

Problem Set 3: Advanced topics in first-principles electronic structure calculations

Assigned: 28/04/2016 – Due: 15/05/2016

In this problem set, we will perform additional first-principles calculations. These calculations will show some aspects of DFT that we did not see in Lab 2. First of all, we will learn how to calculate the electronic band structure for diamond and other carbon allotropes. In this case the non self-consistent technique implemented in Quantum ESPRESSO will be adopted. In the same exercise we'll also learn how to run advanced structural relaxation. In the second exercise we will explore metallic and magnetic systems (using iron as a test case), highlighting all the necessary calculation parameters. In these exercises we will use ultrasoft pseudopotentials (US-PP) as opposed to norm-conserving pseudopotentials (NC-PP) that we used in the last lab. Ultrasoft pseudopotentials give accurate answers with lower wavefunction cutoff (however, charge density cutoffs must remain the same), which means that calculations can be cheaper.

Problem 1 (60 points): Band structure of carbon's allotropes

Band-structure calculations are a fundamental tool in material science, allowing us to have a deeper understanding on how electrons behave in solids. In this problem we will focus on three most import carbon's allotropes: diamond, graphite and graphene. You will calculate band structures along their respective high-symmetry lines using non-self-consistent-field (NSCF) methods. Another important quantity that can be easily obtained in NSCF calculations and that you are asked to compute is the density of states (DOS).

- A Using PWscf, perform a self-consistent-field (SCF) calculation for diamond. Since you already learned how to search for optimal energy cutoffs and \mathbf{k} -point grid sufficient for convergence in the previous Lab, these parameters will be given in the class materials.
- B Run a NSCF calculation to compute the band structure of diamond (see Handout). In the input files, you will have to specify the path in reciprocal space along which bands are computed. Informations about this paths can be found in the Handout. Be careful about the choice of the number of bands to be evaluated and how many points you put on each line. Estimate the band gap of diamond. Is it direct or indirect? How does your value compare with the experimental gap of 5.46 eV at zero temperature? Can you give a reason for this?
- C Perform an additional NSCF calculation as specified in the Handout. Then compute the DOS of diamond running the Quantum ESPRESSO executable `dos.x`.
- D Plot the results for the band structure and the DOS. Can you see any relation between them? Can you explain for instance why the DOS of diamond goes like $\sqrt{E - E_0}$ as a function of energy E close to the bottom of the valence bands E_0 ?

We will now look at an other allotrope of carbon. Graphite is the stable structure of carbon under normal conditions. Graphite is a layered material in which the layers weakly interact with

each other via van der Waals interactions. See Handout for more informations. Up to now, those type of interactions were not included. In the following, you are asked to find the optimal structure for graphite, with or without van der Waals interactions. You will then compute the band structure and density of states of graphite.

- E 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 graphite, those two parameters can be optimized separately. Start by fixing the interlayer distance (for example, at the experimental value) and study the ground state energy as a function of the in-plane lattice parameter, with and without accounting for 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.
- F 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 to find the optimized interlayer separation in both cases. How do these values compare with each other and with experimental results?
- G Compute and plot the band structure and DOS for graphite with van der Waals interactions. Can you see a band gap in the band structure? What about in the DoS? Try to increase the k-points and see the effect on the DoS. Is there a gap in reality? Graphite is a highly anisotropic material, with different in-plane and out-of-plane properties. Can you see this?

We now look at one last allotrope of carbon, graphene. Graphene is a single layer of graphite. See Handout for more informations. It was the first of the 2D materials to be isolated, in 2004. Since then, it has been one of the most studied material in condensed matter, due to its exotic electronic properties.

- H One should be careful when simulating 2D materials. Remember Lab 1 and the study of surfaces. What choice of structure parameters do you propose to simulate graphene? You should have all the information you need from what you have done for graphite without van der Waals interactions.
- I Compute and plot the band structure and DoS of graphene. Is there a gap, in the bands and DoS? The peculiarity of graphene resides in the linearity of the band structure near the Fermi level. Can you see the so-called Dirac cones? Considering linear bands in a 2D material, what should be the behaviour of the DoS in the region of the cones?

Problem 2 (40 points): Iron: stability under pressure and magnetism

You will calculate energies of different structures using the Perdew-Burke-Ernzerhof(PBE) GGA exchange-correlation functional. Use a wavefunction cutoff of 55 Ry along with charge density cutoff 240 Ry. For time reasons, a good **k**-point mesh is already given to you (see the Handout). We are going to compare the energies of the HCP and BCC structures. In addition you will be asked to compute the total energy of BCC iron in different magnetic configurations.

- A Using PWscf, optimize the lattice parameters for both BCC and HCP Fe (i.e., a for BCC and a and c for HCP). Remember that BCC iron is ferromagnetic in its ground state.
- B Plot the energy as a function of volume for the two structures and find when the HCP structure becomes more favorable than the BCC one. (note that: At pressure greater than 15 GPa the HCP-Fe phase is more stable [see “Possible thermal and chemical stabilization of body-centred-cubic iron in the Earth’s core”, L. Vocadlo *et al.* Nature **424**, 536 (2003); Xianwei Sha and R.E. Cohen, Phys. Rev. B **73**, 104303 (2003); M. Friak and M. Sob, Phys. Rev. B **77**, 174117 (2008)]).
- C Using PWscf, calculate and compare the total energy for BCC iron in the ferromagnetic, antiferro-magnetic, and nonmagnetic states after having properly optimized the structure. For each structure perform then a non-self consistent calculation on a finer grid and compute the density of states using the dos.x program and the projected density of states using the projwfc.x program. An example of the input is provided in the PostProcessing folder.