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 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.

Testing the kmesh at 15 bohr vacuum

layers	E(Ryd)	kmesh	E/atom(Ryd)
7	-29.18439382	4x4x1	-4.169199117
7	-29.21509442	5x5x1	-4.173584917
7	-29.23644406	6x6x1	-4.176634866
7	-29.21839403	8x8x1	-4.17405629
7	-29.21470693	9x9x1	-4.173529561
7	-29.21989717	10x10x1	-4.174271024
7	-29.22022603	11x11x1	-4.174318004

Roughly a 8x8x1 mesh is suitable. Slightly higher might be better. On the other hand, as number of layers increase, the kpoint requirements go down. So 8x8x1 is probably fine. This mesh is chosen because of the geometry of the lattice. In real space $c>a$, so in reciprocal space $a^*>c^*$. To get an even sampling of kpoints in reciprocal space, we chose the a^* mesh to be finer than the c^* mesh.

Testing vacuum at 4x4x1 kpoint mesh.

layers	vac(bohr)	E(Ryd)
7	10	-29.18182343
7	15	-29.18422165
7	20	-29.18439382
7	25	-29.18440714
7	30	-29.18468776

Roughly 15 bohrs is fine. We will use 20 bohrs so that I can add a layer of atoms without worries. Probably should've test kpoints first before doing vacuum, but we will assume this is fine. In the literature, typically 10-20 bohrs are used as vacuum.

Surface area is 2.805 Angstroms. So Surface energy is given by
$(Eslab_{n\ atoms}-n*Ebulk)*13.6$ eV/Ryd /2 /2.805 Angstroms/ 2.805 Angstroms

Unrelaxed, all energies in eV/Angstrom^2.

vac(bohr)	layers	E(ryd)	Ebulk(n+1 method)	Ebulk normalized	Esurface n+1 way	Esurface bulk way
	4	-16.65719496	-4.19040017	-16.76160068	0.090233432	0.075886169
	5	-20.84759513				0.072299353
20	7	-29.21839403	-4.18532459	-29.29727213	0.068170993	0.073769541
16.25	8	-33.40371862				0.074569334
20	9	-37.59052007	-4.18552073	-37.66968657	0.068420245	0.074092739
16.25	10	-41.7760408				0.074723016
20	11	-45.96232076	-4.18574555	-46.04320105	0.069901401	0.074697123
16.25	12	-50.14806631				0.075133098
20	13	-54.33518829	-4.18571917	-54.41434921	0.068415423	0.074379483
16.25	14	-58.52090746				0.074838256

Energies converged at ~7-9 layers of bulk to 1 meV/angstrom sq. ~6 meV/A^2 difference between the two methods of finding the energy of one Al atom. Relaxed, all surface energies in eV/Angstrom^2

vac(bohr)	layers	E(ryd)	Ebulk(n+1 method)	Ebulknormalized	Esurface n+1 way	Esurface bulk way
20	7	-29.2191334	-4.18513651	-29.29595557	0.06639414	0.073130535
16.25	8	-33.40426991				0.074092877
20	9	-37.59135856	-4.18547553	-37.66927977	0.067343994	0.073368068
16.25	10	-41.77683409				0.074037409
20	11	-45.96298763	-4.18586457	-46.04451027	0.070456557	0.074120776
16.25	12	-50.1488522				0.074453886
20	13	-54.33560253	-4.18571029	-54.41423377	0.067957643	0.074021472
20	14	-58.52131282				0.074487921

Surface energies are converged ~7-9 layers to 1 meV/angstrom sq. Surface energies are ~1 meV/Angstrom^2 lower than by the unrelaxed method.

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 $\bar{k}$-points. General hint: Metals, such as Al, generally require more $\bar{k}$-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.

Testing kpoints:

|			
al.out.2:!	**total energy**	**=**	**-4.23022618 ryd**
al.out.4:!	**total energy**	**=**	**-4.16672975 ryd**
al.out.6:!	**total energy**	**=**	**-4.19065385 ryd**
al.out.8:!	**total energy**	**=**	**-4.18542955 ryd**
al.out.9:!	**total energy**	**=**	**-4.18400756 ryd**
al.out.10:!	**total energy**	**=**	**-4.18523585 ryd**
al.out.11:!	**total energy**	**=**	**-4.18644523 ryd**
al.out.12:!	**total energy**	**=**	**-4.18639867 ryd**
al.out.13:!	**total energy**	**=**	**-4.18574679 ryd**
al.out.14:!	**total energy**	**=**	**-4.18560793 ryd**
al.out.15:!	**total energy**	**=**	**-4.18585761 ryd**

al.out.16:! total energy   = -4.18608264 ryd
al.out.17:! total energy   = -4.18600728 ryd
al.out.18:! total energy   = -4.18587188 ryd
al.out.19:! total energy   = -4.18586296 ryd
al.out.20:! total energy   = -4.18591535 ryd

Energy is converged at ~15x15x15 k-grid. A finer mesh is needed for metals (such as Al) than for semiconductors or insulators (such as GaP). This is because metals have sharply varying electron densities as a function of energy.

