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

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Assigned: 01/05/2018 – Due: 13/05/2016

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 magnesium oxide and magnesium. In this case the non self-consistent technique implemented in Quantum ESPRESSO will be adopted. We will then learn how to run advanced structural relaxations, using two allotropes of carbon (diamond and graphite) as a study case. In the last exercise we will explore magnetic systems using cobalt 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 (30 points): Band structure of MgO and Mg

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 magnesium oxide, which you have already studied in Lab 2, and magnesium. You will calculate the band structure along their respective high-symmetry lines using the non-self-consistent-field (NSCF) method. 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 MgO. Since you already searched for optimal energy cutoffs and **k**-point grid in the previous Lab, these parameters will be given in the class materials.

B Run a NSCF calculation to compute the band structure of MgO (see handout). In the input files, you will have to specify the path in reciprocal space along which bands are computed. Information about this path 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 MgO. Is it direct or indirect? How does your value compare with the experimental gap of 7.9 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 MgO running the Quantum ESPRESSO executable `dos.x`. Plot the results for the band structure and the DoS. Can you see any relation between them?

D Compute now the band structure and the density of states for bulk magnesium (HCP structure) after having optimized the corresponding lattice parameters (i.e. a and c, follow the procedure described in the handout). Suitable energy cutoffs values and **k**-point grid are given in the class material. Can you explain why the DoS of Mg goes like $\sqrt{E - E_0}$ as a function of energy E

close to the bottom of the valence bands E_0? How do the band structure and the DoS of Mg differ from the MgO ones?

Problem 2 (40 points): The graphite-diamond transition under pressure

In this problem we will focus on two carbon's allotropes which are widely used in a variety of industrial applications: diamond and graphite. Graphite is used to produce extremely strong fibers, easily sheared lubricants, gas-tight barriers, and gas adsorbers. Moreover, graphite can be exfoliated to produce graphene, which is among the nanoscale building blocks for next-generation materials. Diamond has very different properties like unusually high index of refraction, extreme resistance to neutron radiation, very high strength and rigidity, and the highest atom-number density. These extreme differences in the properties are related to the different hybridization state of the carbon atoms: sp^3 in diamond and sp^2 in graphite.

Van der Waals interactions in DFT

Graphite is the stable structure of carbon under normal conditions. It is a layered material in which the layers weakly interact with each other via van der Waals forces. Including such dispersive interactions in DFT is highly non-trivial and special functionals have been developed to cope with these systems (see the handout for more information). In the following, you are asked to find the optimal structure for graphite, with or without van der Waals interactions.

A You have to optimize the two parameters of the graphite structure, one defining the configuration within each layer (in plane), the other the separation between the layers (out of plane). Using a vdW-compliant functional, determine the equilibrium cell parameters following the procedure described in the handout. Fit the curve (energy as a function of the two lattice parameters, a surface in 3D space) to find the two optimized lattice parameters. How do the lattice parameters compare with the experimental results? Can you comment/explain the shape of the curve that you have obtained?

B Repeat the optimization of the lattice parameters using a functional which does not account for the vdW interaction. What happens to the energy when you increase the interlayer distance? Compare the resulting curve with the previous case and comment.

Graphite-diamond transition pressure

Unlike graphite, diamond is very rare and precious. Many attempts were made to synthesize diamonds by trying to mimic the high pressure and high temperature conditions of the volcanic shafts where graphite is naturally transformed into diamond.

C Optimize the structure of diamond using the vdW-compliant functional that you used previously for graphite. (You need to use the same functional used for graphite since in the following you will be asked to compare the energy per atom in the two structures). How many parameters do you have to optimize in this case?

D For diamond, plot the ground state energy per atom versus the volume per atom. You have to expand the volume around the optimized value that you have found in the previous point. Fit

this relation with the appropriate functional form (you can produce an energy-volume file and use the program `ev.x` in the QE software suite to perform the fit).

E Repeat the procedure for graphite keeping into account the vdW interaction. How many parameters do you have to vary in order to vary the volume? Note that once you have chosen a volume variation, there are several ways to obtain this value and you need to find the configuration that corresponds to the minimum total energy. See the handout for details.

F Plot the energy versus volume for the two structures and find the pressure at which the diamond configuration becomes more favorable than the graphite one. How does this compare with the experimental value? Comment the results.

Problem 3 (30 points): Phase Stability and Magnetism in Cobalt

You will calculate energies of different structures using the Perdew-Burke-Ernzerhof(PBE) GGA exchange-correlation functional (no vdW required). Suitable energy cutoffs values and **k**-point grid are given in the class material. We are going to compare the energies of the HCP and FCC structures. In addition you will be asked to compute the total energy of HCP cobalt in different magnetic configurations.

A Using PWscf, optimize the lattice parameters for both HCP and FCC Co (i.e., a and c for HCP and a for FCC). Assume a ferromagnetic ordering for the two structures.

B Compare the energy of the two optimized structures. Which phase is most stable?

C Using PWscf, calculate and compare the total energy for HCP cobalt in the ferromagnetic, antiferro-magnetic, and nonmagnetic states. 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.