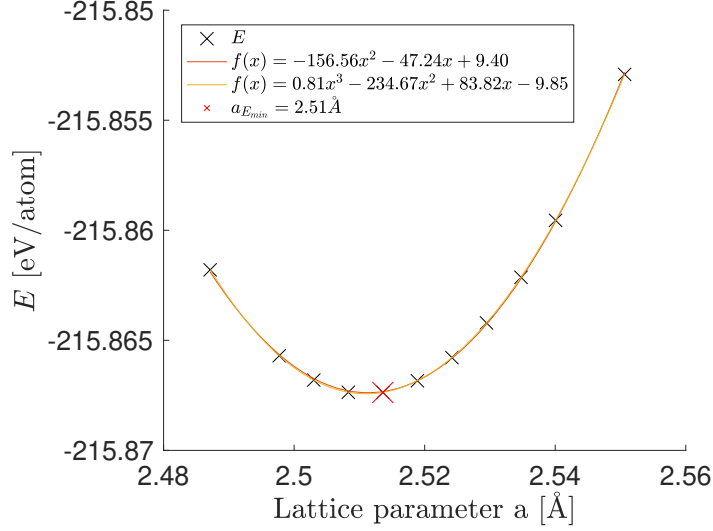

Figure 6: Energy E [eV/atom] as a function of the in-plane lattice parameter a [Å], by taking account of the WdV interactions

In Fig.5 and 6, two fits have been applied in order to find the analytical solution of the Energy as a function of the lattice parameter. As the function is plotted for close values of a, both are good approximations, but when some higher or lower values of a are taken, the polynomial of order 2 will no longer be a good approximation as it is a pair function.

3.1.2 Interlayer lattice parameter

The interlayer parameter c represents the distance between two planes of BN. It is thus much more related to the Van der Waals interactions than the in plane parameter. Both cases are studied here to see the importance of those interactions.

Without Van der Waals interactions the value found for $c = 7.46$Å, shown in Fig.7, is significally (13%) different than the experimental value.
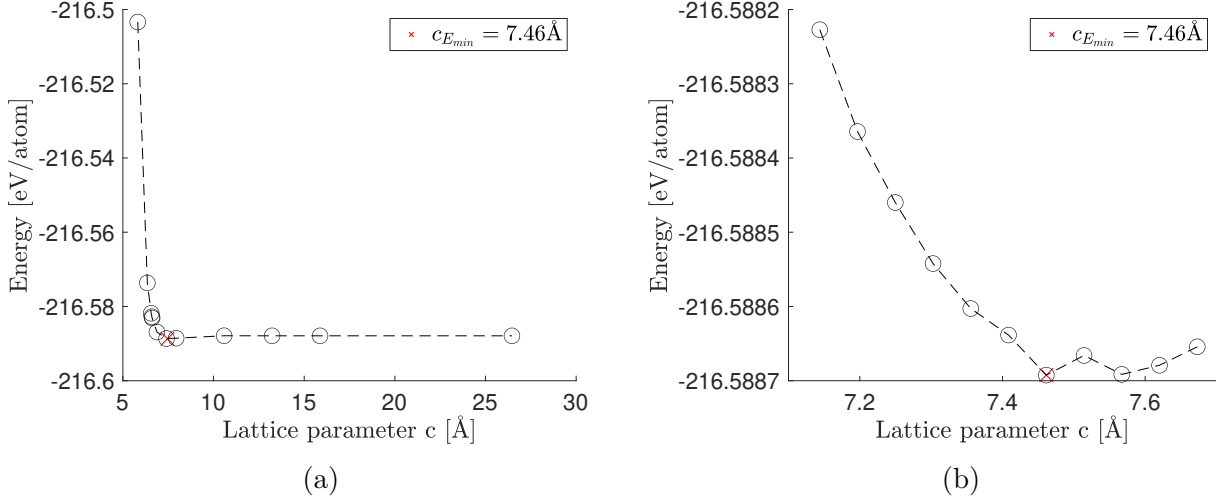
6

Figure 7: a) Energy E [eV/atom] as a function of the interlayer lattice parameter c [Å], without taking account of the WdV interactions, b) same situation but close up

It is interesting to note that on the contrary of the in plane parameter, there is for this case not a clear minima: as demonstrated on both Fig.7a,7b.

