NANO266 Lab 3 - Bulk properties from Quantum Mechanics

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1 Introduction

In this lab, we will look at obtaining bulk properties from quantum mechanics. We will still be using QuantumEspresso. We will also introduce you to the basics of running calculations on supercomputing resources, e.g., how to submit jobs, handle queues, etc.

2 Initial setup

By this stage, you should already have everything set up. Make sure you are in the lab3 folder by doing:

cd <path/to/repo>/labs/lab3

3 Submitting jobs to the Comet queues

Comet uses the SLURM queuing system. For more information, you may read the guide at https://www.sdsc.edu/support/user_guides/comet.html. For the purposes of this lab, a sample *submit_script* has been provided. It is imperative that you understand how the script works as you will be using this for the rest of this and the next lab. Read the user guide to understand what each of the options in the preamble means. You can then modify them to suit your needs.

To submit the job, just simply run:

sbatch submit_script

You may check on the status of your job using the following command:

squeue −u <username>

4   Q1 (20 points): The bcc-hcp transition in iron

In this problem, you will look at the bcc to hcp transition in iron. We will be using the PBE GGA functional that we used in the earlier lab. Use an energy cutoff of 50 Ry with a charge density cutoff of 250 Ry. You will need to determine an appropriate k-point mesh for both the bcc and hcp structures. The energy differences are very small; choose parameters to converge your energies to within 1 meV.

1. Calculate the ground state energy of Fe in both the bcc and hcp structure. Two template files are provided for bcc and hcp. A run_pw.py file is also provided that works for bcc, but you need to modify it as appropriate to work for hcp.

2. Varying the volume of the cell calculate when the hcp structure becomes more favorable than the bcc one. Note that it is important when comparing energies that the k-point samplings for both systems are comparable and converged. Determine an appropriate k-point grid for both structures. Optimize the lattice parameters for both bcc and hcp Fe (i.e., a for bcc and a and c for hcp).

3. Calculate and compare the total energy for the BCC structure in the ferromagnetic, anti-ferromagnetic, and nonmagnetic states. (10 points)

Note that you will need to read the PWSCF manual to figure out how to set various options to do this work. At this stage of the course, we will not be providing complete scripts and you need to work through the manuals to figure out what to do. This is part and parcel of computational modeling work.

5   Q2 (40 points): Stability of the PbTiO$_3$ perovskite

PbTiO$_3$ is a perovskite oxide which is ferroelectric. The ferroelectric response of PbTiO$_3$ is the result of a displacive transition where a low temperature tetragonal phase is preferred over the cubic phase.

For this question, it is important that you note several differences in the `PbTiO3.pw.in.template` file.

- The `calculation` parameter is set to `relax`, which means we are allowing atoms to move.

- There is an addition IONS section where the `ion_dynamics` is set to `"bfgs"`, which chooses the quasi-Newton minimization method.

- At the end of the atomic positions for Pb and Ti, there are three additional 0s. These indicate that the Pb and Ti are not allowed to move in any of the coordinates. Conversely, no such restriction is placed on the O atoms, which are allowed to relax accordingly.

Please answer the following questions.

1. Calculate and plot the energy of cubic $PbTiO_3$ as a function of lattice parameter. Use a $4 \times 4 \times 4$ k-point mesh with a 1, 1, 1 offset. Sample lattice parameters with a sufficiently fine grid to get a reliable value for the equilibrium lattice constant. To get an idea where to begin, note that the room-temperature experimental lattice constant is about 3.97 Å.

2. Using the equilibrium lattice parameter from part (1), plot the energy as a function of displacement of the Ti atom along one of the cubic lattice directions, allowing the O atoms to fully relax for each displacement. Report the Ti displacement at which the total energy is at a minimum. What is the energy difference between this configuration and the minimum-energy configuration from part (1)? Be aware that for $PbTiO_3$, the Ti displacement will be very small.

3. Now allow both the Ti atom and the O atoms to relax and find the minimum energy structure, using the minimum-energy Ti displacement from part (B) as your starting configuration. Report the final atomic positions and final energy.

4. Which phase is the most energetically stable for $PbTiO_3$ and how does that relate to the ferroelectric behavior of this material?

6   Q3 (40 points): Formation Energy of the $Cu_{1-x}Au_x$ intermetallics

In this problem, we will investigate the formation energies of the $Cu_{1-x}Au_x$ for $x = 0.25$, 0.5 and 0.75. See Ozolins et al. Cu-Au, Ag-Au, Cu-Ag and Ni-Au intermetallics: First-principles study of phase diagrams and structures, Phys. Rev. B, 1997, 57, 19, doi:10.1103/PhysRevB.57.6427.

1. Calculate the ground state energy for fcc Cu, Au and $Cu_{1-x}Au_x$ Here, we will use PWSCF's *vc-relax* option to avoid having to manually do a equation of state analysis. Start with the end members and the CuAu ($x = 0.5$) intermetallic and do a k-point convergence such that your formation energies are within 5 meV /atom. Start with a relatively small grid, e.g., 4×4 $\times

2. For CuAu, you should use the L10 phase, which is a body-centered tetragonal (bct) with two atoms in the unit cell, and lattice parameters are $a = b \neq c$. A sample file is provided. You may search the internet for the experimental lattice parameters and use those to set your initial guesses for $a = $ celldm(1) and $c/a = $ celldm(3). You should use good guesses to minimize the computational time.

3. Calculate the formation energy of $Cu_{1-x}Au_x$:
$$\Delta H_f(Cu_{1-x}Au_x) = E(Cu_{1-x}Au_x) - (1-x)E(Cu) - xE(Au)$$
where E(Cu) and E(Au) are the total energies for Cu and Au in their fcc bulk phase. Note that you must normalize the energies accordingly. We want the formation energies per atom, i.e., $0.5 \times$ the formation energy per CuAu.

4. Repeat the calculations for Cu_3Au and $CuAu_3$. For both these structures, start with a fcc Cu or Au structure, and replace all corner atoms with atoms of the other type. For example, to create the Cu_3Au, you can start from the fcc Cu unit cell, and set the Cu atoms to be on the faces, which gives one Au (1 /8 × 8) and three Cu (1 /2 × 6). Note that in order to create this structure, you need to decrease the symmetry from the fcc to simple cubic, and then add an atom. Review your crystallography and PWSCF's input file format so that you understand how to do this.

5. Plot the formation energy of the $Cu_{1-x}Au_x$ phases you have calculated against x. Discuss which of the ordered intermetallic structures are stable at 0K.