Finding lattice parameter:
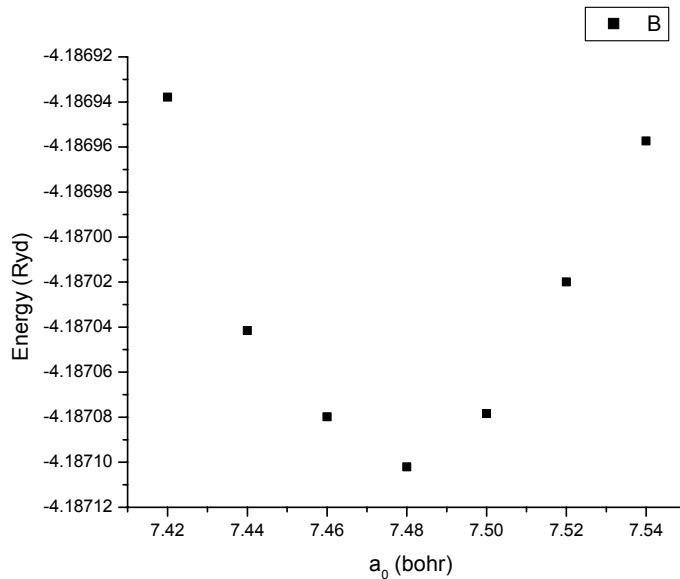
The lattice constant is approximately 7.48 bohr. This is ~3.96 Angstroms, slightly smaller than experiments. This is expected when using LDA.

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.

Convergence of BCC (45 Ryd cutoff, 5.1 bohr lattice parameter)

Kpoints(even mesh)	E
2	-55.43418668 ryd
4	-55.56715995 ryd
6	-55.56473174 ryd
8	-55.56362132 ryd
9	-55.56413313 ryd
10	-55.56432337 ryd
12	-55.56412203 ryd
14	-55.56414651 ryd
16	-55.56415602 ryd

 Energy is converged to ~5 meV/atom at a 10x10x10 mesh

Convergence of FCC (45 Ryd cutoff, 5.5 bohr lattice parameter)

Kpoints(even mesh)	E
2	-55.14820702 ryd
4	-55.36825753 ryd
6	-55.36426651 ryd
8	-55.37169301 ryd
10	-55.36832514 ryd
12	-55.36971125 ryd
14	-55.36917069 ryd
16	-55.36935237 ryd

 Energy is converged to ~5 meV/atom at a 14x14x14 mesh

It is well known (in first-principles literature) that the FCC structure converges poorly with respect to kpoints, unless a shift in kpoint origin is used. We do not use kpoint shifts in this lab.