With Van der Waals interactions As before there is not a clear minima, as shown in Fig.8, the difference in the energy level is of the order 10^{-4}eV (lower than the precision of the energy, then the best value for c is not well define). It will be considered here that it is still possible to take the lower value for the energy found to have the better lattice parameter $c = 6.49$eV.
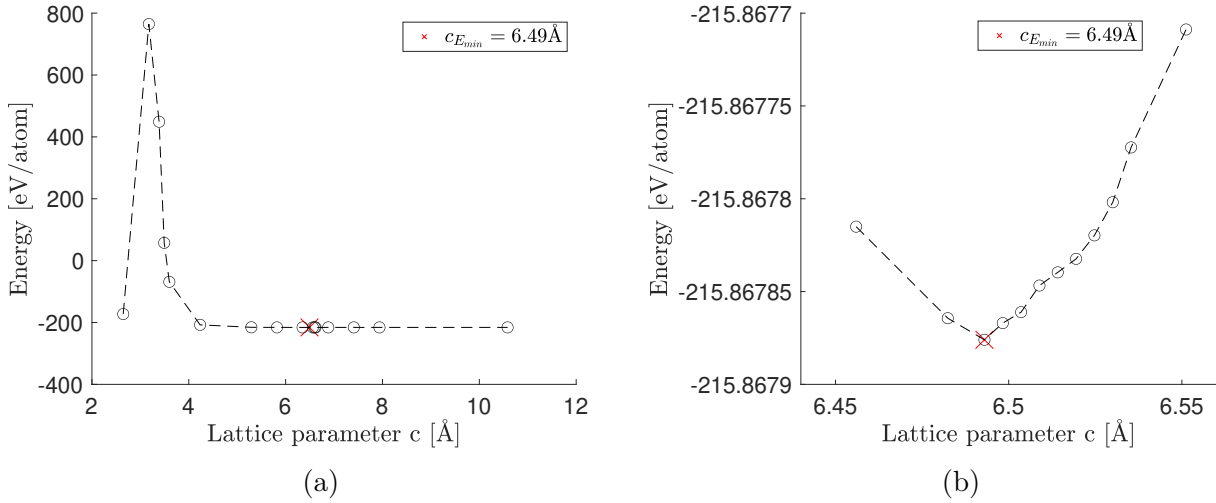

Figure 8: a) Energy E [eV/atom] as a function of the interlayer lattice parameter c [Å], by taking account of the WdV interactions, b) same situation but close up

The effect of the Van der Waals interactions are directly visible in Fig.8a, as the difference with the experimental value is now only of 1.7%, a much more convincing value.
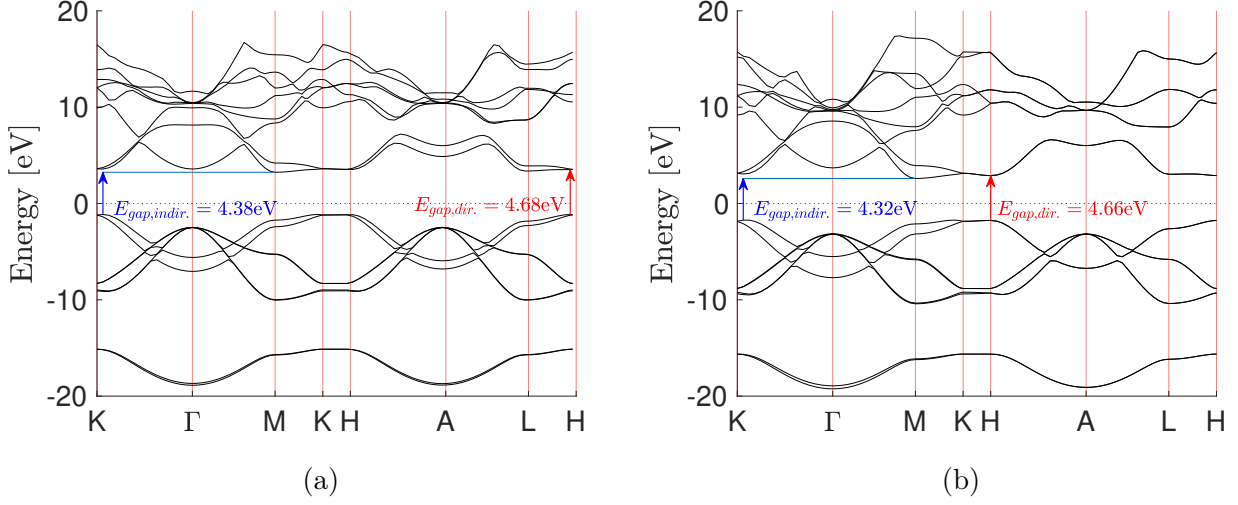
3.1.3 Plotbands

