

3.320 Atomistic Modeling of Materials Spring 2005

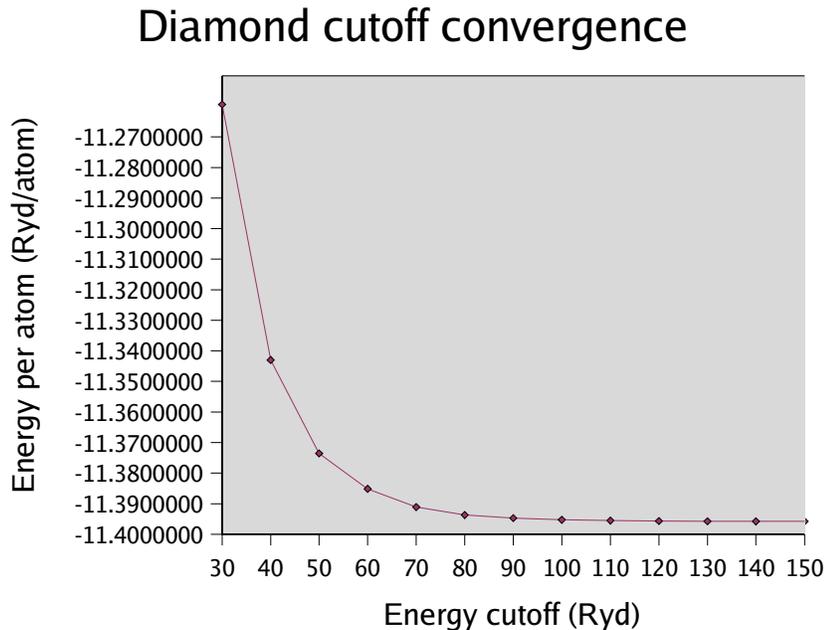
Solution set 2: First-principles energy methods

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

- A. Using PWSCF, calculate the energy of diamond as a function of cutoff energy. A good increment might be ~ 10 Ryd, in the range of 10-140 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.

Note that 5meV is approximately 0.0004 Ryd

Using a lattice constant of 6.60 bohr and a 4x4x4 kpoint grid.



Energy cutoff (Ryd)	Cell Energy (Ryd)	Energy per atom (Ryd/atom)	Delta E (Ryd/atom)
30	-22.5188058	-11.2594029	0.1364080
40	-22.6859706	-11.3429853	0.0528256
50	-22.7470911	-11.3735456	0.0222653
60	-22.7703286	-11.3851643	0.0106466
70	-22.7822043	-11.3911022	0.0047087
80	-22.7874363	-11.3937182	0.0020927
90	-22.7894369	-11.3947185	0.0010924
100	-22.7905116	-11.3952558	0.0005551
110	-22.7910740	-11.3955370	0.0002739
120	-22.7913723	-11.3956862	0.0001247
130	-22.7915112	-11.3957556	0.0000553
140	-22.7915795	-11.3957897	0.0000211
150	-22.7916218	-11.3958109	0.0000000

Delta E is the difference from the most accurate number (at cutoff of 150 Ryd). The converged energy cutoff appears to be approximately 110 Ryd for this particular lattice constant and k-grid.

- 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?

Yes, the energy is monotonically decreasing with increasing cutoff. This behavior is a direct result of the variational principle. By not including an infinite number of basis functions we will always overestimate the ground state energy. However, we can get arbitrarily close to the ground state energy as the number of basis functions approaches infinity.

- 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?