In part A, you will look at energies using the Perdew-Zunger LDA exchange-correlation. This is the most commonly used LDA exchange-correlation.
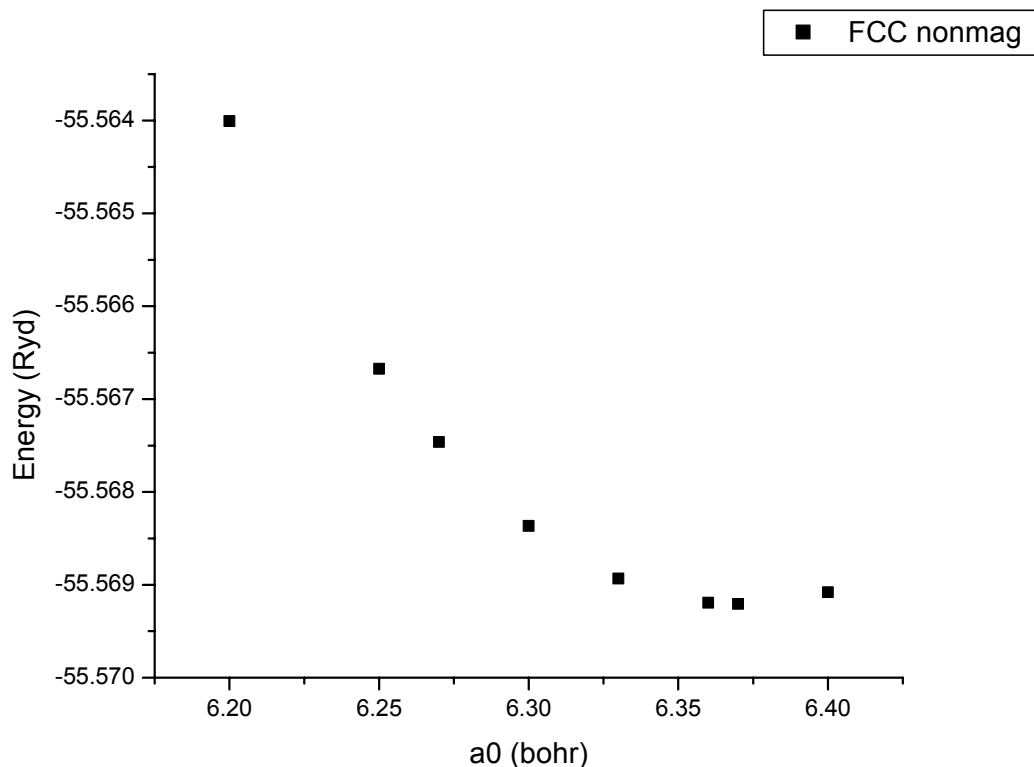
1. Calculate the energy of BCC iron as a function of lattice parameter. Make a