Figure 9: Bands structure and Energy gap E_{gap} (in eV) of the h-BN a) without taking account of the VdW interactions and b) with these interactions

Both cases, direct and indirect bands gap have been computed in Fig.9 in order to compare whether the h-BN is a direct or indirect bandgap semiconductor. It is clear that in both cases, without and with the Van der Waals interactions, the indirect band gap ($E_{gap,indir.} = 4.38$eV, $E_{gap,indir.} = 4.32$eV respectively) are lower than the direct band gap ($E_{gap,dir.} = 4.68$eV, $E_{gap,dir.} = 4.366$eV respectively). Thus the h-BN has an indirect bandgap where the top of the valence band is at the point K of the reciprocal space and the bottom of the conduction band is at the point M. The fact that the hexagonal Boron Nitrite is an indirect band gap conductor was also verify experimentally[11].
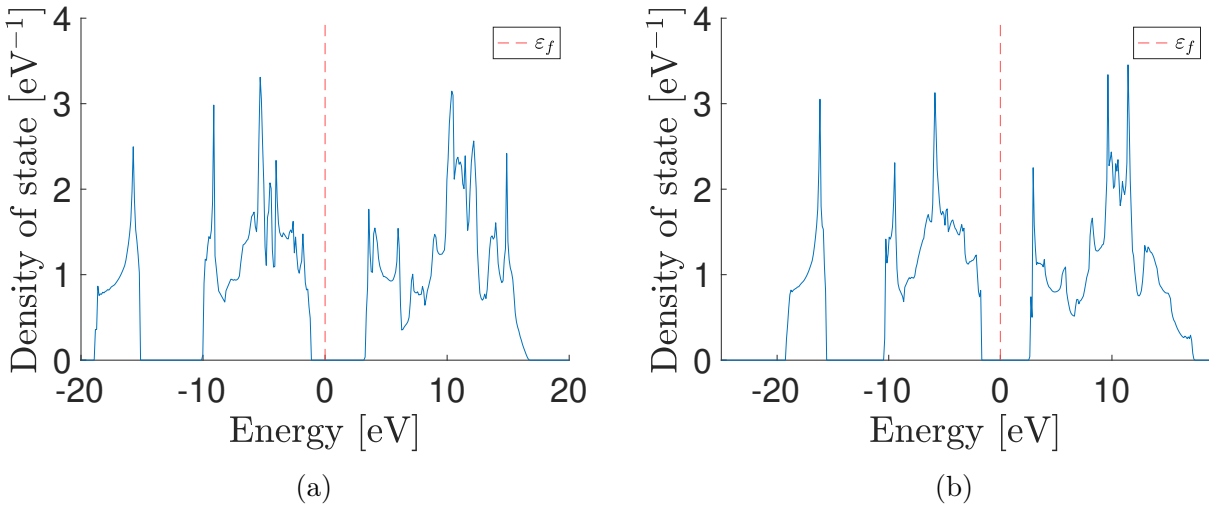
3.1.4 DOS

Figure 10: Density of state $[\text{eV}^{-1}]$ as the function of the energy [eV] in the h-BN a) without taking account of the VdW interactions, b) with these interactions

8

Both Density of state in Fig.10, are composed of the same structure, meaning that the density of states in both cases are more or less equivalent for any energy E. But it is worth noting that when taking account of the Van der Waals interactions, the lowest electrons in the conducting band are more likely to have a lower energy than without these interactions.

