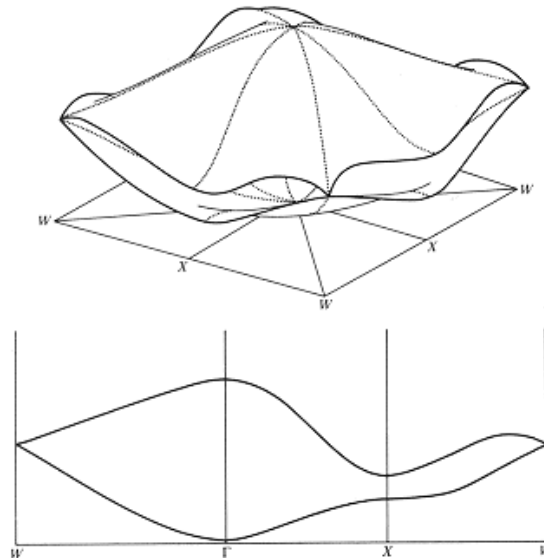


HOMEWORK 7
HF, Band Diagrams, Pseudopotentials
Due March 16, 2009

Problem 1: Silicon Band Diagrams

In the previous calculations that we have done using Quantum espresso, we considered self consistent computations that required integration over a k-point grid. This is used to calculate the total energy, charge density, etc. In band diagram computations, we stop with computing the energies at the different k-points. This is a non-scf computation. The band diagram is a simplified representation of the energy vs k vector plot. In actuality, it will be a 3D plot. But, it would be sufficient for most purposes to know the $E_n(\mathbf{k})$ curves - the dispersion relations - along the major directions of the reciprocal lattice.



http://www.tf.uni-kiel.de/matwis/amat/semi_en/index.html provides a very elegant description of the choice of k points. The notations for the points of symmetry in the BZ are:

The center of the Wigner-Seitz cell is always denoted by a Γ

The intersection point with the $[100]$ direction is called **X**.

The intersection point with the $[110]$ direction is called **K**.

The intersection point with the $[111]$ direction is called **L**

Compute the band diagram for silicon by explicitly providing the k points along regions of high symmetry (say, **L- Γ -X-K- Γ**).

A sample code is given in `siband.in` in the attached Examples directory.

Problem 2: FCC and HCP cobalt

1. Calculate the energy of FCC cobalt as a function of the lattice parameter and make a plot.

2. Calculate the energy of HCP cobalt. Start from the ideal c/a ratio. Find the equilibrium parameter a for that ratio and then change c at the corresponding fixed a . Also try several values of a around the equilibrium a that you found to ensure you are at the minimum-energy configuration. In particular, for each a , you should make a plot of the energy vs. the c lattice parameter and select the minimum-energy configuration from among these plots. How do the lattice parameter and the c/a ratio compare with the experimental values?

3. Calculate the energy difference between HCP and FCC cobalt. Which one is more stable? Can you expect a phase transition when you increase the pressure?

4. The difference between HCP and FCC is in the stacking sequence along $\langle 111 \rangle$ directions of cubic cell or $\langle 0001 \rangle$ directions of hexagonal cell.

FCC : ABCABCABC.....

HCP : ABABABABA.....

In our previous construction, we considered the FCC in a cubic cell and the HCP in the hexagonal cell. Now we will construct an FCC structure in a hexagonal cell. Assuming that the atoms (A and B) are placed at $(1/3, 2/3, 1/2)$ and $(2/3, 1/3, 3/4)$ for the HCP in a hexagonal cell, where should the third atom (C) go, to make this cell FCC?

What is the relationship between the lattice parameter a for the FCC in a cubic system and the corresponding value for FCC in a hexagonal system? Calculate the hexagonal FCC parameter from the cubic parameter you computed in 1, and compare that result with the HCP value you computed in 2.

Fix c/a to the ideal value and construct FCC in a hexagonal cell. Calculate the total energy and compare it with that of HCP.

5. We want to introduce a stacking fault in the HCP structure.

That is, go from a ABABABABA..... structure to

a AB|CABABAB..... structure

Make a plot which shows how the energy varies as a function of the number of atomic layers in the unit cell. To make it simpler, fix a and c/a to the values from the HCP structure, and fix the atomic positions. Do not go above 10 layers of atoms even if your calculation does not converge

Note:

a) Look at the model input files provided (Co.HCP.scf.in, Co.FCC.scf.in)

b) There are two independent lattice parameters in a hexagonal lattice. `celldm(1)` is a in bohr (not angstrom) and `celldm(3)` is c/a (not the absolute value of c). Find an appropriate value of `celldm(3)` from your knowledge of the ideal HCP structure. Two atoms comprise one unit cell

c) As discussed in class, calculations of metals converge very slowly due to the presence of the Fermi level. Since there is a discontinuity of the occupation number for the bands around the Fermi energy, total energy with respect to the number of k-points converges