plot of the energy vs. lattice parameter. How does this compare to the experimental value? (You should find this value yourself)
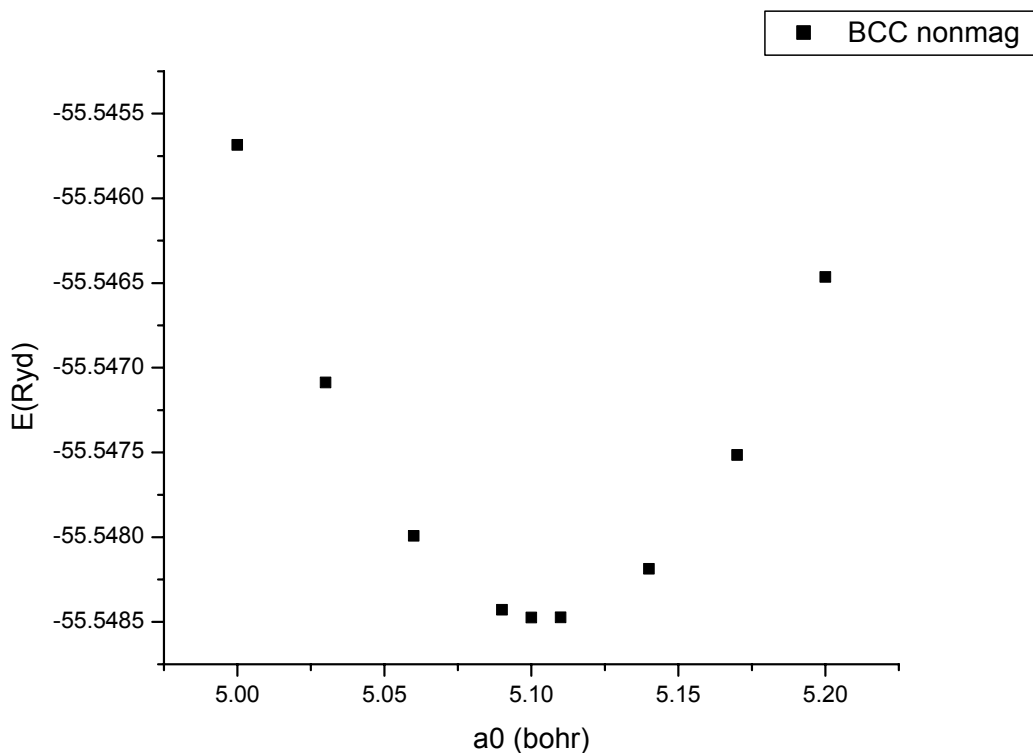
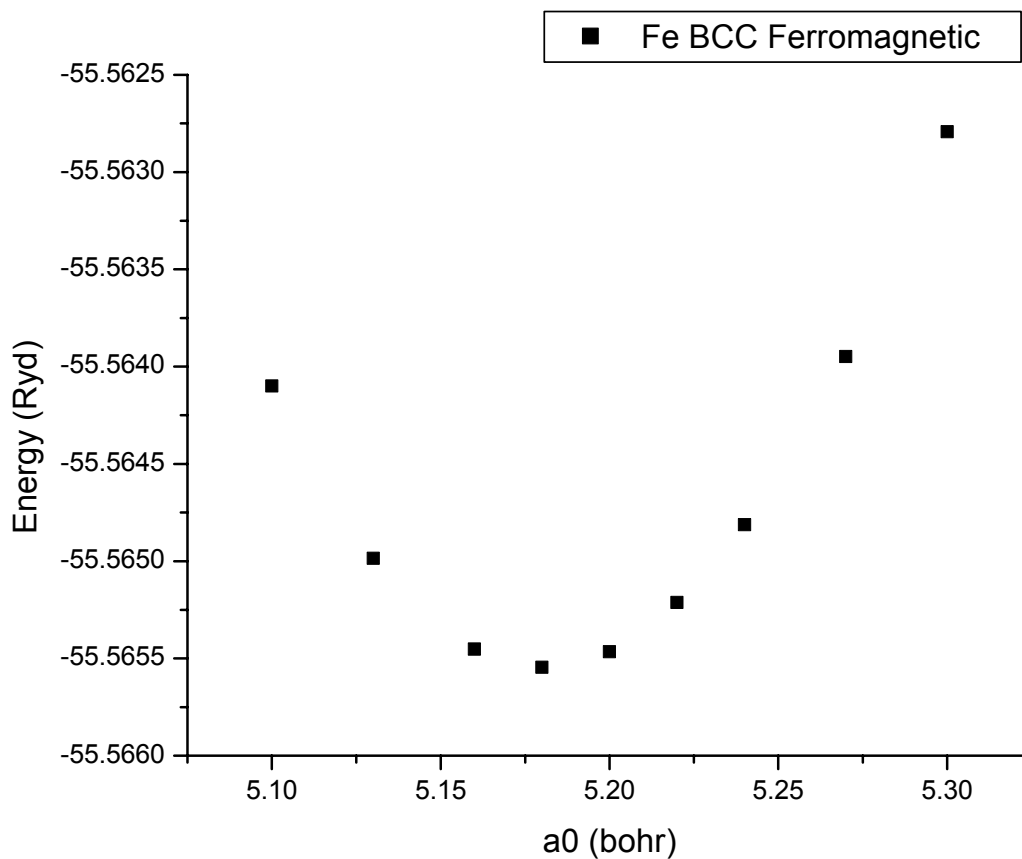**Cutoff of 40 Ryd, 14x14x14 $\bar{k}$ -points grid.**

