

MatSci 331 Homework 6

Lithium Pseudopotentials and Plane-wave DFT for Graphene and Graphane: Exchange-Correlation Functional, Pseudopotential, Band Structure, Atomic Relaxation

Due Friday, Mar. 15 at 5 pm in Durand 110.
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In this homework, you will first explore the generation of a simple pseudopotential for a lithium atom in the single-particle picture using MATLAB. You will then use it in your single particle band structure code to see how well it works.

Next, you will use Quantum Espresso, a plane-wave DFT code, to calculate properties of graphene and graphane. Andre Geim and Konstantin Novoselov received the 2010 Nobel prize in Physics for isolating graphene (a single hexagonal symmetry plane of graphite) and demonstrating some of its unique properties.

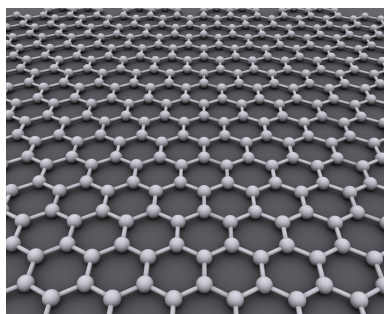


Figure 1: Graphene. (<http://en.wikipedia.org/wiki/File:Graphen.jpg>)

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 from the HW 5 distribution for some help on this if you are unfamiliar. 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 sufficient run times.

1 Lithium pseudopotential

On coursework, find two MATLAB codes associated with this HW distribution. These compute the eigenstates of an atom with nuclear charge Z by finding the eigenvalues and eigenvectors of the radial wave equation,

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - \frac{Z}{r} \right] \psi_{n,\ell}(r) = \epsilon_{n,\ell} \psi_{n,\ell}(r) \quad (1)$$

Here, $\psi_{n,\ell}(r) = r\phi_{n,\ell}(r)$ where ϕ is the full radial wave function. We will neglect electron-electron interactions to simplify the calculations. The MATLAB code solves this eigenproblem on a real-space mesh by discretizing the kinetic energy operator - take a look at the Hamiltonian H to see how it looks.

1. Set $Z = 1$ and $\ell = 0$ for the hydrogen atom and compute the lowest three eigenvalues and eigenvectors. Verify that the energies obey the hydrogen atom spectrum $E(n) = \frac{Z^2}{2n^2}$ in Hartrees. Plot the wave functions and give the number of nodes in each.
2. Now repeat for a lithium atom where $Z = 3$. Plot the radial wave functions of the lowest energy states. Qualitatively, how does the lowest energy state change relative to hydrogen? Generally, as Z increases, the lowest energy states (core orbitals) become more tightly localized and therefore require the use of a high plane wave cutoff to converge.
3. For lithium, the occupied states are the 1s and the 2s states, both of which have $\ell = 0$, zero angular momentum. The bonding and electronic properties of most interest are determined entirely by the 2s state which is much more delocalized than the 1s. We would like to develop a pseudopotential that describes the 2s state with lower spectral content than the Coulomb potential, and we don't need it to describe the 1s state because it does not participate in chemical bonding. In this case we can describe the electronic structure (approximately) by developing a pseudopotential for only the $\ell = 0$ radial wave functions. (If you are so inclined, you can compute the radial wave functions for $\ell \neq 0$ by introducing the centrifugal term in the radial Hamiltonian.)

Consider a pseudopotential of the form

$$V^{ps} = \begin{cases} -\frac{Z}{r}, & \text{if } r \geq r_c \\ -\frac{Z}{r_c}, & \text{if } r < r_c \end{cases} \quad (2)$$

where r_c is a cutoff radius. This is a one parameter pseudopotential. Maximizing r_c minimizes the plane wave cutoff required to converge wavefunctions, but making r_c too big could potentially impact the chemical bonding between atoms. We want to ensure that r_c isn't much bigger than half the distance between atoms to satisfy the latter constraint.

Make a plot of the lowest 5 eigenvalues of the radial wave equation for values of r_c ranging from zero to 3 atomic units. Determine a value of r_c such that the lowest eigenvalue is within 10^{-2} Hartrees of the 2nd lowest eigenvalue of the full Coulomb potential.