3.2   Singler Layer BN

In order to simulate a single layer of a Boron Nitrite, one have to ensure that the interlayer parameter is large enough to avoid interlayer interactions. For this part a value $\frac{c}{a} = 25$ has been chosen as the total energy has already converge for such a value (see Fig.8,7).
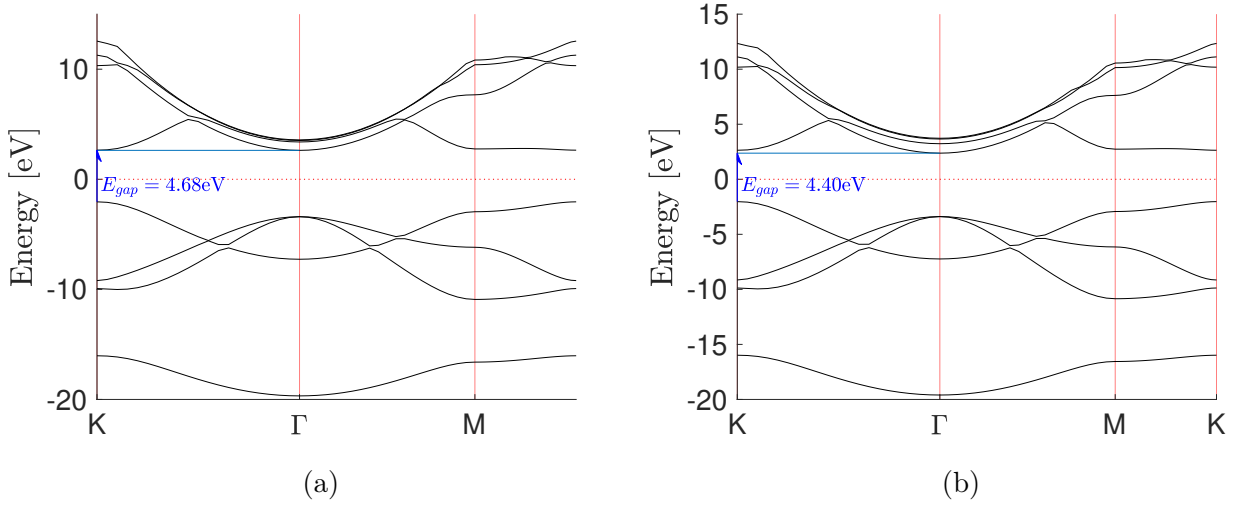

Figure 11: Bands structure and Energy gap E_{gap} (in eV) of the 2D BN a) without taking account of the VdW interactions and b) with these interactions
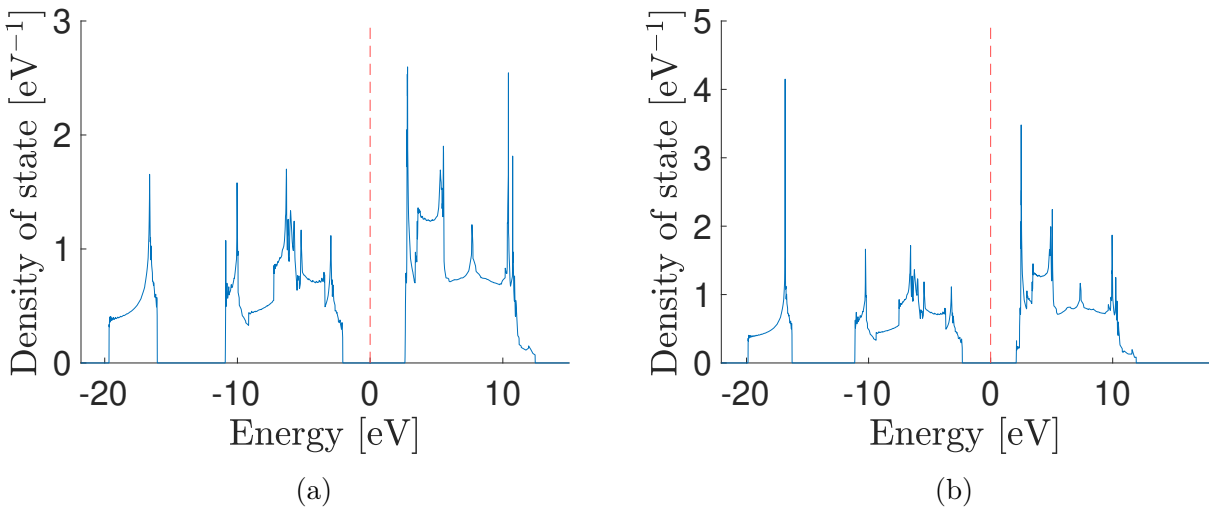
3.2.1   DOS

Figure 12: Density of state [eV^{-1}] as the function of the energy [eV] in the 2D BN a) without taking account of the VdW interactions, b) with these interactions

9

The density of state of the one layer Boron Nitrite is represented with and without the Van der Waals interactions in Fig.12. It is clear that both have similar DOS, but it should be notice that for 1 peak in the valence band, we have a higher density with the VDW interactions, whereas for a peak in the conduction band, the density of state is higher without the VDW interactions. Both cases should have the exact same DOS as the Van der Waals interactions act at an interlayer level and here it is supposed to be a 2D material with a unique layer, nevertheless as it is impossible to simulate an infinite value for c in order to have a single layer, it is possible that some artefacts of the VDW interactions are still visible on these plots.

