3.320 Atomistic Modeling of Materials Spring 2003
Problem set 2: First-principles energy methods

In the empirical energy lab, we looked at problem-specific convergence issues, such as supercell size. We did not look at energy-calculation convergence issues, such as potential cutoff range. In Problem set 2, we will examine energy-calculation convergence issues of first-principles calculations. The two issues we will examine are energy cutoff and $\vec{k}$ -point grid size.

Problem 1 (10 points): Convergence of *absolute energies* with respect to cutoff energies.

A. Using PWSCF, calculate the energy of GaP as a function of cutoff energy. A good increment might be ~5 Ryd, in the range of 5-50 Ryd. When changing the cutoff, make sure to keep the other variables (lattice constant, $\vec{k}$ - points, etc..) fixed. Record all relevant parameters such as lattice constant, $\vec{k}$ -points, and so on. Record and plot your final results. A good absolute energy value is converged to ~5 meV/atom (convert this to Ryd). Specify when you reach this level of convergence. Note that PWSCF calculates energy per primitive cell.

B. Do you see a trend in your calculated energies with respect to cutoff? If you see a trend, is this what you expect and why? If not, why?

C. In Problem Set 1, we used a cubic cell. Here, we use the primitive cell. What are the advantages and disadvantages of both methods?

Problem 2 (10 points): Convergence of *absolute energies* with respect to $\vec{k}$ -points.

A. Using PWSCF, calculate the energy as a function of $\vec{k}$ -point grid size. For each grid, record the number of unique $\vec{k}$ -points. This gives a measure of how long your calculation will take - calculations scale as K, where K=number of unique $\vec{k}$ -points. When changing the size of the $\vec{k}$ -point grid, make sure to keep your other variables (lattice constant, cutoff, etc..) fixed. HINT: To save time, you can choose a lower cutoff than the "converged" cutoff in the last problem. There are some "cross effects" in doing so, however we assume these are small.

B. Do you see a trend in your calculated energies with respect to grid size? If you see a trend, is this what you expect and why? If not, why?

Problem 3 (10 points): Convergence of *forces* with respect to cutoff energies.

A. Sometimes, we are interested in quantities other than energies. In this problem, we will be calculating forces on atoms. Displace the P atom +0.10 in the *z* direction (fractional coordinates). Keeping other parameters fixed, calculate the forces on P as a function of cutoff. A good force value would be converged to within ~10 meV/A (convert this to Ryd/bohr - PWSCF gives forces in Ryd/bohr). Don't forget to record relevant parameters (lattice parameter, $\vec{k}$ -points, unique $\vec{k}$ -points etc..). A good $\vec{k}$ -point grid to use is 3x3x3. Plot and record your results.

Problem 4 (10 points): Convergence of *forces* with respect to $\vec{k}$ -points.

A. Using PWSCF, calculate the force on the P atom (displaced +0.10 in fractional coordinates) as a function of $\vec{k}$ -point grid size. Keep all other parameters fixed. Record relevant your conditions (lattice parameter, cutoffs, etc..). HINT: To save time, you can choose a lower cutoff than the "converged" cutoff in the last problem, say 15 Ryd. There are some "cross effects" in doing so, however we assume these are small.

Problem 5 (5 points): Convergence of *energy differences* with respect to energy cutoffs.

A Using PWSCF, calculate the energy difference between GaP at two lattice parameters as a function of cutoff. For example, you could calculate the energy for GaP at the experimental lattice parameter, calculate the energy for GaP at 10.15 bohrs (or any lattice parameter close to the minimum), take the difference between the two, and repeat for many energy cutoffs. Make sure to keep your other variables (lattice constant, $\vec{k}$ - points, etc..) fixed while changing the cutoff. Record all relevant parameters such as lattice constant, $\vec{k}$ -points, and so on. A good energy difference is converged to ~5 meV/atom (convert this to Ryd).

Problem 6 (10 points) Comparing Probs. 1, 2, 3, and 4, and 5:

How do the cutoff requirements change when looking at absolute energies vs. looking at forces vs. energy differences? How do the $\vec{k}$ -point grid requirements change?

Problem 7 (45 points): Equilibrium lattice constant and bulk modulus.

This problem has you calculating the equilibrium lattice constant and bulk modulus of GaP.

Usually, we are interested in quantities such as forces or energy differences. We are not usually interested in absolute energies. For this reason, use the cutoff and $\vec{k}$ -point criteria that you determined for the force and energy difference calculation for this problem.

Note, to be absolutely safe you should test for the quantity you are interested in. Ideally, we would test convergence of lattice constant as a function of energy cutoff and $\vec{k}$ -point grid size. For now, just use the force criteria.

A. Calculate the equilibrium lattice constant of GaP using PWSCF. The experimental value is 5.45 Angstroms. Use the cutoff and $\vec{k}$ -point grid criteria you obtained from the force convergence calculations. How does the experimental value compare with the calculated value? Is this expected? Make sure to record all the relevant parameters ($\vec{k}$ -points, cutoffs, etc..).

B. Calculate the bulk modulus of GaP. This problem will have you derive some (simple) equations and then apply them to solving a problem. This type of procedure (derive and calculate) happens all the time in the computational sciences.

The bulk modulus is a measure of the stiffness of a material. The bulk modulus is defined as

$$B=-V_0 \frac{dP}{dV}, \text{ where } V_0 \text{ is the equilibrium volume.}$$

Derive an expression for the bulk modulus, and calculate it.
How does your value compare with the experimental value of $8.8\text{x}10^{11}$ dyn cm^{-2}?

Hint1 : Remember $P = pressure = -\frac{dE}{dV}$.
Hint 2: Remember the program calculates energies per primitive unit cell.

The following page may help with units:

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

Extra credit question (but longer and harder, OPTIONAL!) (40 points):

For GaP, calculate C11, C12, and C44 using first-principles energy methods. To do this, you will need to compute the energetics of deformation, and fit the resulting energy curves. The following links may help you:

http://cst-www.nrl.navy.mil/bind/static/example15/index.html
http://www.tfkp.physik.unierlangen.de/~oli/physics/downloads/elasthowto.pdf