MSE760 Lab 3 Report

Abinit Convergence study and defect properties

Lijing Yang

Mechanical Engineering Department, University of Wisconsin – Madison

March 21, 2018

1 Total energy of Si with respect to cutoff energy

Convergence study was performed with respect to the energy cut-off in order to find the minimum ecut required for a convergence of total energy. Ecut is defined to be used for kinetic energy cutoff which controls number of plane waves at given k point [1], and is always suggested to be determined with several calculations at the beginning as a convergence test.

It is shown in Fig. 1 that when ecut reaches 8.0 Ha, total energy is converged. Here a k-point mesh of 2x2x2 grid is applied in the Brillouin zone with a primitive unit cell (2 Si atoms in a unit cell). It's also found that the total energy after convergence is not the same as cohesive energy since an isolated atom is still given some energy in DFT.

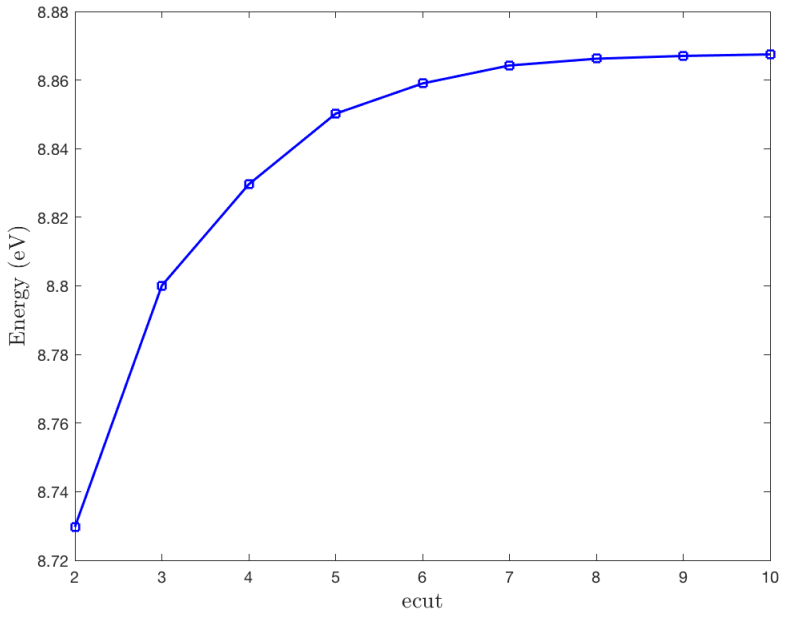

Figure 1: Total energy with varied ecut, Note that units of ecut and total energy should both in Ha instead of eV

2 Total energy of Si with respect to k-points

A convergence of total energy can be found at k-point mesh 6x6x6 as shown in Fig. 2

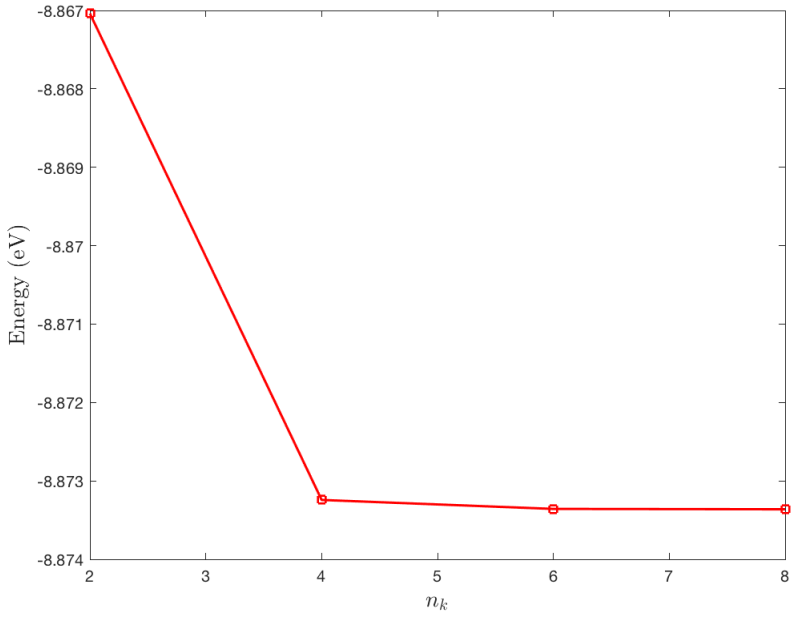

Figure 2: Convergence study with respect to k-points. the energy unit should also be in Ha instead of eV

3 Determine lattice parameter with varied k-points

optcell is enabled to optimize the volume of unit cell only, with it set to 1, only the volume is optimized excluding rprim, which brings up a difference in output of acell compared to the fixed volume in convergence test of part 1. A slightly larger dilatmx sets the effective ecut to be 1.05 times of ecut=9.0. ecutsm (smearing) is set to smooth the total energy.

