Module 2: Quantum Espresso Project – Aluminum

<u>Goals</u>

In this project, we will continue using the PWSCF code and look at convergence with respect to the k-point mesh, how to relax crystal structures, and how to compute mechanical and optical materials properties. Successful completion of this work will demonstrate mastery of Quantum Espresso DFT calculations for condensed systems.

<u>Deliverables</u>

You will produce a short report documenting some of your findings and you will submit some of your findings to PrairieLearn. This is indicated in red below and the points allocated for each deliverable are enumerated below.

The report part will train you in creating proper figures. When you make your figures, please pay attention to two things (these will be graded and you will lose points if you do not pay attention to these!):
  (i) The figure and its formatting itself:
- Make sure axis labels and tick labels are large enough.
- Axis labels should be of the format: "Quantity (unit)"
- Tick labels should all use the same number of digits after the decimal point.
- Use major ticks and subticks. Use 4 subticks if your major ticks are "1", "5", 10", etc. Use 3 subticks if your major ticks are "1", "2", "3" as well as "0", "2", "4" etc.
- Make sure the data points are clearly visible and color coded if you show multiple data sets. Avoid using red and green as color code in the same figure (color-blindness!). You can also use different line styles, if you prefer.
- Include error bars if you know errors!
  (ii) The figure caption:
- Explain what the quantities are that are plotted on both axes: If your y axis label is, for instance "E (eV)", include in the caption an explanation such as "Total energy from DFT E in eV".
- Put into the caption explicitly and concisely what you learn from the figure: Do not confuse this with the previous bullet point (e.g. by stating "Total energy versus k-points.")! Say instead: "The minimum of this curve corresponds to the equilibrium lattice constant and total energy and the curvature allows to extract the bulk modulus." Use as many sentences as needed to explain what you learn from the figure!

Please note that we will again use peer feedback and make sure to meet those deadlines, which will be posted on CampusWire. Not sending your report for feedback, or not providing feedback will lead to a 20 point penalty.

Your final report should be formatted as a **single pdf document comprising your report and all requested files**. Submit your final report via Gradescope (link on course web site) by **11:59 pm on October 2, 2020. Late submissions will not be accepted.**

Convergence in E_{cut} and k-point mesh

For all first-principles calculations for solids, you must pay attention to two convergence issues. The first is the *cutoff energy*, E_{cut}, which is the cutoff for the wave-function expansion. The second is k-point mesh, which determines how well your discrete grid approximates the continuous integral.

Background for *k*-point convergence

Remember that we are dealing with infinite systems using periodic boundary conditions. This means that we can use the Bloch theorem to help us solve the Schrödinger equation. The Bloch theorem says:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\,\mathbf{k}\cdot\mathbf{r})\,u_{n\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}}\exp(i\,\mathbf{G}\cdot\mathbf{r})$$

In these equations, $\psi_{n\mathbf{k}}(\mathbf{r})$ is the wave function and $u_{n\mathbf{k}}(\mathbf{r})$ is a function that has the same periodicity as the lattice. In the walkthrough we studied the plane wave expansion and convergence with respect to the maximum G_{max} vector given by the cutoff energy

$$E_{cut} = \frac{\hbar^2 G^2}{2m}$$

Because of the Bloch theorem, we need to solve a Schrödinger-like Kohn-Sham equation (*i.e.* iterate until self-consistency the diagonalization of an MxM matrix, where M is the number of basis functions) everywhere in the Brillouin Zone. In practice, we do it for a finite number of k values, and get a value for E at each k.

The figure shows an example of an electronic band structure for a semiconductor – the eigenvalue $\varepsilon(k)$ – of the Kohn-Sham equation as a function of *k* value. The *k* value goes over the first Brillouin zone. (If you don't remember or don't know what a Brillouin zone is, refresh yourself with the concepts of direct and reciprocal lattice.)
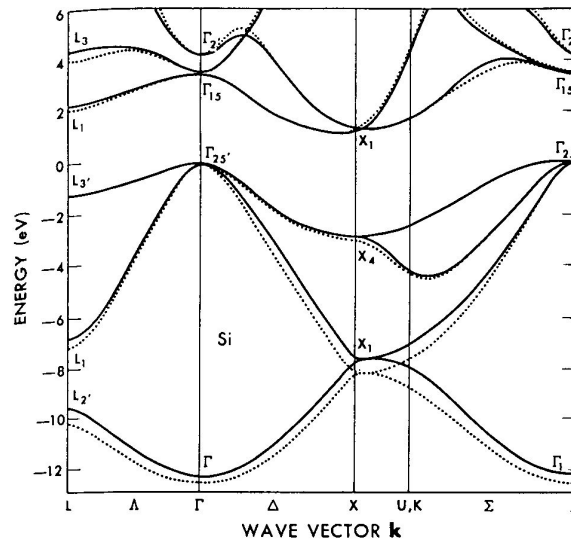
https://wiki.fysik.dtu.dk/gpaw/exercises/band_structure/bands.html