The lattice constant is 5.10 bohr (2.70 Angstroms). This is slightly lower than the experimental value of 2.87 Angstroms. The energy is Ryd.

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?

Cutoff of 40 Ryd, 14x14x14 $\bar{k}$ -points grid.
The equilibrium lattice constant is 6.37 bohr. The energy is -55.56920542 Ryd.

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?

Cutoff of 40 Ryd, 14x14x14 $\vec{k}$ -points grid.
The lattice parameter is 5.18 bohr (2.74 Angstroms). The magnetic moment
is 1.97 bohr/cell. E= -55.56554552 Ryd.

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?
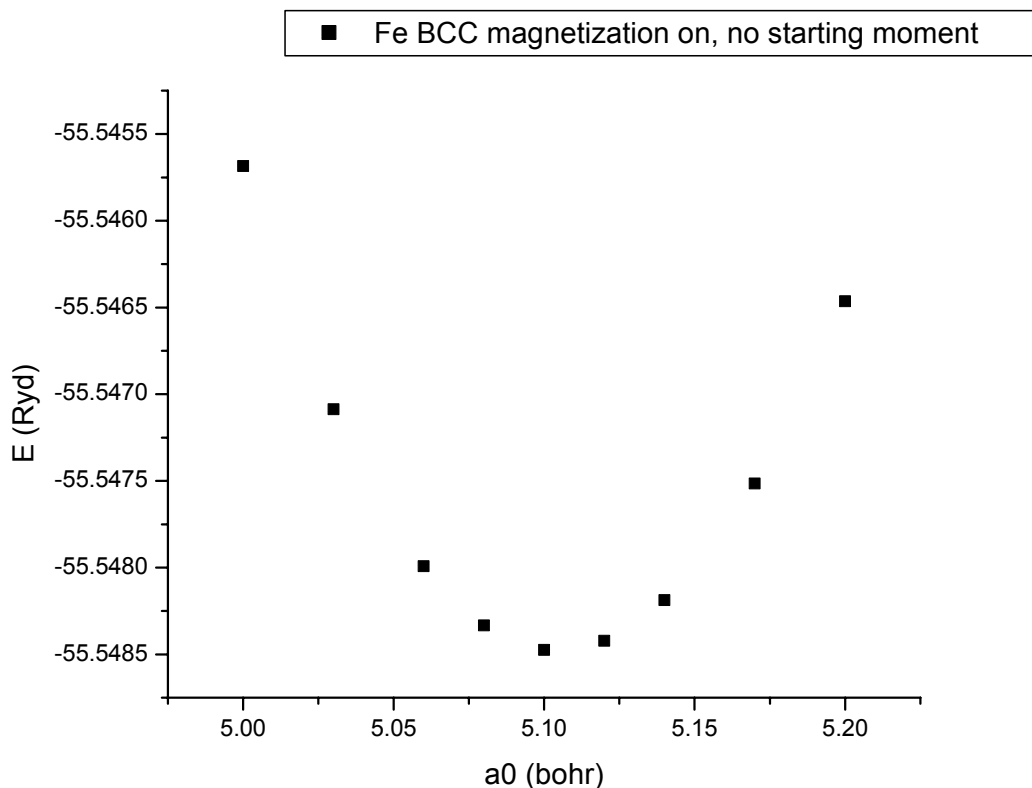
**Cutoff of 40 Ryd, 14x14x14 $\vec{k}$ -points grid.
The lattice parameter is 5.10 bohr, same as in part A. The
magnetic moment is zero, same as when magnetism is turned
off.   This problem shows that there are local minimum that
we can reach, depending on where we start. E= -55.54847489
Ryd, same as before.**

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.

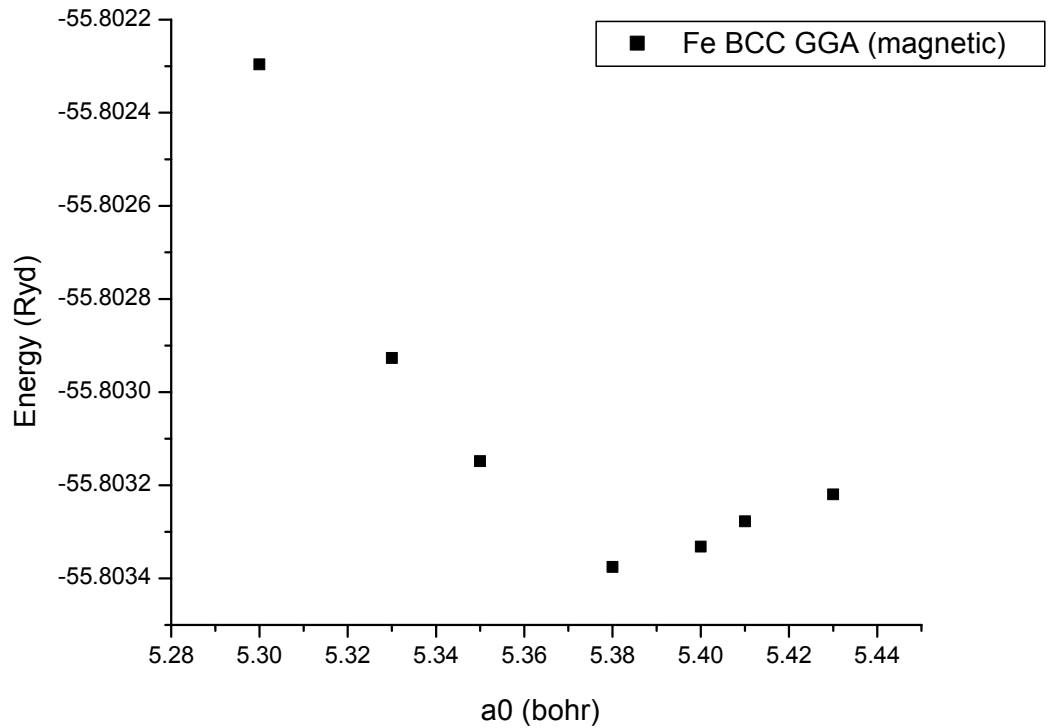**All calculations used cutoff of 40 Ryd, 14x14x14 $\vec{k}$ -points grid.**