It can be seen from Fig. 3 that as n_k increases, lattice parameter will reach to a steady value close to 10.1995 Bohr, which is 5.397Å, whereas the experimental value is 5.431Å. The difference might be due to the way optcell 1 works, since it introduces a homogeneous dilatation of the three components of a cell, which is normally not the actual condition, especially in experiments. If optcell is set to 2, which allows a full optimization of cell geometry (both volume and rprim), the result of acell might become closer to experimental value.

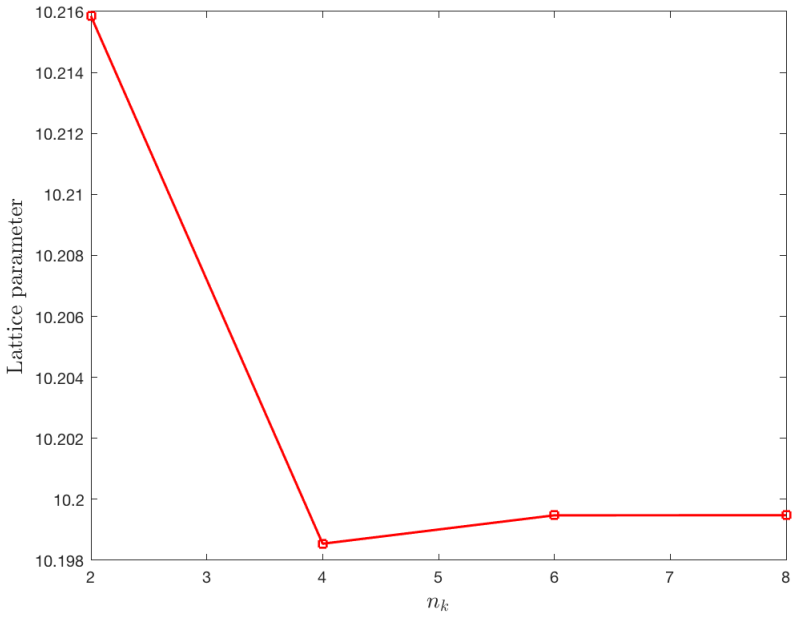

Figure 3: Convergence of lattice parameter with optcell enabled and relaxed ecut through dilatmx larger than 1.0

4 Vacancy formation energy of Si

As a change of set up, conventional unit cell is used instead of primitive unit cell used for the previous tests. 8 and 64 atoms are used, with 1x1x1 unit cell and 2x2x2 unit cells associated respectively, while ecut is set to 8.0, as the minimum value leading to a convergence of total energy from the first test. LDA (Local Density Approximation) method is applied.

The vacancy formation energy can be obtained from:

$$E_f[V_{Si}] = E_{def} - (N_{Si} - 1)\frac{E_{perf}}{N_{Si}} \tag{1}$$

which gives a result of 3.2433eV for vacancy formation energy of 8 atom supercell, and 3.8084eV for vacancy formation energy of 64 atom supercell.

Compared with the result from 215 atoms supercell shown in [2], as for a k-point mesh of 2x2x2, that gives 3.517eV. It is clear that neither 8 atom nor 64 atom supercell performs well on the convergence. The reason could be that k-point needs to be adjusted according to the choice of number of atoms. As presented in [2], a 215 atom supercell requires n_k=5, a 511 atom supercell requires n_k=4, and a 999 atom supercell requires n_k=3 in order to converge. This result implies that the smaller the supercell is, the larger n_k is required to reach a convergence. Therefore, it can be seen from the convergence tests in [2] that a k-point mesh

of 2x2x2 cannot qualify as a large enough n_k value, which leads to a significant variation in achieved vacancy formation energy in the test results.

5 Discussion on the goodness of vacancy formation energy calculation via DFT compared to empirical potential

From the aspect of computational cost, empirical potential is less intensive to fit different experimentally obtained properties, i.e. the lattice constant and bulk modulus, which requires *a priori* knowledge on the problem. In contrast, *ab initio* method, though demands rigorous computational power, could provide a more general and broader solution while no clear *a priori* knowledge presents [3].

Empirical potential tends to be specific, i.e. works only for particular property. An example could be the upgrade from tersoff to modified tersoff in Lab 2. Thus, empirical potential is lack of flexibility, however, it could provide accurate, though narrow results.

References

[1] https://www.abinit.org/sites/default/files/infos/8.0/input_variables/html_automatically_generated/varbas.html#ecut.

[2] AF Wright. Density-functional-theory calculations for the silicon vacancy. *Physical Review B*, 74(16):165116, 2006.

[3] http://cmt.dur.ac.uk/sjc/thesis_prt/node13.html.