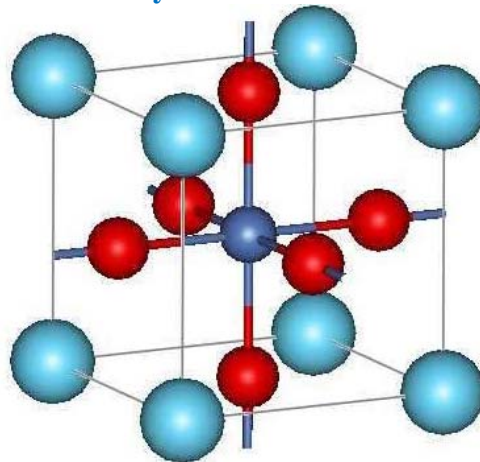
very slowly. Adding electronic temperature (`degauss`) smooth out the abrupt change of the occupation number and as a result total energy converges with fewer number of k -points. (This is given in the sample input file)

d) `nspin=2` turns ON spin polarization while `nspin=1` turns it OFF. We will use `nspin=2` throughout Problem 1.

e) The number of K points for HCP can be reduced in one direction (because the z direction is longer, so the reciprocal cell in the z direction is smaller)

f) This problem requires you to run the program multiple times. It helps to use a `.bat` file. A bat file is just a sequence of shell commands that the computer sequentially executes. Attached is a simple Batch job generating program and a sample batch file (`BatchJobCreate.cpp`, `CoHCPrun.bat`).

Problem 3: Perovskite Oxide Stability



BaTiO_3 is a perovskite oxide which is known to behave as a ferroelectric. The ferroelectric response of BaTiO_3 is commonly thought to be the result of a transition where a tetragonal phase is preferred over the cubic phase. In this problem, we will study the energetics of cubic BaTiO_3 and use first principles calculations to gather information pertaining to the transition to the tetragonal phase.

1. Calculate and plot the energy of cubic BaTiO_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.

2. Using the equilibrium lattice parameter from part (a), 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 (a)? Be aware that for BaTiO_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.

Note:

- a) The first part of the problem is a scf calculation. Look at the sample file provided. (Prob3.in)
- b) The other parts are ‘relaxation’ problems. That is they are a sequence of scf calculations to find the minimum energy basin. This is very similar to the ‘opti’ command that was used in GULP. This requires changing the text of the input file from ‘scf’ to ‘relax’ and add the ion-dynamics tag. Look at the sample input file provided (DistrotProb3.in).
- c) For the relaxation computation, the ions are allowed to move. These degrees of freedom can be given in the ‘ATOMIC POSITIONS’ column, following the positions. A value of 0 fixes that particular coordinate.
- d) Again, the use of batch jobs will be very useful.

Problem 4: Creating a Simple Pseudopotential

When generating pseudopotentials, it is necessary to solve the Schrodinger equation for individual atoms. One can assume that the electron density is spherically symmetric and perform a spherical averaging of the density. This also means that the electron potential is also spherically symmetric (this is only valid in a closed shell system). By splitting the electron wavefunction into the radial part R and spherical harmonics and by introducing a new function

$$\phi(r) = rR(r)$$

the radial Schrodinger equation can be transformed into a simple second order differential equation.

$$-\frac{1}{2} \frac{d^2 \phi}{dr^2} + \left[U(r) + \frac{l(l+1)}{2r^2} \right] \phi = E\phi$$

where U is the potential (the core potential plus screening due to other electrons).

1. For Coulomb potential $U=-1/r$ calculate the ground state energy ($l=0$) and the function ϕ numerically by using a finite differences method (or use the method of your choice). You will have to solve an eigenvalue problem.
2. Make sure you get the correct energy and function by comparing your results to the analytical solutions for the hydrogen atom.
3. Replace the Coulomb potential with an Ashcroft-type potential: $U(r)=-1/r$ only for values of r greater than R_c . For all other values of r , $U(r)=0$. Calculate the ground state energy and the energy of the first excited state for $R_c = 1.0$ a.u.
4. Now we will construct an Abarenkov-Heine type pseudopotential to replace the real Coulomb potential.

$$U(r) = \begin{cases} -1/r & \text{for } r > R_c \\ A & \text{for } r \leq R_c \end{cases}$$

For $R_c=1.5$ a.u. find the best value of A to get the correct ground state energy. Using this value of A , what is the energy of the first excited state? What is the wavefunction you get using your pseudopotential?