4   Phase stability and magnetism in Nickel

4.1   Phase stability for ferromagnetism

In first part it will be assumed that the right ground state magnetic order of the two structures is ferromagnetic. Using the experimental lattice parameter for the Nickel[4], $a = 3.466$Å for the FCC phase and $a = 2.450$Å, $c = 4.018$Å for the HCP phase, a self-consistent calculation is computed for both phases. For the FCC composed of 1 atom in the primitive cell, the total energy found is $E = -4.6680 \cdot 10^3$eV (or $E = -343.08793385$Ry).
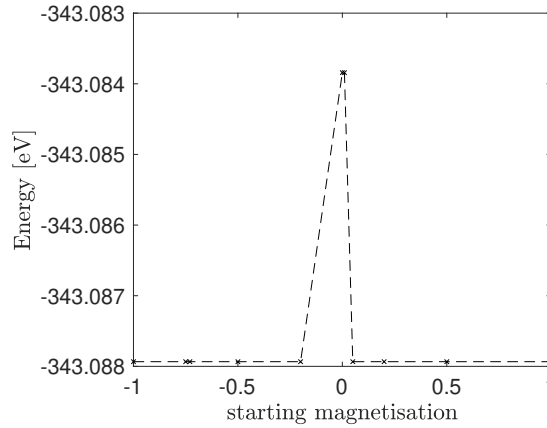

Figure 13: Total Energy E in a Ni lattice as a function of the starting magnetisation

In both cases the energy per atom does not depend on the initial magnetisation parameter 'starting_magnetization'[2]. One thing to notice it that the energy, in Fig.13 has a different value when the starting magnetisation is zero because it will not converge to any magnetic state.
Then the HCP configuration is composed of two atoms and the total energy per atom found is $E = -4.6679 \cdot 10^3$eV (or $E = -343.0862$Ry) thus just a bit above the FCC phase. Then it makes sense to say that the FCC phase is a stable phase whereas the HCP phase is a metastable phase.

4.2   Energy for different magnetisation configurations

For the anti-ferromagnetic configuration, it is important to define two type of atoms in the cell, (NiU) and (NiD) with associated spin-up and spin-down starting magnetization. It is then essential to have a 2x1x1 supercell, and thus extend the first cell vector two times long ($v = (-3.46603.466)$). The total energy found is $E = -4.6680 \cdot 10^3$eV (or $E = -343.08793385$Ry). The last magnetic configuration studied here is the Non magnetic configuration with a total

energy $E = -4.6679 \cdot 10^3$eV or $E = -343.08384393$ Ry.

Magnetic configurations:	Energy per atom [Ry]	Energy per atom [eV]
Ferromagnetic	-343.08793385	$-4.6680 \cdot 10^3$
Antimagnetic	-343.0840	$-4.6679 \cdot 10^3$
Non magnetic	-343.08384393	$-4.6679 \cdot 10^3$