The energy of the crystal, E, is computed by integrating over the occupied bands of the first Brillouin zone. Thus, summing over a finite number of k points is an approximation to performing an integral. You will need to make sure you have enough k-points to have a converged value for the energy computed by this integral.

Input Files

Log into your EWS Linux account.

We will be using a special pseudopotential for Al. Let's take a look at our choices. Navigate your browser to http://www.quantum-espresso.org/pseudopotentials/.

You will see a periodic table, where you can click on any element to see all of the pseudopotentials that are available for that element; you can also filter to downselect to particular sets. If you select Al, you will see many (many) options. We are going to use Al.pbe-n-van.UPF which means the

- potential for **aluminum** using the
- **PBE** = Perdew-Burke-Ernzerhof Generalized Gradient Approximation (GGA) for the exchange correlation potential
- with **nonlinear** core corrections (for the treatment of the exchange-correlation)
- as a **Vanderbilt** ultrasoft pseudopotential
- in the **UPF** format (for Quantum Espresso)

The electron configuration of Al is $[Ne]3s^23p^1 = 1s^22s^22p^63s^23p^1$. This particular functional has 3 electrons in the valence, so the filled $[1s^22s^22p^6]$ shells are in the "core" while the $3s^23p^1$ electrons will be considered valence electrons; this is like treating Al as a lumped Al^{3+} ion with $3e^-$. Since this particular pseudo potential does not come prepackaged, we need to download this pseudopotential into a local pseudopotential directory. For example:

$ cd ~/QE/espresso-5.0.2/pseudo
$ wget http://www.quantum-espresso.org/wp-content/uploads/upf_files/Al.pbe-n-van.UPF

When we run QE, we will tell the code where to find this pseudopotential on our local disc. You may want to export your ESPRESSO_PSEUDO environment variable (see walkthrough); else, you'll need to make sure that the pseudo_dir variable in each input file points to the correct directory.

After downloading, you can look at the pseudopotential file using "less"; the information inside of PP_HEADER reiterates much of what is described above.

Next create a directory to store your files. You should create a new subdirectory in your "Runs" directory that you created last time. For example

$ cd ~/QE/Runs
$ mkdir Al
$ cd Al

Now download the appropriate input file from the course web site and upload these files to this directory.
Al.scf.inp Al.relax.inp Al.band.inp

We will look first at the Al.scf.inp input file. This input file is for Al in the fcc crystal phase.

