# 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 factors we will examine are energy cutoff and number of $\vec{k}$ -points.

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 7-50Ryd. 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, etc… Plot your final results. A good value for energy convergence is ~5 meV/atom (convert this to Ryd). Specify when you reach this level of convergence. Note that PWSCF calculated energy per primitive cell.

2x2x2 $\vec{k}$ - grid, 3 unique $\vec{k}$ - points, converged to 5 meV/atom at 45-50 Ryd
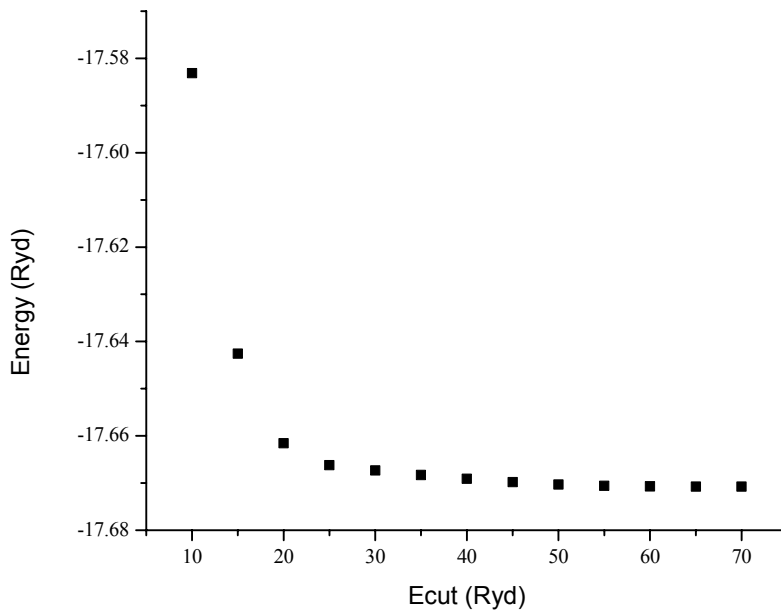
Ecut	E(ryd)		E/atom(Ryd)	E/atom(eV)		convergence(eV)

(Ryd)

5	-17.30666196	-8.65333098	-117.6853013	2.475962172
10	-17.58315472	-8.79157736	-119.5654521	0.595811404
15	-17.64257973	-8.82128987	-119.9695422	0.191721336
20	-17.66159937	-8.83079969	-120.0988757	0.062387784
25	-17.66622302	-8.83311151	-120.1303165	0.030946964
30	-17.66734786	-8.83367393	-120.1379654	0.023298052
35	-17.66829436	-8.83414718	-120.1444016	0.016861852
40	-17.66909222	-8.83454611	-120.1498271	0.011436404
45	-17.66982375	-8.83491188	-120.1548015	0.006462
50	-17.67033414	-8.83516707	-120.1582722	0.002991348
55	-17.67059928	-8.83529964	-120.1600751	0.001188396
60	-17.67076625	-8.83538313	-120.1612105	5.3E-05
65	-17.67076625	-8.83538313	-120.1612105	5.3E-05
70	-17.67077404	-8.83538702	-120.1612635	0

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

Yes, the trend is monotonically (same direction always) decreasing. This is expected from the variational principle, which says any "guessed" wavefunction will always be above the "true" energy. As your "guessed" wavefunction improves with expanded basis, you will approach the true energy.

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?

Using a cubic cell is easier conceptually.
Using a primitive cell makes computations go faster.

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 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.

Ecut=20 Ryd, a0= 10.3043 Bohr
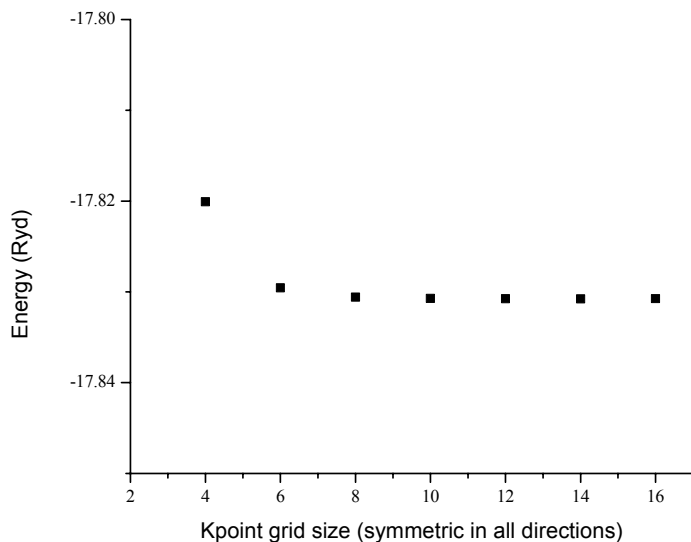
For 4, 6, 7, 8, 10, 12,14, and 16 $\vec{k}$ -grids, there are 8, 16, 20, 29, 35, 47, 72, 104, and 145 unique $\vec{k}$ -points respectively. Converged to ~5meV/atom at ~8x8x8 grid, but a 7x7x7 might work too.