Table 1: total energy E per atom for different magnetic configurations

The Tab.1 shows that the magnetic ground state (the magnetic configuration with the lowest energy) is the ferromagnetic configuration with $E = -4.6680 \cdot 10^3$ eV per atom, followed by the Non magnetic and finally the antimagnetic configurations (for a smaller difference than 2.2meV).
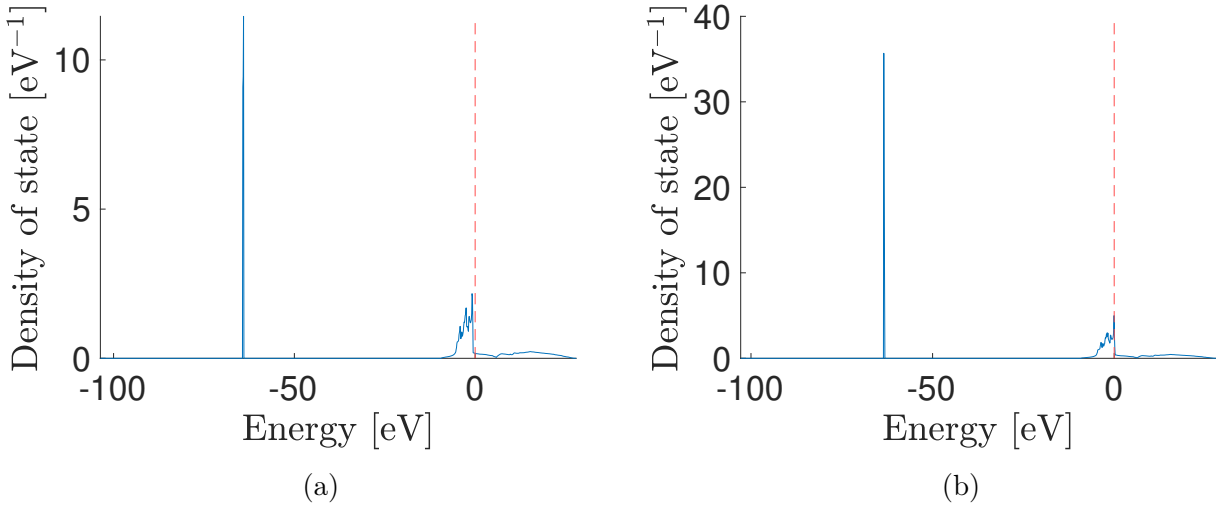
4.2.1 DOS

(a)	(b)

Figure 14: Density of state $[\text{eV}^{-1}]$ as the function of the energy [eV] in Nickel a) for a ferromagnetic system, b) for a non magnetic system

The Density of state of the Nickel are plotted for the ferromagnetic case and the non magnetic case in Fig.14. Some states, in both cases, are at the Fermi energy implying that the valence band is full and then that Nickel is indeed a metal. Furthermore in both DOS, a single peak appears for a value of $E = -63.3$eV, but with a higher intensity in the non magnetic case.

References

[1] Jorge Kohanoff and Nikitas Gidopoulos. *Density Functional Theory: basics, new trends and application.* URL: https://moodle.epfl.ch/pluginfile.php/3325646/mod_resource/content/0/Kohanoff%20Gidopoulos.pdf.

[2] *User's Guide for Quantum ESPRESSO.* URL: https://www.quantum-espresso.org/Doc/user_guide_PDF/user_guide.pdf.

[3] Yu Hang Leung a Aleksandra B. Djurišić Xinyi Chen a and Alan Man Ching Ng. "ZnO nanostructures: growth, properties and applications". In: *Royal socity of chemistry* (2012). URL: https://pubs.rsc.org/en/content/articlehtml/2012/jm/c2jm15548f.

[4] *Lab 3: Advanced topics in first-principles electronic structure calculations*. EPFL.

[5] Dhirendra Kumar Sharma et al. "A review on ZnO: Fundamental properties and applications". In: *Materials Today: Proceedings* (2020).

[6] Gianluca Prandini et al. "Precision and efficiency in solid-state pseudopotential calculations". In: *npj Computational Materials* 4.1 (2018). http://materialscloud.org/sssp, p. 72. ISSN: 2057-3960. DOI: 10.1038/s41524-018-0127-2. URL: https://www.nature.com/articles/s41524-018-0127-2.

[7] G.S. Orudzhev V.N. Jafarovaa. "Structural and electronic properties of ZnO: A first-principles density-functional theory study within LDA(GGA) and LDA(GGA)+ U methods". In: *Elsevier* (2020). URL: http://www.elsevier.com/locate/ssc.

[8] Stefano de Gironcoli Burak Himmetoglu Andrea Floris and Matteo Cococcioni. "Hubbard-corrected DFT energy functionals: The LDA+U description of correlated systems". In: *International Journal of Quantum Chemistry* (2014). URL: https://onlinelibrary.wiley.com/doi/epdf/10.1002/qua.24521.

[9] "Visible spectrum". In: *Wikipedia* (). URL: https://en.wikipedia.org/wiki/Visible_spectrum.

[10] M. Knapp W. Paszkowicz J.B. Pelka. "Lattice parameters and anisotropic thermal expansion of hexagonal boron nitride in the 10-297.5 K temperature range". In: *Applied Physics A Materials Science and Processing* (2002).

[11] P. Valvin G. Cassabois and B. Gil. "Hexagonal boron nitride is an indirect bandgap semiconductor". In: *nature* (2016). URL: https://www.nature.com/articles/nphoton.2015.277.