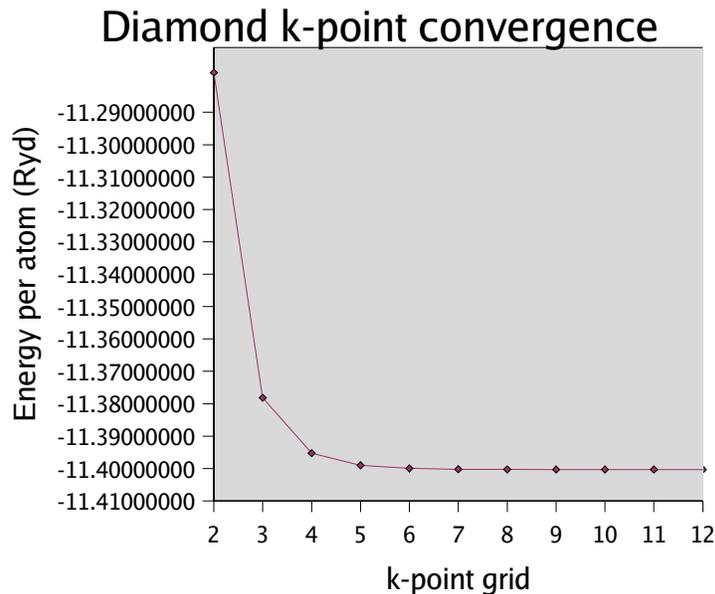
A cubic or conventional cell tends to be easier to work with conceptually. Most materials scientists and physicists have a clear mental picture of a cubic lattice. Most properties of interest are also communicated with reference to the conventional cell(i.e. [100] direction, (111) plane, etc. use the lattice vectors of a conventional cell, not a primitive one). The cost of the simplicity is a larger volume cell and a bit of redundancy since symmetrically equivalent atoms may need to be declared multiple times.

The primitive cell takes the most advantage of the symmetry of the crystal. Atoms in the asymmetric unit need only be declared once which is more efficient computationally.

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.

Using a lattice constant of 6.60 bohr and an energy cutoff of 100 Ryd:



k-point grid	unique k points	Cell energy (Ryd)	Energy per atom (Ryd)	Delta E (Ryd)
2	3	-22.55551018	-11.27775509	0.12256136
3	4	-22.75628990	-11.37814495	0.02217150
4	8	-22.79051162	-11.39525581	0.00506064
5	10	-22.79803329	-11.39901665	0.00129981
6	16	-22.79992168	-11.39996084	0.00035561
7	20	-22.80042493	-11.40021247	0.00010399
8	29	-22.80057082	-11.40028541	0.00003104
9	35	-22.80061578	-11.40030789	0.00000856
10	47	-22.80062788	-11.40031394	0.00000251
11	56	-22.80063077	-11.40031539	0.00000106
12	72	-22.80063290	-11.40031645	0.00000000

Convergence is achieved with a 6x6x6 k-point grid for this lattice constant and cutoff.

- 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?

One might argue that the energy is monotonically decreasing but that does not necessarily happen all the time. No systematic trend can be predicted from just increasing the sampling points for the approximation to the integral.

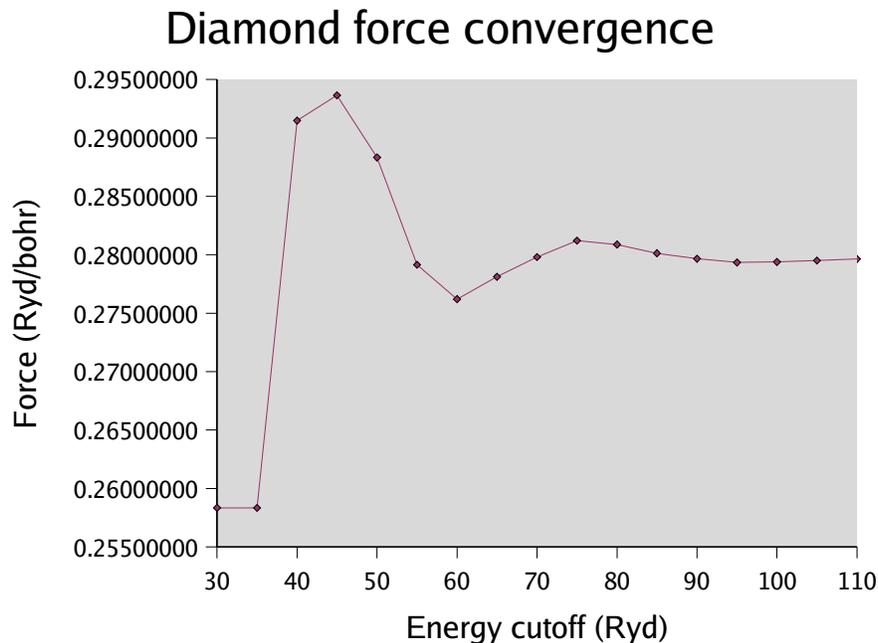
Problem 3 (10 points): Convergence of *forces* with respect to cutoff energies.