4. Now make a plot comparing the radial wave functions for the 2s state of the full Coulomb potential, and the lowest eigenstate of your pseudopotential. Qualitatively, how do they compare for the region $r < r_c$ and $r > r_c$? It may be necessary to multiply one of the radial wave functions by -1 to directly compare.
5. The 2p states are usually close in energy to the 2s states and could play a role in bonding. In fact, because we are neglecting electron-electron interactions, the 2s and 2p states have the same energy. You can verify this by comparing the lowest energy $\ell = 1$ eigenvalue to the 2nd lowest energy $\ell = 0$ eigenvalue. We would like our pseudopotential to describe these states in addition to the 2s to accurately describe bonding.

Set $\ell = 1$ and compare the lowest energy eigenvalues of your pseudopotential and the full Coulomb potential. These should be equivalent if the pseudopotential does a good job describing the 2p states. Is the performance of your pseudopotential acceptable? Acceptable deviations here are under 0.1 eV.

Pseudopotentials can be (and usually are) defined in a non-local form such that a separate radial potential applies to each ℓ angular momentum component. This exploits the full form of the pseudopotential matrix, including the off-diagonal elements.

6. The reciprocal-space form of the pseudopotential considered here is

$$\tilde{V}(\vec{G}) = -\frac{4\pi Z}{|\vec{G}|^2} \frac{\sin(|\vec{G}|r_c)}{|\vec{G}|r_c} \quad (3)$$

Overlay a plot of this potential as a function of $|\vec{G}|$ with a plot of the bare Coulomb potential for lithium. Note that higher frequency components are suppressed in the pseudopotential, resulting in a calculation that should converge to a given level of precision at a lower plane wave cutoff energy. Larger values of r_c lead to more diminished high frequency components.

7. Now revisit the single-particle bands code that you developed in HW 5. Using a primitive BCC lattice (lattice vectors $a_1 = a_{\text{lat}}(-0.5, 0.5, 0.5)$, $a_2 = a_{\text{lat}}(0.5, -0.5, 0.5)$, $a_3 = a_{\text{lat}}(0.5, 0.5, -0.5)$ where a_{lat} is the conventional cell BCC lattice constant), set the conventional cell lattice constant to 20 atomic units and compute the bands for lithium using the full Coulomb potential. The lowest couple of bands should be rather flat. Make a plot of the lowest two energy bands at the Γ point (i.e. $\vec{k} = (0, 0, 0)$) versus plane wave cutoff energy up to a cutoff as high as you can go.

8. Now make a new function that computes your pseudopotential and plot the lowest energy eigenvalue as a function of the plane wave cutoff energy. This energy should converge much more quickly with cutoff energy than the full Coulomb potential. Overlay your pseudopotential plot on top of the full Coulomb potential plot from the previous part.
9. Set the conventional cell lattice constant to 6.60 atomic units, the experimentally measured lattice constant. Compute the bands for both the Coulomb potential and pseudopotential along the path from Γ to P : $\vec{k} = (k_x, k_x, k_x)$ (same path as HW 5), ensuring that both are converged with respect to cutoff energy. You will probably need to consider higher cutoff energies of, e.g. 40 Hartrees for the Coulomb potential. The best we can expect here is for the lowest energy band in the pseudopotential case to reproduce the 2nd to lowest energy band for the full Coulomb potential. How does the energy dispersion of these bands compare? Can you explain any discrepancies in terms of our approximations here? What could be done to improve the agreement?
10. Now set the potential part of the Hamiltonian to zero and plot the free-electron bands. How does the energy dispersion from Γ to P compare with that of the pseudopotential calculation? Is this consistent with the relatively high conductivity of solid lithium, which is a metal?
11. In terms of the pseudopotential you've developed, explain how this lithium Coulomb potential can give valence electron bands that look similar to free-electron bands, i.e. why do the valence electrons behave as if there is no potential when there are very sharp features in the potential? Note that this is an intrinsically quantum effect, and does not simply result from screening of the nuclear charge by core electrons! Recall that there is no screening here in this single-particle picture.

2 Espresso Preliminaries

You can find the Espresso documentation in the file `/espresso-4.2.1/doc-def/INPUT_PW.def` or http://www.quantum-espresso.org/input-syntax/INPUT_PW.html. There are a variety of text editors available on corn, including gedit which may be the easiest to use if you are unfamiliar with the others.

