

# MatSci 331 Homework 5

## Plane-wave DFT Preliminaries: Brillouin zone sampling, plane-wave cutoff energy, and bulk modulus

Due Monday March 4 at the beginning of class.  
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In this homework, you will write and utilize a simple MATLAB single-particle electronic structure code with periodic boundary conditions. You will also start using Quantum Espresso, a research-level plane-wave basis set DFT code, to explore the role of some of the most important convergence parameters. You will need to log into corn.stanford.edu to run Espresso and be able to do some basic editing of text files on corn. Please see the additional information in this HW distribution for some help on this if you are unfamiliar.

### 1 Single-particle bands

Find the set of MATLAB codes in this homework distribution (on Coursework) to compute the electronic bands in a periodic system for a single electron. These utilize a plane wave basis with the Hamiltonian derived in class,

$$\mathcal{H}_{\vec{k},\vec{G}\vec{G}'} = \frac{\hbar^2}{2m}|\vec{k} - \vec{G}|^2 \delta_{\vec{G},\vec{G}'} + \tilde{V}(\vec{G} - \vec{G}') \quad (1)$$

The single-particle wavefunctions expanded in a plane wave basis have the form,

$$\psi_{\vec{k},n}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}, |\vec{G}| < G_{\max}} \alpha_{\vec{k},n}(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad (2)$$

where the sum is over integer combinations of computational cell reciprocal lattice vectors  $\vec{G} \equiv \ell\vec{b}_1 + m\vec{b}_2 + n\vec{b}_3$  of magnitude less than some specified cutoff  $G_{\max}$ . The cutoff is usually expressed in terms of the energy of the equivalent free particle electron,  $\hbar^2 G_{\max}^2 / 2m$ . Higher  $|\vec{G}|$  components of the wavefunction correspond to smaller scale spatial features.

An advantage of using a plane wave basis set over other types, like Gaussian functions, is that the accuracy of the basis can be systematically increased by increasing  $G_{\max}$  since the plane waves are a complete set of functions and Gaussians are not.

The MATLAB code uses atomic units, where  $e = 1$  (electronic charge),  $m = 1$  (electron mass),  $\hbar = 1$  and the distance units are  $a_0 = 0.529177 \times 10^{-10}$  m and energy units are

Hartrees= 27.2 eV. The main MATLAB program sets the lattice vectors to be those of a face-centered cubic primitive cell and computes the reciprocal lattice vectors. A call to a function **get\_plane\_waves** is made to compute all  $\vec{G}$  vectors that have  $\frac{\hbar^2}{2m}|\vec{G}|^2 < \mathbf{ecut}$  or  $|\vec{G}|^2/2 < \mathbf{ecut}$  in atomic units. The kinetic and potential parts of the Hamiltonian matrix are constructed for each  $\vec{k}$  value on a line from  $\Gamma$  to  $L$  in the first Brillouin Zone, i.e.  $\vec{k} = (k_x, k_x, k_x)$  along this direction. The eigenvalues are computed at each of the points and the bands can be plotted.

1. Add a section to the main code that computes the kinetic part of the Hamiltonian along the diagonal. Set **ecut** = 3.0 Hartree and plot the bands from  $\Gamma$  to  $L$ . Set the fcc conventional cell lattice constant to be 7.65 atomic units, the lattice constant for aluminum. Compare your lower energy bands with those (computed) for the aluminum (Al) valence electrons on the class slides. Specifically, compare the energies of the lowest energy bands at the  $\Gamma$  and  $L$  points. What does this comparison suggest about the electronic conductivity of Aluminum? The remarkable correspondence between free-particle electronic states and the valence states of some metals (where the potential is hardly constant!) is a consequence of the pseudopotential effect, to be discussed in class.
2. Increase **ecut** to 6.0 and run the calculation again. How many plane waves are in the calculation now? Plot the bands; what has changed? Have the lowest energy bands changed?
3. Now increase the cubic conventional cell lattice constant to 20.0 and compute the bands. What is the number of plane waves and has it changed? Make a plot of the lowest energy bands. What features of the lowest energy bands have changed. Explain why.
4. Did it run any slower with the larger cutoff? The time required to compute all the eigenvalues of a matrix of dimension  $N \times N$  typically scales like  $N^3$ .
5. Now add an atom to the potential part of your Hamiltonian. The hydrogen atom has  $V_{\text{atom}}(\vec{r}) = -e^2/r$  so the full potential for the crystal is,