- A. Sometimes, we are interested in quantities other than energies. In this problem, we will be calculating forces on atoms. Displace a C atom +0.05 in the z direction (fractional coordinates). Keeping other parameters fixed, calculate the forces on C as a function of cutoff. A good force value would be converged to within ~ 10 meV/Angstroms (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 $4 \times 4 \times 4$. Plot and record your results.

Using a lattice constant of 6.60 bohr and a $4 \times 4 \times 4$ k-point grid.

Displacing the C atom at (0.25,0.25,0.25) to (0.25,0.25,0.30).

Note that 10meV/Angstrom is approximately 0.0004 Ryd/bohr.

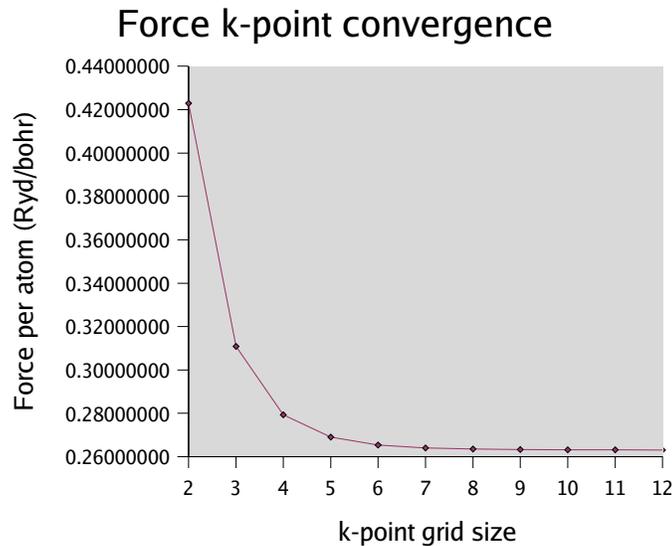


Energy cutoff (Ryd)	z-force per atom (Ryd/bohr)	Delta force (Ryd/bohr)
30	0.25834978	-0.02129270
35	0.25833872	-0.02130376
40	0.29147917	0.01183669
45	0.29364139	0.01399891
50	0.28832961	0.00868713
55	0.27914217	-0.00050031
60	0.27620612	-0.00343636
65	0.27811338	-0.00152910
70	0.27980402	0.00016154
75	0.28120779	0.00156531
80	0.28088179	0.00123931
85	0.28013161	0.00048913
90	0.27966108	0.00001860
95	0.27934565	-0.00029683
100	0.27938801	-0.00025447
105	0.27951065	-0.00013183
110	0.27964248	0.00000000

Convergence is achieved in this case at approximately 90 Ryd. The oscillations can be reduced by choosing a denser k-grid.

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

Using PWSCF, calculate the force on a C atom (displaced +0.05 z direction in fractional coordinates) as a function of \vec{k} -point grid size. Keep all other parameters fixed. Record your relevant conditions (lattice parameter, cutoffs)
Using a lattice constant of 6.60 bohr and an energy cutoff of 100 Ryd.

