3.320 Atomistic Modeling of Materials Spring 2003
Problem set 3: First-principles energy methods II

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. In this lab, 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 cutoffs, which means that calculations go faster. Note, this lower cutoff only applies within the same atom type. That is, a US-PP for Si will have a lower cutoff than a NC-PP for Si. But a US-PP for Si does not necessarily have a lower cutoff than NC-PP for Al.

In Problem 1, we will calculate surface energies again. In problem 2, we will examine different exchange-correlations, and see how they affect the energetics and lattice parameters.

Problem 1 (50 points): Surface energy of Al (001) surface.

Often, the developers of a first-principles code will give you a good cutoff for a particular element. Cutoffs are generally transferable between different compounds and structures. On the other hand, the number of $\bar{k}$ -points required for convergence of energy depends highly on both structure and chemistry. Thus, you should always check convergence with respect to $\bar{k}$ -points in any new calculation.

In this lab, we will give you the cutoff for Al (14 Ryd), as well as the lattice parameter for Al (7.50 bohrs). You will have to determine a suitable $\bar{k}$ -point mesh for both supercell Al and FCC Al.

A. Using the lattice parameter from part A, edit the given files to create supercells of FCC Al with surfaces. Calculate the energies of these slabs, with layers removed. Calculate the energies both relaxed and unrelaxed. You will need to test the convergence of energies with respect to slab size and vacuum size. Explain the rationale for the $\bar{k}$ -point mesh chosen.

B. Calculate the bulk energy of FCC Al. You will do this in two ways.

1. First, obtain a bulk energy by calculating the energy of FCC Al (both at 7.50 bohr and relaxed). You will have to test the convergence of energies with respect to $\vec{k}$ -points. General hint: Metals, such as Al, generally require more $\vec{k}$ -points than insulators or semiconductors , such as GaP. You need the finer mesh to capture the effects of sharply varying electron densities as a function of energy.

2. Calculate the energy of the bulk by taking the limit of the change in energy, when you add a layer. That is,

$$E_{bulk} = \lim_{n\to\infty} E_n - E_{n-1}$$

Compare the energy of the bulk you calculated using both methods.

C. From these calculations, you can obtain a value for the surface energy of Al(001).   Convert this value to eV/Angstrom^2. How does your choice of "bulk energy" affect your calculated surface energy? Hint: It is better to calculate the surface energy at each step, and for each supercell, rather than calculating many supercells and waiting until the end to calculate the surface energy. If you calculate the surface energy at each stage, you will have a better idea of when your value is converged with respect to supercell and vacuum size.   Thus, you can avoid calculating supercells that are too large, vacuums that are too large, and so on.

The units webpage may help you:

http://www.chemie.fu-berlin.de/chemistry/general/units_en.html

Problem 2 (50 points): Magnetic and non-magnetic iron in the FCC and BCC structures.

A cutoff of 25 Ryd is given to you. You may want to raise this (if using scripts) to produce a smoother energy vs. lattice parameter curve. A good $\vec{k}$ -point mesh is not given to you: you will have to find this yourself.

A. In part A, you will look at energies using the Perdew-Zunger LDA exchange-correlation. This is the most commonly used LDA exchange-correlation.

1. Calculate the energy of BCC iron as a function of lattice parameter. Make a plot of the energy vs. lattice parameter. How does this compare to the experimental value? (You should find this value yourself)

2. Calculate the energy of FCC iron as a function of lattice parameter. Make a plot of the energy vs. lattice parameter. What is the equilibrium lattice parameter?

3. Now, recalculate the energy of BCC iron as a function of lattice parameter, but this time turn on the spin polarization (magnetization). Set the starting magnetization value to a value between -1 to +1. Make a plot of the energy vs. lattice parameter. How does the equilibrium lattice parameter compare with experiments? Record the magnetic moment. (How does turning on magnetism change the lattice parameter?

4. Recalculate the energy of BCC iron as a function of lattice parameter (one more time), and again turn on the magnetization. This time, set the starting magnetization value to 0. Make a plot of the energy vs. lattice parameter. What is the equilibrium lattice parameter? Record the magnetic moment. How can you reconcile this answer with part 3?

B. Repeat parts 1, 2, and 3 of section A, this time using the Perdew-Burke-Ernzerhof (PBE) GGA exchange correlation. There are many commonly used GGA exchange correlations- this is one of the most popular.

C. For LDA calculations, make a table (or a diagram) showing the energies in the system. Repeat this for the GGA calculations. How do LDA and GGA answers compare? How do magnetic moments compare? How do lattice constants compare? What is the experimental equilibrium state of Fe? How do all of your results compare with experiments? Are any of the calculated results expected or unexpected?

Extra credit (20 points): Antiferromagnetic iron in the FCC and BCC structures..

A. Calculate the energy of antiferromagnetic iron in BCC and FCC configurations, using GGA and LDA. To do this, you will need to create a supercell with an antiferromagnetic configuration. Refer to the INPUT_PW file for more details on input parameters that you may need to change (such as Bravais lattice, the meanings of the various celldm, nat, ntyp, etc…) . To break the symmetry, you will need to define two types of iron atoms: one type iron with a positive initial spin, and one type iron with a negative initial spin.