BCC:
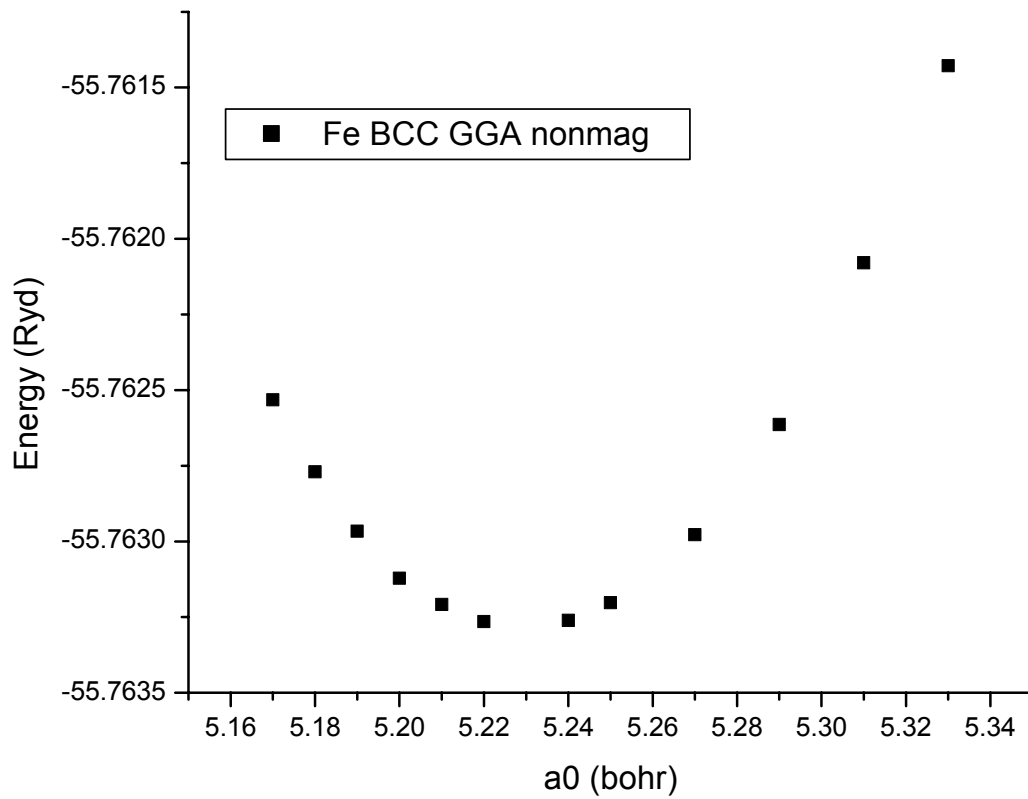
BCC – The lattice parameter was ~5.23 bohr (2.77 Angstroms), slightly less than experiments, but greater than the LDA. E=-55.76326454 Ryd.
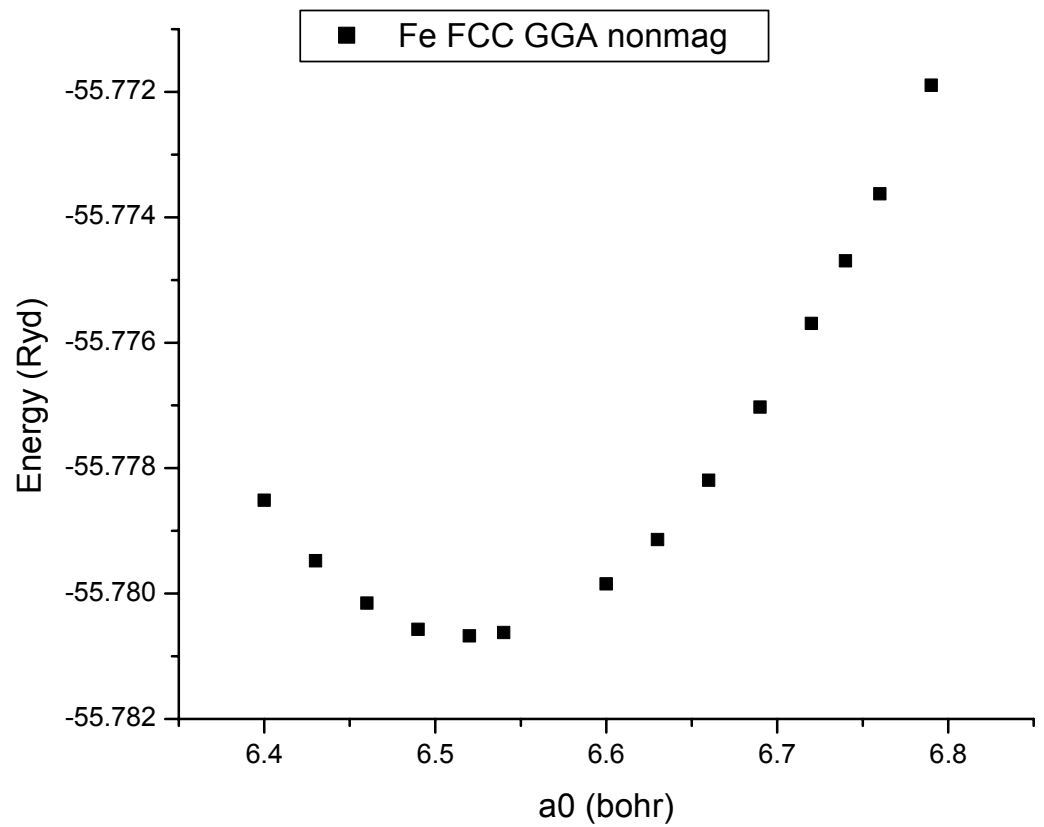
FCC – The lattice parameter was ~6.52 bohr
**E= -55.78067551**