Aluminum exists under standard conditions as a face-centered cubic (FCC) structure with four Al atoms in the conventional unit cell at [0 0 0], [0 0.5 0.5], [0.5 0 0.5], and [0.5 0.5 0], in units of the lattice constant, alat. (Of course, there would be no difference in having these atoms at [0.5 0.5 0.5], [0.5 1.0 1.0], [1.0 0.5 1.0], and [1.0 1.0 0.5], why not?)
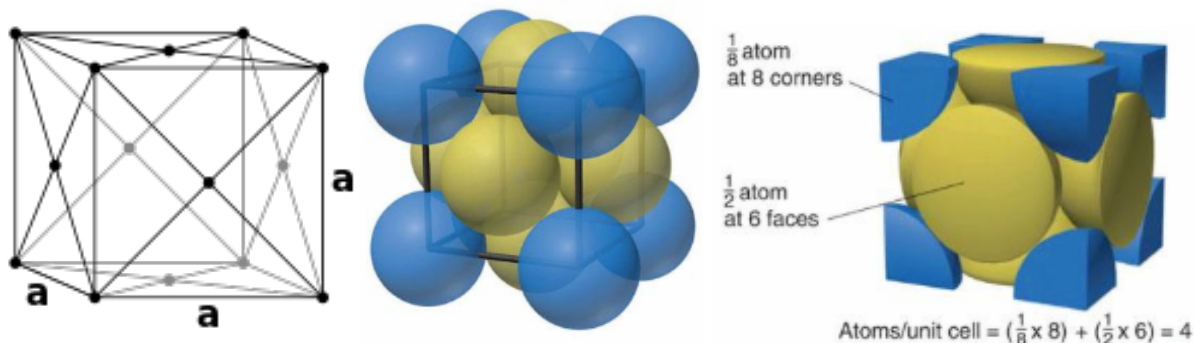
QE operates using not the conventional unit cell, but the *primitive unit cell* based on the primitive axis vectors as the most economic way to define a unit cell. In the case of FCC lattices, this allows us to define our periodic crystal containing just a single Al atom at the origin [0 0 0].
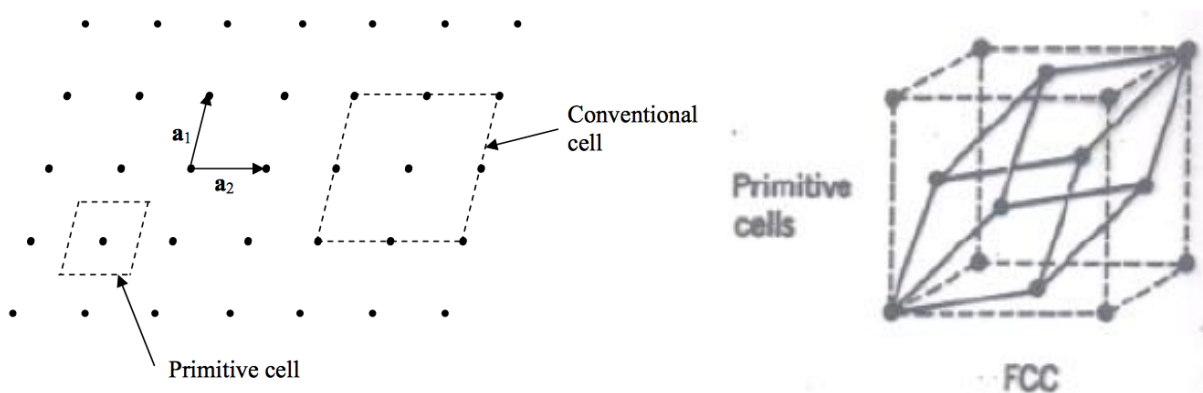
Look at the input file, which you have copied over to your directory.
$ less Al.scf.inp

The file will look similar to the one for the H_2 molecule in the walkthrough. Here we highlight some key points:

Cell:

```
...
  ibrav= 2,
...
ATOMIC_POSITIONS alat
 Al 0.00 0.00 0.00
…
```

Here we specify a FCC lattice using ibrav=2 (cf. http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html#idp82000) and locate a single Al atom at the origin of our primitive cell.

Smearing:

```
...
  occupations = 'smearing',
  smearing = 'methfessel-paxton',
  degauss = 0.05,
...
```

A metal is a system with unoccupied bands near the Fermi energy (the energy of the highest occupied e⁻ level) meaning that bands may cross at the Fermi surface. The DFT calculation scales quadratically with the number of bands in the calculation. To reduce computational costs, the DFT algorithm only considers the occupied bands, and a few unoccupied bands. At T = 0 K, there is a step discontinuity in the e⁻ occupation numbers of the bands, but at finite temperature (i.e., T > 0 K) the function is no longer discontinuous.
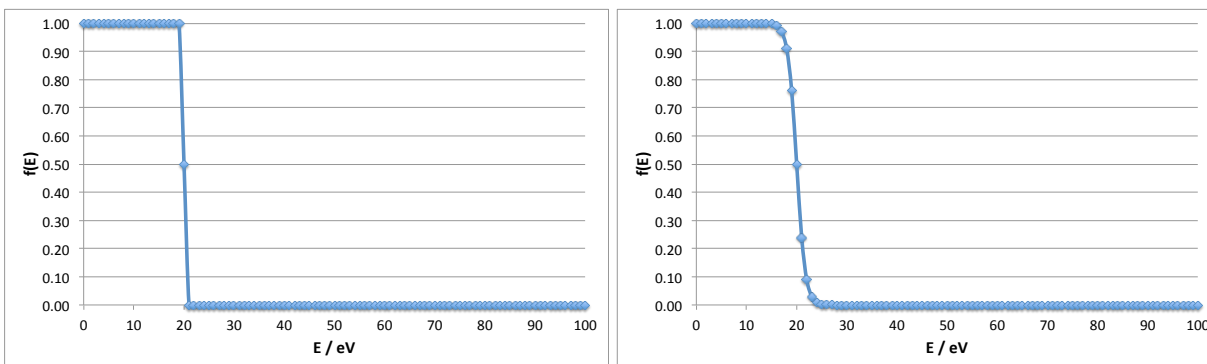
Fermi distribution, $f(E) = 1 / [\exp((E-E_F)/k_BT)+1]$ for a Fermi energy $E_F = 20$ eV at (left) T = 0 K and (right) T = 5000 K.