mesh	E(ryd)	E/atom(Ryd)	E/atom(eV)	convergence(eV)
2	-17.66159937	-8.83079969	-120.0988757	1.150232184
4	-17.82007597	-8.91003799	-121.1765166	0.072591304
6	-17.82955562	-8.91477781	-121.2409782	0.008129684
8	-17.83057695	-8.91528848	-121.2479233	0.00118464
10	-17.83072445	-8.91536223	-121.2489263	0.00018164
12	-17.83075779	-8.9153789	-121.249153	4.5072E-05
14	-17.83076898	-8.91538449	-121.2492291	0.000121164
16	-17.83075116	-8.91537558	-121.2491079	0

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

No trend. This is no big deal. There are no systematic effects from replacing a continuous integral with a discrete set of points.

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). Calculate the forces on P as a function

of cutoff, while keeping other parameters fixed. 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, $\bar{k}$ -points, unique $\bar{k}$ -points etc..). A good $\bar{k}$ -point grid to use is 3x3x3. Plot your results.

kgrid 3x3x3, a_0= 10.3043 bohr
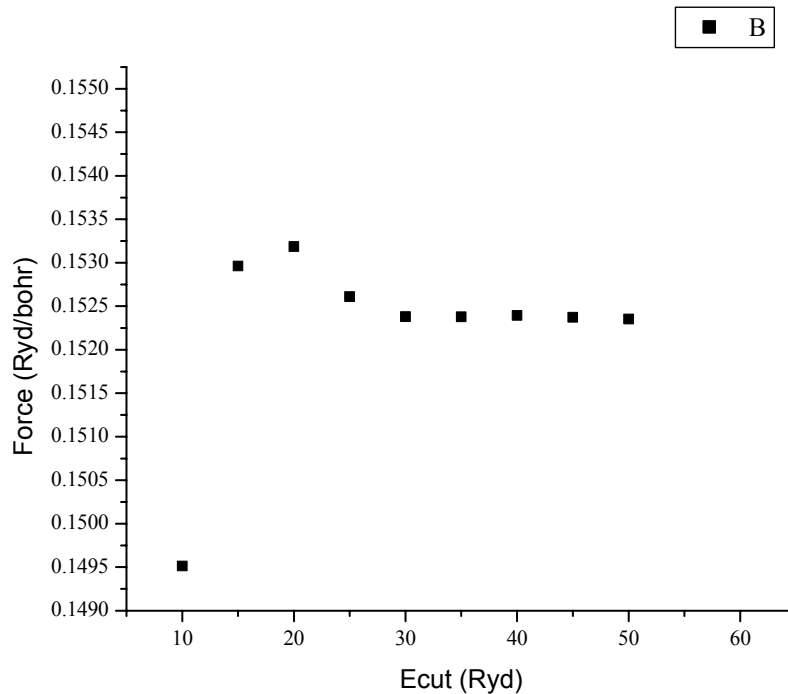
Forces are converged to ~5 meV/Angstrom at ~25 Ryd.

Ecut (Ryd)	F(Ryd/bohr)	F(eV/Ang)	convergence(eV/Ang)
5	0.15421035	2.09726076	0.02524704
10	0.14951243	2.033369048	0.038644672
15	0.15296318	2.080299248	0.008285528
20	0.15318559	2.083324024	0.011310304
25	0.15261039	2.075501304	0.003487584
30	0.15237915	2.07235644	0.00034272
35	0.1523775	2.072334	0.00032028
40	0.15239486	2.072570096	0.000556376
45	0.15237196	2.072258656	0.000244936
50	0.15235395	2.07201372	4.44089E-16

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

A. Using PWSCF, calculate the force on the P atom (displaced +0.10 in fractional coordinates) as a function of $\bar{k}$-point grids. 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.