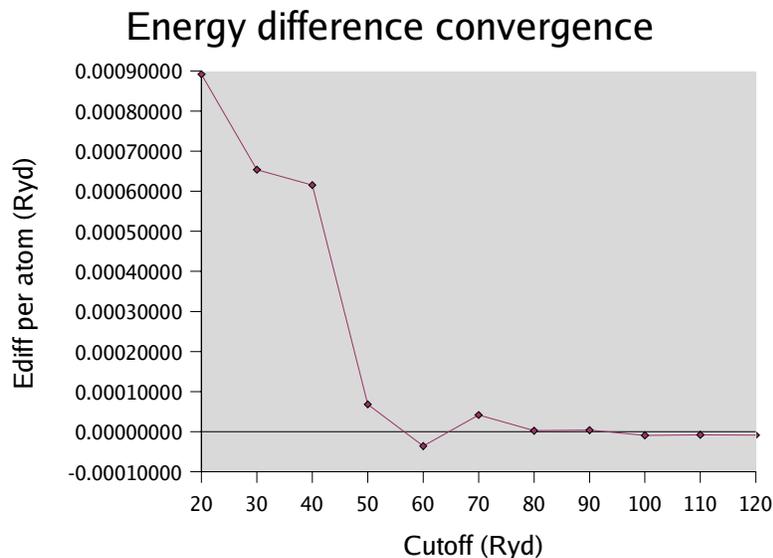


k-point grid size	Force per atom (Ryd/bohr)	Delta force (Ryd/bohr)
2	0.42290533	0.15975365
3	0.31082503	0.04767335
4	0.27938801	0.01623633
5	0.26903441	0.00588273
6	0.26536995	0.00221827
7	0.26402655	0.00087487
8	0.26350561	0.00035393
9	0.26329463	0.00014295
10	0.26324349	0.00009181
11	0.26319027	0.00003859
12	0.26315168	0.00000000

Convergence at cutoff of 100 Ryd is achieved at a gridsize of 8x8x8. If you chose the cutoff too low, you may see some outliers and oscillations.

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

Using PWSCF, calculate the energy difference between diamond structures at two lattice parameters as a function of cutoff. For example, you could calculate the energy of diamond at the experimental lattice parameter (6.74 bohr), then calculate the energy at 6.70 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).



Cutoff (Ryd)	energy per cell (6.70) (Ryd)	energy per cell (6.74) (Ryd)	Energy per atom (6.70) (Ryd)	Energy per atom (6.74) (Ryd)	Ediff per atom (Ryd)	Delta Ediff (Ryd)
20	-22.144063	-22.145846	-11.072031	-11.072923	0.00089184	0.00090056
30	-22.499623	-22.500930	-11.249811	-11.250465	0.00065361	0.00066233
40	-22.654622	-22.655852	-11.327311	-11.327926	0.00061522	0.00062394
50	-22.715673	-22.715809	-11.357837	-11.357905	0.00006802	0.00007674
60	-22.740049	-22.739977	-11.370024	-11.369988	-0.00003612	-0.00002740
70	-22.750784	-22.750867	-11.375392	-11.375433	0.00004161	0.00005034
80	-22.755554	-22.755558	-11.377777	-11.377779	0.00000219	0.00001091
90	-22.757813	-22.757820	-11.378907	-11.378910	0.00000374	0.00001246
100	-22.758890	-22.758872	-11.379445	-11.379436	-0.00000908	-0.00000036
110	-22.759391	-22.759375	-11.379696	-11.379688	-0.00000796	0.00000076
120	-22.759672	-22.759655	-11.379836	-11.379827	-0.00000872	0.00000000

For lattice constants of 6.70 bohr and 6.74 bohr and a k-point grid of 8x8x8, convergence can be claimed at an energy cutoff of 50 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? Can you explain this?