When bands are near the Fermi level – as in metals – this means that small changes in the wavefunction can cause large changes in the band occupancy, making the algorithm unstable. To stabilize the algorithm, better reflect the continuous nature of the band occupancies at finite temperature, and reduce the number of Fourier components (i.e., E_{cut}) and k-points required for convergence, we employ a *smearing function* to the energy bands.

Here we are telling QE to use a smearing potential for the atoms in the metal with Methfessel-Paxton first-order spreading (cf. PRB 40, 3616 (1989)) and a 0.05 Ry value for the Gaussian spreading for Brillouin-zone integration.

k-points:

```
...
K_POINTS {automatic}
 4 4 4  0 0 0
```

After the keywork K_POINTS, "automatic" tells PWSCF to automatically generate a k-point grid.

The format of the next line is

nkx nky nkz offx offy offz

where nk* is the number of intervals in a direction and off* is the offset of the origin of the grid.

If we now do

$ less Al.relax.inp,

you will see similar changes to what we had to relax the hydrogen molecule; now, however, we use "vc-relax" (or **variable cell** relaxation, to relax the unit cell), and there is also a new card for &CELL, which takes the default values.

You can read the documentation for the input file in the INPUT_PW file; this is in the Docs subdirectory under the espresso-5.0.2 directory, or online.

A1. SCF energy Calculation

If using the EWS workstations, in order to use the scratch space and not to overwrite each other's files, please edit your input files (using, for example, vi) to set

prefix='aluminum-<username>'

outdir='/tmp/<username>'

where you replace <username> with your netid.

Also remember to set pseudo_dir to point to your local pseudopotential directory.

Using the Al.scf.inp input file, run the PWSCF code to calculate the energy of the Al phase.

✤ PRAIRIELEARN: What is your calculated value of the total energy of the system in:
    a) Rydbergs?   b) eV?   c) Joules?

[10 pts]

✤ PRAIRIELEARN: How long did the calculation take in
    a)   CPU time?   b) wall time?

[5 pts]

A2. Geometry Relaxation

Using the Al.relax.inp input file, run the PWSCF code to relax the lattice parameter.

N.B. Remember to make the same modifications to prefix, outdir, and pseudo_dir as you did above.

✤ PRAIRIELEARN: What is your calculated value of the total energy of the system in:
    a) Rydbergs?

[5 pts]

✤ PRAIRIELEARN: How long did the calculation take in
    a)   CPU time?   b) wall time?

[5 pts]

✤ PRAIRIELEARN: What is the value of the input lattice constant in a.u.?

[10 pts]

✤ PRAIRIELEARN: Near the top of your output file you will see a block:

crystal axes: (cart. coord. in units of alat)

6

```
a(1) = ( -0.500000  0.000000  0.500000 )
a(2) = (  0.000000  0.500000  0.500000 )
a(3) = ( -0.500000  0.500000  0.000000 )
```

Towards the end of your output file (just below the line reading "End of BFGS Geometry Optimization") you will see the block that looks something like:

```
CELL_PARAMETERS (alat= 10.20000000)
 -0.509955391  0.000000000  0.509955391
  0.000000000  0.509955391  0.509955391
 -0.509955391  0.509955391  0.000000000
```

In units of the input lattice constant alat, the lattice vector of the relaxed crystal geometry has grown – in this case – from 0.5 to 0.509955391. The lattice constant, alat, scales in direct proportion to this change (i.e. by a factor of 0.509955391/0.5).