20 Ryd, experimental lattice constant
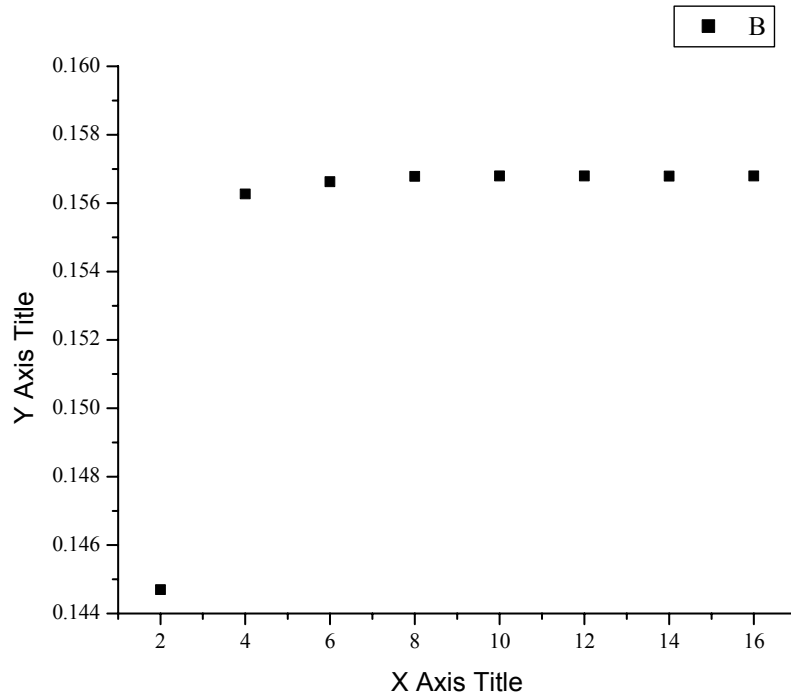
Forces are converged to ~5 meV/Angstrom at cubic grids at ~6x6x6.

mesh	F(Ryd/bohr)	F(eV/Ang)	convergence(eV/Ang)
2	0.14469736	1.967884096	0.164507096
4	0.15626735	2.12523596	0.007155232
6	0.15662718	2.130129648	0.002261544
8	0.15678161	2.132229896	0.000161296
10	0.15679671	2.132435256	4.4064E-05
12	0.1567926	2.13237936	1.1832E-05
14	0.15678836	2.132321696	6.9496E-05
16	0.15679347	2.132391192	0

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.   Specifically, 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 value for energy convergence is ~5 meV/atom (convert this to Ryd). Note, this should be done for atoms at equilibrium positions (as in Problems 1 and 2).
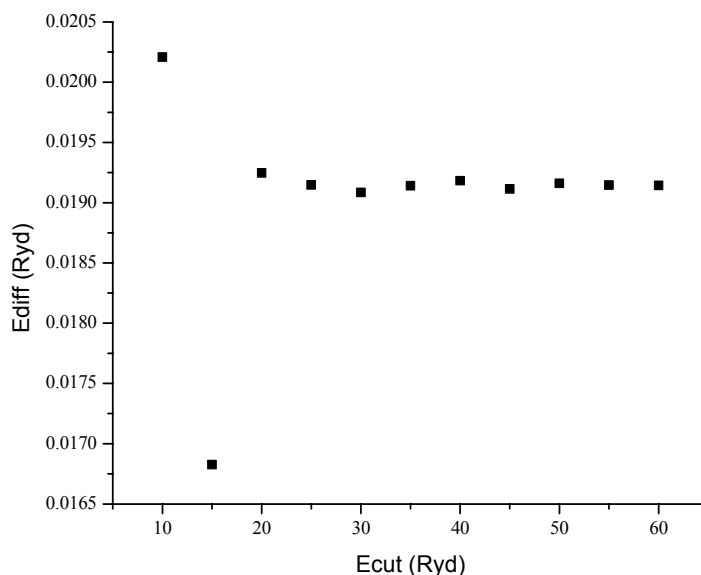
Energy differences are converged to 5 meV at between 20-25 Ryd

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?

The cutoff requirements are lower when calculating at forces and energy differences. The cutoff requirements are higher when calculating absolute energies. On the other hand, the $\vec{k}$ -point requirements are roughly the same.   These problems show that different problems have different convergence issues.   Note that we often care about energy differences and forces, but we almost never care about absolute energies.

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. That would take a long time, so just use the force criteria for now.

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..). This should be done for atoms at equilibrium positions (as in Problems 1, 2, and 5).

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

$$\text{B=-}V_0\frac{dP}{dV}$$

Where V_0 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 $P = pressure = -\dfrac{dE}{dV}$.