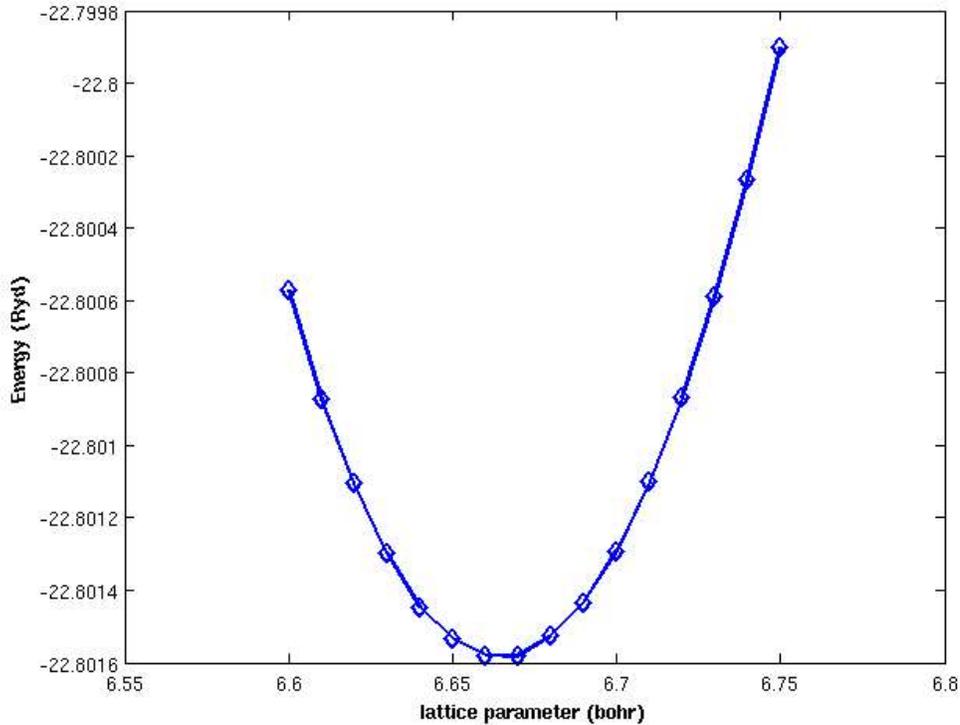
Energy cutoffs can be set to a lower value when we are only interested in the forces or for energy differences. Convergence of the absolute energy is the hardest to achieve.

k-point requirements are roughly the same for the calculations shown here, however the kpoint requirements for the broken symmetry used for the displaced carbon atom are higher than the kpoint requirements for the completely symmetric case. It is generally true that different geometries will require different k-point meshes in order to reach convergence. However, the change in required k-point density for a slight shift in atoms is expected to be far less than the change in required k-point density if we completely change the crystal symmetry(e.g. fcc to bcc).

The key point here is that different calculations will have different convergence issues. (i.e. calculations of absolute energies require stricter conditions for convergence and are therefore more expensive.)

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

- A. Calculate the equilibrium lattice constant of diamond using PWSCF. The experimental value is 6.74 bohr. 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..).



Using an energy cutoff of 100 Ryd and a 8x8x8 kpoint grid, the lattice constant is calculated using energies to be about 6.67 bohr. This value is smaller than the experimental lattice constant of 6.74 bohr. This result is expected since we know that LDA will typically overbind.

- B. Calculate the bulk modulus of diamond. 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.

One way of getting an expression is just to plug in P:

$$B = -V_0 \frac{dP}{dV} = V_0 \frac{d^2 E}{dV^2}$$

Now just obtain the curvature of your energy versus volume curve and multiply by your equilibrium volume to get bulk modulus. Note that your origin must be located at the equilibrium volume in order to use this method. Also note that the primitive cell volume is 1/4th the volume of the conventional cell.

A slightly more involved but just as simple is to use a Taylor expansion with respect to volume in the region near V_0 .

$$E(V) = E(V_0) + (V - V_0) \left(\frac{dE}{dV} \right)_{V=V_0} + \frac{(V - V_0)^2}{2} \left(\frac{d^2 E}{dV^2} \right)_{V=V_0} + O((V - V_0)^3)$$

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

We used MATLAB to fit the data to this equation but any spreadsheet/stats package should be able to spit out the fitting parameters and residuals. Our value for B using this method is 0.03137 Ryd/bohr³. The conversion factor from these units is 1.47x10¹³. The final answer in the appropriate units is about 461 GPa.

The obtained value compares quite well with the experimental value of 442 GPa. Using the argument that LDA overbinds, one usually expects moduli which are higher than experiment.