Using your terminal values for the CELL_PARAMETERS block, what is the lattice constant of your final relaxed geometry in a.u.?

[10 pts]

A3. E_{cut} convergence

To speed up the convergence calculations, we use scripts. For the cutoff energy convergence we can use the script from the last lab. Keep the lattice constant fixed at alat = 9.0 a.u.

✤ REPORT: Consider a range of energy cutoffs, E_{cut}, and make a plot of your scf energy as a function of E_{cut}.

[15 pts]

✤ PRAIRIELEARN: Suggest an appropriate value for E_{cut} for a given accuracy.

[15 pts]

Hint: It may not be necessary to fit a decaying exponential if you can adequately substantiate your answer by inspection of your numerical data. For example: "Assuming $E_{true} = E$ @ E_{cut} = XX Ry, then beyond an E_{cut} of YY Ry, the system energy is converged to within the desired accuracy of ZZ Ry/atom."

A4. k-point convergence

Modify the script from A3 to loop over *k*-point meshes ranging from 1×1×1 to 12×12×12 and calculate the energy for the different *k*-point meshes. Use the optimal E_{cut} value computed in A3, and keep the lattice constant fixed at alat = 9.0 a.u.

Hint: To scan over 1×1×1 to 3×3×3 k-point meshes, the beginning of the do loop in your modified file might look something like:

```
for kpts in "  1 1 1  0 0 0" "  2 2 2  0 0 0" "  3 3 3  0 0 0" ; do

        sed "/  4 4 4  0 0 0/s/.*/ $kpts/" $INPUTFILE  | $PWSCF > out
```

✤ REPORT: Make a plot of your scf energy as a function of the resolution of your k-point mesh.

✦ PRAIRIELEARN: Suggest an appropriate k-point mesh for a given accuracy.

[15 pts]

Hint: It may not be necessary to fit a decaying exponential if you can adequately substantiate your answer by inspection of your numerical data. For example: "Assuming E_{true} = E @ k-point mesh with resolution X-by-X-by-X, then for k-point meshes with resolution higher than Y-by-Y-by-Y, the system energy is converged to within the desired accuracy of ZZ Ry/atom."

A5. Converged geometry relaxation

Once you have selected your cutoff energy and *k*-point mesh size to be within 2 mRy/atom, modify Al.relax.inp to reflect these values and re-run the relaxation.

Hint: If you get the error "Error in routine scale_h (1): Not enough space allocated for radial FFT: try restarting with a larger cell_factor" try a better initial guess for your lattice parameter.

✦ PRAIRIELEARN: What is your calculated value for the relaxed lattice constant in a.u. using your converged E_{cut} and k-point mesh?

[10 pts]

✦ REPORT: Find (from an appropriate reference) the lattice constant for aluminum at room temperature. Discuss in one paragraph in your report how your value compares with the experimental value!

[10 pts]

A6. Bulk modulus

You've computed the lattice constant for Al with density functional theory; now, let's compute some additional properties. First, a mechanical property – the bulk modulus.

The bulk modulus is defined to be the (linear) change in pressure with a small change in volume per atom. We will use a finite difference approximation to extract this. Edit your Al.scf.inp script to use your converged values of Ecut, kpoint mesh, and your calculated lattice constant.

Run this calculation and extract the computed pressure (derivative of total energy with respect to volume) using

$ grep 'P=' Al.scf.out

you will see a line that looks something like

    total   stress (Ry/bohr**3)   (kbar)   P=   -0.73

though your number may be different.

✦ PRAIRIELEARN: Now, create two new input files, one with with a *unit-cell volume* that is 1% smaller than that corresponding to your calculated relaxed lattice constant, and one with a *unit-cell volume* 1% larger. What are these two new different pressure values?

[20 pts]

✤ PRAIRIELEARN: You will now have the pressure at three different volumes. Use this data to compute the bulk modulus, defined as,

$$K = -V \frac{dP}{dV}$$

at the volume, V, corresponding to the equilibrium volume (where P=0).

[20 pts]

Hint: The unit-cell volume, v, and alat are related as: $v = 2 \times (0.5 \times alat)^3$.