Before you run the input files in this HW, 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/'
```

Run the input scripts with the command,

```
../..../bin/pw.x < input_script.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).

3 Brillouin zone sampling and plane wave cutoff

A sample graphene input is set up in the **examples/graphene/scf** directory. As in HW 5, determine a k-space mesh and plane wave cutoff energy that converges the total energy to within around 0.01 eV/atom.

4 Minimum energy lattice constants

The input file chooses a hexagonal computational cell. There are two unique lattice constants to specify: a and c . One determines the lattice constant of the graphene. The other determines the separation between the graphene planes. This is a case where we don't really want or need fully periodic BC's, but we get them anyway due to the use of plane waves. If the c lattice constant is too small, the planes will interact with each other. We want to study the energetics of only 1 plane. Note that the input specifies the a and c/a ratios. The a value is in a.u. (Bohr radii a_0).

1. Find the critical value of the c lattice constant above which the energy does not change (to within 0.01 eV) with variations in c . For our purposes here, choose a value of c that is about 3 Angstroms larger than the critical value that you determine. This will allow for the introduction of hydrogen atoms (later) without needing to change the size of the computational cell.
2. Vary the a lattice constant to find the minimum energy value (minimal $P_{xx} = P_{yy}$ in this case). How does it compare to the experimental value of 2.46 Angstroms?
3. Is your calculated lattice constant a prediction of this computational method or does the empiricism here incorporate the lattice constant? While there is a lot of empiricism in practical DFT, it is significantly less empirical than the interatomic potentials we covered at the beginning of this class.

4. Is there a dipole moment in this computational cell? Dipole moments on surfaces result in fictitious electric fields with periodic boundary conditions. These electric fields can alter the energetics if they are sufficiently large.

5 Exchange correlation functional

1. What type of exchange correlation functional are you using? You'll need to look in the pseudopotential file to find out. Espresso uses the exchange correlation functional listed in the pseudopotential file.
2. Now utilize a similar ultrasoft pseudopotential that was created using a different exchange-correlation functional. Use the potential **C.pz-rrkjus.UPF** in the **/pseudo** directory. Look at the details of this pseudopotential file. This potential was created using the Perdew-Zunger parameterization of LDA.
3. Do you think convergence of your results will require a larger or smaller plane wave cutoff for this potential? Or about the same?
4. Using the k-point mesh and cutoff you used for the previous problem, calculate the stress P_{xx} in the graphene plane using the computational cell dimensions from the previous problem. Is this an acceptably small stress? If not, find the a lattice constant that minimizes the energy. How different is it from the experimental lattice constant of 2.46 Angstroms?
5. Which exchange-correlation functional would you expect to be typically more accurate for this lattice constant?

6 Pseudopotential type

Now try a pseudopotential that is norm-conserving: **/pseudo/C.pbe-mt_gipaw.UPF** Norm-conserving pseudopotentials have higher spatial frequencies in the core than ultrasoft or PAW potentials and therefore require the use of higher cutoff energies. Norm-conserving potentials are generally, if anything, slightly more accurate than the ultrasoft and PAW potentials.

1. Find the cutoff energy required to converge the calculation using this pseudopotential.
2. How does the speed of the calculation compare with the ultrasoft pseudopotential case when using the cutoff energy appropriate for the ultrasoft potential?

7 Band structure

Looking at the band structure can be revealing for high-symmetry systems. For lower symmetry systems, an electronic density of states may be more appropriate. Since we're dealing with a high symmetry system here, let's calculate the bands.

Band structure calculations typically start by doing an ordinary ground state calculation to obtain the self-consistent electronic density. You can use a k-space mesh to do this calculation. Once the density is obtained, it is possible to calculate the bands at any point in the Brillouin zone without having to do another SCF calculation. To make a clear band structure plot that looks good, you typically want to calculate the bands at more points in the BZ than you used for your SCF calculation. Furthermore, the points that you want for a band structure plot are along high symmetry points in the BZ, probably not what you used for your mesh. We will use a post-processing code to do this part of the calculation. For more info on this process, see the Espresso tutorial distributed with this HW.