BCC Ferromagnetic

BCC magnetic – The lattice parameter was ~5.38 bohr (2.84 Angstroms), almost the same as experiments experiments, but greater than the LDA. E= -55.80337544 Ryd. The magnetic moment was 2.32 bohr/cell.

C. For LDA calculations, make a diagram showing the hierarchy of 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?   Are any of the calculated results expected or unexpected?

LDA:
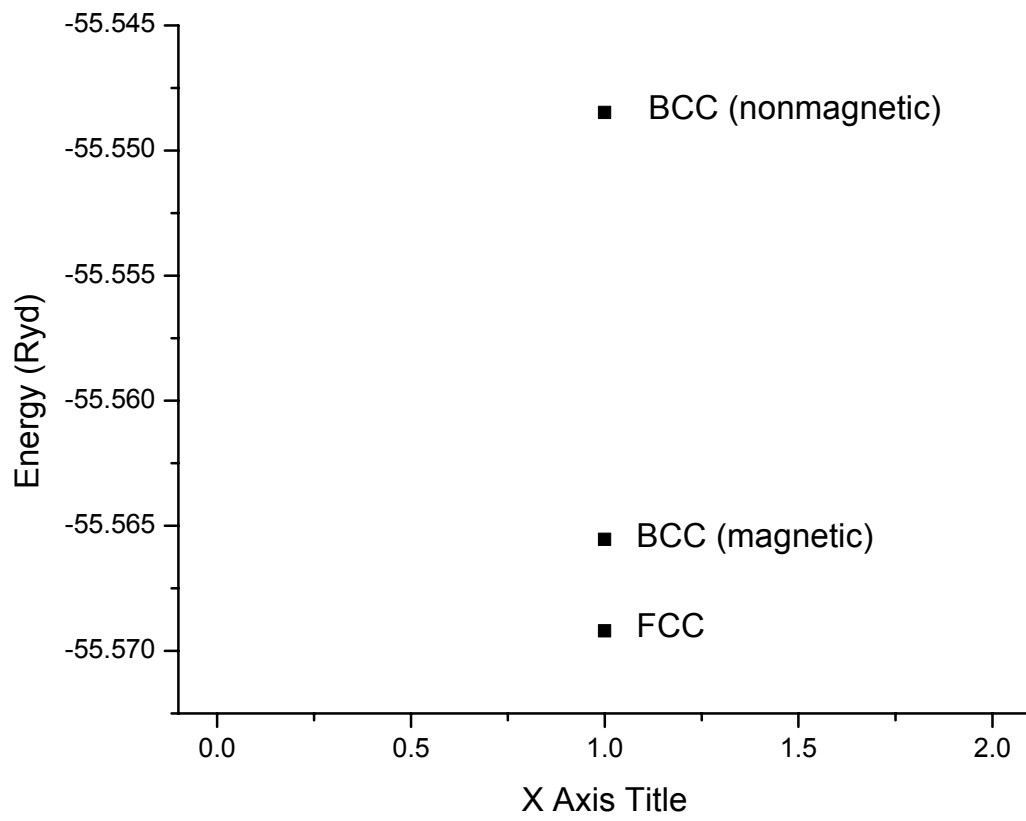
GGA:
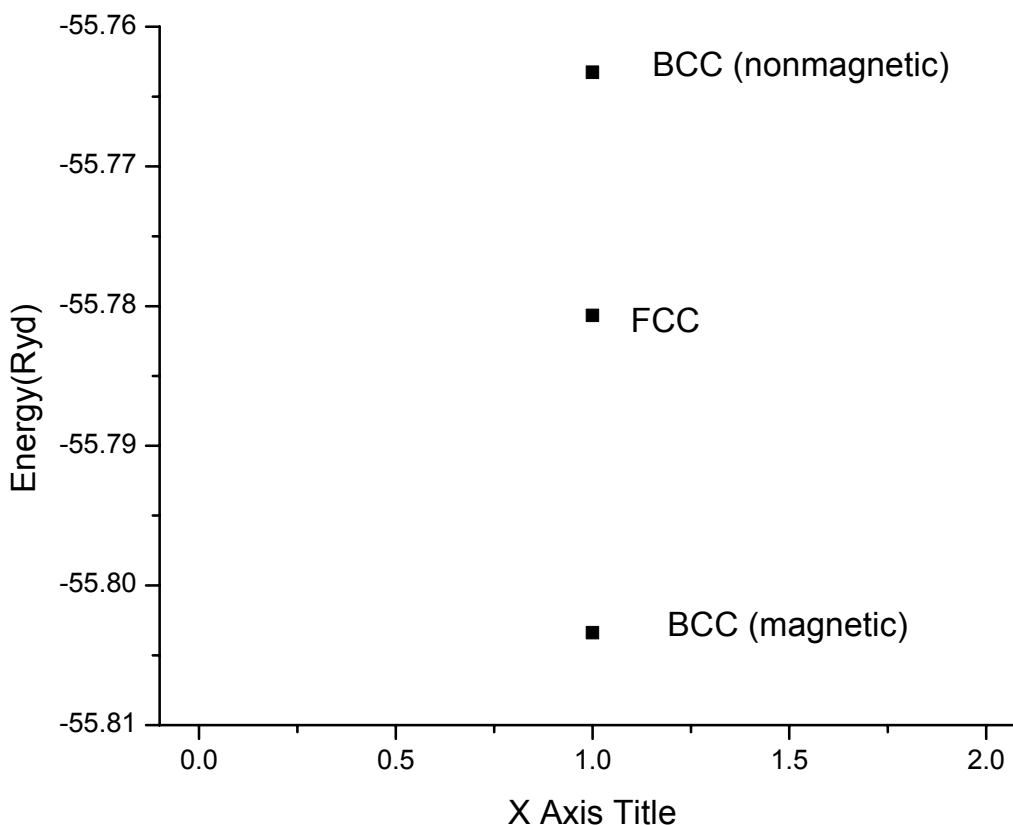
For all cases, the lattice parameters using GGA are larger than using LDA. This is well-known effect of using LDA vs. GGA.   Note, that although GGA agrees better with experiments this time, sometimes GGA will overestimate the lattice constant. Magnetic moments calculated using the GGA are higher than LDA, which agrees with previous calculations (Kresse, Joubert Phys. Rev. B. 59 1758 (1999)).

When spin polarization is turned on, the magnetic moment will depend on the initial conditions. This shows that there are local minima. Note, first principles codes always find local minima. If the code always found global minima, every structure would relax to FCC (LDA) or magnetic BCC (GGA).

Experimentally, Fe is observed to be magnetic and BCC. This is in agreement with the GGA calculations, but in disagreement with the LDA calculations. The Fe example in this problem is *the* classic case of LDA failing. Although the LDA works most of the time, it does not work all of the time. This problem shows the importance of testing first!

Keep in mind GGA works better in this problem but this is not always so. Also, GGA runs take around ~50% longer than LDA runs.

Note, you should never compare absolute GGA numbers directly with absolute LDA numbers.   This would be like comparing apples and oranges, since both have systematic differences that do NOT cancel. However, you can compare differences between structures using the same method. When taking differences, systematic errors and constants will cancel out. If both methods are good for the problem you are investigating, differences between two numbers (done with LDA and done with GGA) should be close.   In this case, the differences are not that close, which shows that both methods are not good for this problem – in this case LDA fails.

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.