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

Expand the energy in a Taylor series as a function of volume.

$$E(V) = E(V_0) + (V - V_0)\frac{dE}{dV} + \frac{(V - V_0)^2}{2}\frac{d^2E}{dV^2}$$

P$= -\dfrac{dE}{dV}$ **=0 at equilibrium**

$$E(V) = E(V_0) + \frac{(V - V_0)^2}{2}\frac{d^2E}{dV^2}$$

Now use P$= -\dfrac{dE}{dV}$

$$E(V) = E(V_0) - \frac{(V - V_0)^2}{2}\frac{dP}{dV}$$

Now use B=-$V_0\dfrac{dP}{dV}$

$$E(V) = E(V_0) + \frac{(V - V_0)^2}{2V_0}B$$

Ecut-25 Ryd, 29 unique kpoints (8x8x8 grid)

Data: Data1_C
Model: user5

Chi^2 = 3.9115E-11
R^2   = 0.9989

P1   -17.83867   ±2.2316E-6
P2   256.75929   ±0.01724
P3   0.00656   ±0.00006
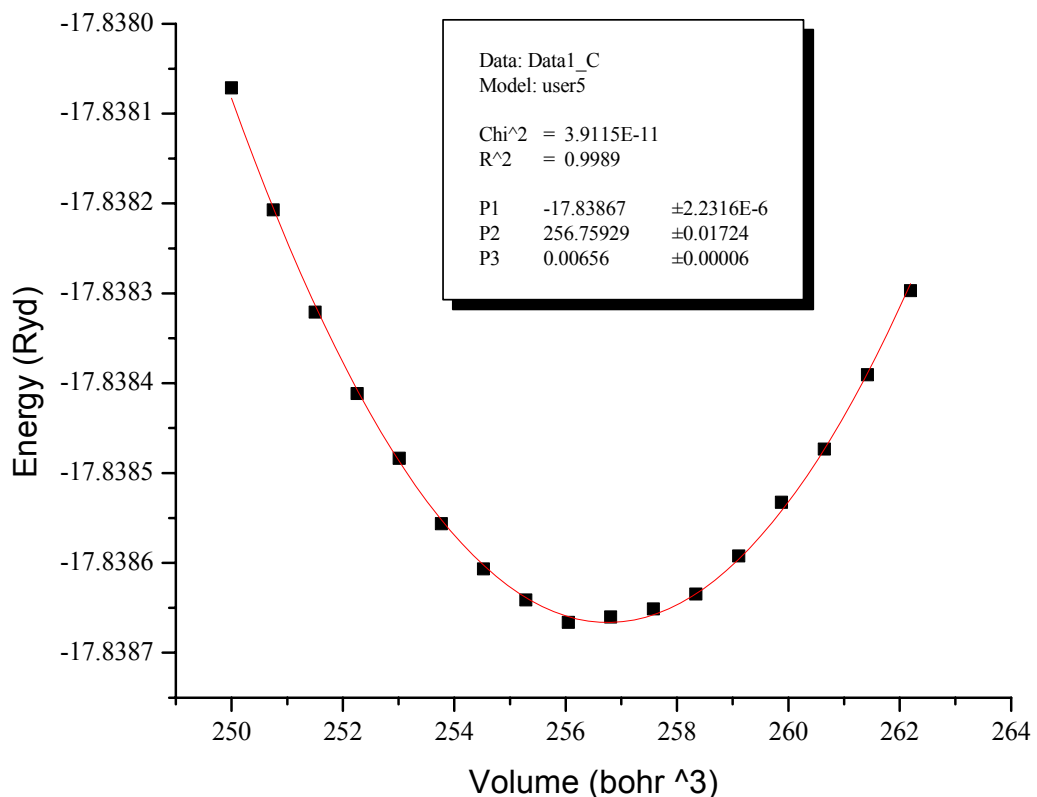
P1=E_0=-17.83867
P2=V_0=256.75929
P3=B=0.00656

The lattice parameter is ~10.089 bohr= 5.34 angstroms. This is slightly below experimental values, which is expected for DFT calculations with the LDA (only LDA!) exchange correlation.

B=0.00656 Ryd/bohr^3. The conversion is 1.47×10^{14} to go from Ryd/Bohr^3 to dyne/cm^2. This gives us B=9.64×10^{11} dyn/cm^2, in good agreement with experiments. The calculated bulk modulus is slightly higher than experimental values. All things being equal (and assuming a good pseudopotential), this is expected because LDA overbinds slightly.

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

For GaP, Calculate C11, C12, and C44 using the 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