$$V(\vec{r}) = \sum_{\vec{R}} \frac{-e^2}{|\vec{r} - \vec{R}|} \quad (3)$$

assuming one of the hydrogen atoms is located at the origin. Recall that  $\vec{R} = t\vec{a}_1 + u\vec{a}_2 + v\vec{a}_3$  where  $t$ ,  $u$ , and  $v$  are integers. Fourier transforming the crystal potential,

$$\tilde{V}(\vec{G}) = \int \frac{d\vec{r}}{N\Omega} V(\vec{r}) e^{i\vec{G} \cdot \vec{r}} = \int \frac{d\vec{r}}{\Omega} V_{\text{atom}}(\vec{r}) e^{i\vec{G} \cdot \vec{r}} = -\frac{1}{\Omega} \frac{4\pi e^2}{|\vec{G}|^2} \quad (4)$$

where  $N$  is the number of atoms in the crystal and  $\Omega$  is the unit cell volume. With a lattice constant of  $30 a_0$  (large enough for interatomic interactions to be relatively weak, compute the bands and verify that they are relatively flat and exhibit the isolated hydrogen atom spectrum. An **ecut** value of 3.0 Hartrees should do a reasonable job, but you can probably do better.

6. Now make the lattice constant smaller,  $10 a_0$ . What happens to the bands in your fcc hydrogen crystal? What happens to the p-like bands?

In the context of DFT, we will discuss how pseudopotentials can be created for  $\tilde{V}(\vec{G})$  that describe the scattering properties of valence electrons from atoms.

## 2 Espresso preliminaries

On corn, copy the Espresso distribution into your home directory. From your home directory, type,

```
cp -rf /afs/ir.stanford.edu/users/e/v/evanreed/public/espresso-4.2.1/ .
```

Change directory to the **example** directory,

```
cd espresso-4.2.1/example/Si
```

In this directory, find the input file for Si. This input file calculates the total energy for silicon. Study the role of each input keyword in this file by consulting the documentation in the file `/espresso-4.2.1/doc-def/INPUT_PW.def`. There are a variety of text editors available on corn, including gedit. gedit may be the easiest to use if you are unfamiliar with the others.

Si has the diamond structure with two atoms in its face-centered cubic (rhombohedral) primitive cell. Since we're not planning to do MD or otherwise break the symmetry of this crystal, it's ok to do a calculation on the primitive cell of the crystal.

Before you run this input, you will need to change the `outdir` and `pseudo_dir` to your own directories by editing the paths in the input files to point to your directories,

```
outdir = '/afs/ir.stanford.edu/users/e/v/evanreed/tmp' ,  
pseudo_dir = '/afs/ir.stanford.edu/users/e/v/evanreed/espresso-4.2.1/pseudo/'
```

You can use **pwd** to find the name of your current directory. Run this input script with the command,

```
../bin/pw.x < si.scf.mesh.in
```

The line in the output with the exclamation point on the left side is where the converged total energy is output. Also look for the stress tensor output in kbar (1 bar is about 1 atm).

If you have problems running Espresso after a period of no problems, try deleting the files in the /tmp/ directory specified in the input file. This directory accumulates files and may exceed your corn quota after sufficiently large number of times running Espresso.