1. Run a graphene SCF calculation with the cutoff and k-space mesh you've chosen. Look in the directory `/example/band/1` to find an example script for a band structure calculation. You will need to change your calculation mode to **calculation = 'bands'**, and use the kpoints specified in the example file. These kpoints are along a high-symmetry path in the BZ for graphene.
2. After running the bands calculation, go to the `/example/band/2` directory and look at the bands.in file. Run the bands.x executable using this input file to produce the file bands.dat containing the band structure info: `../../bin/bands.x ;bands.in ; bands.out`. The executable bands.x does some formatting of the data, no calculations. You will need to change the directory path as appropriate in **bands.in**.
3. You can plot bands.dat using a program of your choice. Or you can run `../../bin/plotband.x` which will prompt you for some info about the postscript plot to make. You will be prompted for some information including the postscript file name (e.g. bands.ps) to produce, energy range, Fermi energy (which you can find in the output of your SCF calculation), energy label spacing, etc. You can view the resulting postscript file **bands.ps** by running, e.g. **display bands.ps**

The unusual feature of graphene is the X-like feature at the Fermi energy, where conduction band valence bands are ordinarily parabolic in other materials. This leads to a semi-metallic character and an optical absorption that is nearly constant across a broad spectrum. Graphene is an atomically thin, nearly transparent electrical conductor.

8 Graphane formation energy

Recent DFT calculations and subsequent experiments have shown that graphene can absorb hydrogen, forming a CH structure, i.e. there is one hydrogen per carbon atom. DFT calculations predicted this stability of this material *before* the experiments were done! See the prediction by Sofo, et al, Physical Review B 153401, (2007) and experiment by Elias, et al, Science 323, 610 (2009). The hydrogen atoms are located above and below the plane of carbon atoms. When hydrogen is absorbed, the sp^2 hybridization of C changes to sp^3 and the bond angles of the carbon atoms change to something closer to tetrahedral.

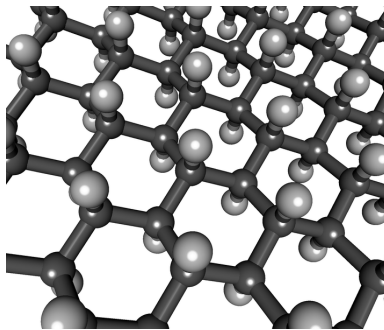


Figure 2: Graphane. (<http://en.wikipedia.org/wiki/File:Graphane.png>)

1. Look in the directory `/example/graphene/opt` to find the input file that is set up for geometry optimization. This input includes 2 hydrogen atoms using a PBE-derived ultrasoft pseudopotential. Note that you should not mix pseudopotentials created with different exchange-correlation functionals. Place the hydrogen atoms out of the plane of the graphene and lined up along the c axis with the carbon atoms. Place them approximately a typical CH bond distance out of plane. Assuming the cutoff for the H-pseudopotential is lower than the C-pseudopotential, use the cutoff energy and k-point mesh that you determined previously for this carbon potential and run the geometry optimization calculation. Note that there is an extra loop in the output file that performs SCF calculations each time the atom positions are moved to minimize energy.
2. What is the resulting CH bond length?
3. What is the P_{xx} component of the stress in the graphene? Why?
4. To determine the zero stress lattice constant for graphane, change the calculation mode to `calculation = 'vc-relax'`. This mode includes the computational cell lattice vectors in the energy minimization process. Note that there are many cases where you would not allow the computational cell lattice vectors to change, e.g.

when studying the surface chemistry of a single isolated reaction. Keeping the lattice constant in the latter case simulates the constant strain condition imposed by the bulk material. Run the calculation and record the total energy - this one might take a few minutes to run.

5. To estimate the graphane formation energy, $\Delta E \approx E_{\text{graphane}} - (E_{\text{graphene}} + E_{\text{H}_2})$ where E_{H_2} is the energy of a hydrogen gas molecule. At the computational cell size, BZ mesh, and cutoff energy used for your graphene calculation, calculate the total energy of an H_2 molecule by performing a geometry optimization. What is the formation energy for graphane, per formula unit? Is it stable?
6. Describe in a sentence how you could include nuclear entropic effects to obtain the free-energy at room T (recall HW 4).
7. What might happen to the hydrogen if this material is heated up? Could it make a good hydrogen storage material?
8. If you want to be sure your result is converged with respect to your cutoff energy and BZ mesh, you might wish to calculate this number using a few different values (not required for this HW).