### 3 Brillouin zone sampling

Within the DFT approach using periodic boundary conditions, the single-particle states must be computed at discrete points in the Brillouin zone. The total electronic density is then given by,

$$\rho(\vec{r}) = \frac{1}{N_{\text{k-points}}} \sum_{\vec{k}, n} f(\vec{k}, n) \psi_{\vec{k}, n}(\vec{r})^* \psi_{\vec{k}, n}(\vec{r})$$

where the occupation of each state  $f(\vec{k}, n) = 2$  if the energy eigenvalue  $\epsilon_{\vec{k}, n} < \epsilon_{\text{Fermi}}$  and  $f(\vec{k}, n) = 0$  if  $\epsilon_{\vec{k}, n} > \epsilon_{\text{Fermi}}$  in the ground state. The DFT total energy is given by,

$$E_{\text{tot}}[\{\psi_{\vec{k}, n}\}] = \frac{2}{N_{\text{k-points}}} \sum_{\vec{k}, n} \epsilon_{\vec{k}, n} - \int d\vec{r} V_{\text{ion}}(\vec{r}) \rho(\vec{r}) - \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} - E_{\text{XC}}[\rho(\vec{r})] + E_{\text{ion-ion}}$$

where the accuracy of both the eigenvalues  $\epsilon_{\vec{k}, n}$  (the single-particle band structure) and density  $\rho(\vec{r})$  is determined the k-space sampling.

1. Determine the k-point mesh density is required for convergence of the total energy. Run a series of calculations with different k-point mesh densities and plot the total energies as a function of k-point mesh size. Use a cubic mesh (i.e.  $n \times n \times n$ ). Do these calculations with a plane wave cutoff energy of 18 Rydbergs. Recall that  $k_b T_{\text{room}}$  per atom sets the relevant energy scale for many materials problems; you would like your energies to be converged to less than this quantity, i.e. less than 0.01 eV per atom, typically 0.005 eV per atom. Convert this quantity to Rydbergs and compare to your total energies. What k-point mesh is required to converge the total energy to this quantity?
2. Now do the same for the pressure. What k-point mesh is required to converge the pressure to within a few kbar? Is this the same energy cutoff required to converge the total energy?
3. Might this k-point mesh need to change if you changed the size of your computational cell? If you increased the volume of your computational cell by a factor of 8 (by doubling each computational cell vector) while preserving the atomic density (now

16 atoms in the computational cell), what would be a good guess for the k-point mesh density to use to achieve the same degree of convergence, based on your results above?

4. Based on your knowledge of dispersion in materials, how would you expect the required k-space mesh to change to achieve similar levels of convergence for a material that is metallic? Increase, decrease, or stay the same?

## 4 Plane wave cutoff

1. With your choice of k-point mesh that converges the total energy to less than  $k_b T_{\text{room}}$ , explore the variation of total energy and stress with the plane wave cutoff energy. Make plots of total energy and stress versus cutoff energy.
2. What cutoff energies converge the total energy to within  $k_b T_{\text{room}}$  and the stress to within a few kbar? Are they the same?

## 5 Convergence of energy differences

The convergence of absolute energies is generally of less practical interest than the convergence of the difference between energies, or related quantities. Convergence of the latter to a given precision may occur at lower cutoff energies due to the subtraction of systematic errors.

1. Decrease the lattice constant by 1% and calculate the total energy as a function of cutoff with the kpoint mesh used for the previous problem. Now plot the difference in energy as a function of cutoff, i.e.  $\Delta E(E_{\text{cutoff}}) = E(V_1, E_{\text{cutoff}}) - E(V_2, E_{\text{cutoff}})$  where  $V_1$  and  $V_2$  are two different volumes.
2. At what value of cutoff energy is  $\Delta E(E_{\text{cutoff}})$  converged? How does this cutoff energy compare to the cutoff required to converge total energies?
3. Where are the highest spatial frequency components of the wave functions located within the computational cell and why might energy differences be converged at a different cutoff energy than the absolute total energy?

## 6 Bulk modulus and zero pressure volume

In this problem, you will calculate the bulk modulus of Si by doing a fit to the total energy curve. To lowest order, the total energy curve around the minimum is,

$$E(V) = E(V_0) + \frac{B}{2V_0}(V - V_0)^2 \quad (5)$$

1. Calculate the total energies for a series of lattice constants around the energy minimum, spaced by about 1% increments in lattice constant. Use Excel or another program to do a quadratic fit to your energy curves. Determine  $V_0$  and  $B$ .
2. How well do they agree with the experimental values for Si? Is this level of agreement good or bad?