*N.B.* Astute users will note that this data can be used to improve your estimate of the equilibrium lattice constant.

✤ REPORT: Find (from an appropriate reference) the bulk modulus for aluminum at room temperature. Discuss in one paragraph in your report how your value compares with the experimental value!

[10 pts]

A7. Band structure

Finally, let's compute an electronic property – the band structure.

We will plot a band structure (similar to what is shown above); this is the energy with respect to *k* along different directions in the Brillouin zone (show to the right). There are particular directions that we will want to plot out: from (000)—called the Γ-point—along the (001) direction to X; then from a symmetry related X point in the 2nd BZ back to Γ along (011); and finally, from Γ out to L along (111). These paths are chosen so that one can see the high-symmetry directions in the Brillouin zone.
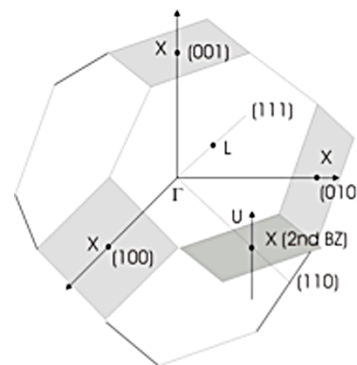
To make a band-structure plot, there are *two steps*: 1. finding the self-consistent charge density (which requires a k-point mesh that fills the Brillouin zone), and 2. without changing that density, solving the Kohn-Sham equation for k-points along particular paths.

So, we will need to do two runs:

1. First, run your self-consistent calculation in a particular directory using Al.scf.inp with optimized lattice constant, E_{cut}, and k-point mesh.

2a. Second, modify the Al.band.inp file to make sure that (a) you use same optimized lattice constant, E_{cut}, and pseudopotential as in Al.scf.inp, and (b) that you use the same prefix and outdir as in Al.scf.inp. When you run your band structure calculation, it will read in the charge density from your SCF calculation and use that as input to its band structure calculation.

N.B. The Al.band.inp file does *not* have the line "restart_mode='from_scratch'"; it is restarting using the output from your previous calculation!

If you look at Al.band.inp, you will see some lines like:

```
  calculation='bands'
...
&SYSTEM
```

...
  nbnd=8
...
K_POINTS
 26
   0.0 0.0 0.0 1.0
   0.0 0.0 0.1 1.0
...
   0.4 0.4 0.4 1.0
   0.5 0.5 0.5 1.0

The "calculation" line tell PWSCF that you'll do a band structure calculation; the "nbnd" line is the number of bands you want to output at each k-point, and then you have 26 k-points along a "path" that you want to evaluate. These k-points are defined in Cartesian coordinates, with units of $2\pi/a$.

2b. Compute the band structure by running PWSCF with the Al.band.inp file.

In Al.band.out you will see lines listing the energies of each of the 8 bands at each of the 26 k-points that look like:

     k = 0.0000 0.0000 0.0000   band energies (ev):

  -5.8405 5.9588 5.9588 5.9588 8.5118 8.5118 8.5118 9.0563

     k = 0.0000 0.0000 0.1000   band energies (ev):

  -5.7976 5.6685 5.7884 5.7884 8.4088 8.7351 8.7351 9.3371
...

✤ REPORT: Make a plot of the band energies moving from the first to last k-point to generate a band structure plot with band energies measured in eV.

The pathway of k-points stored in Al.band.inp passes through a number of special points in the Brillouin zone. The first k-point at (0,0,0) corresponds to the Γ point. The 11th k-point at (0,0,1) corresponds to the X point. The 21st k-point at (0,0,0) also corresponds to the Γ point. The 26th k-point at (0.5,0.5,0.5) corresponds to the L point. **Label these special points on the x-axis.**

[20 pts]

A *band gap* is defined as the energy gap between the highest energy of the highest occupied orbital and the lowest energy of the lowest unoccupied orbital. In a *direct band gap* material (e.g., GaAs), this energy gap occurs at a single k-point; in an *indirect band gap* material (e.g., Si), the highest energy of the highest occupied orbital occurs at one k value, while the lowest energy of the lowest unoccupied orbital occurs at another.

✤ REPORT: At absolute zero, the bottom three bands of Al are fully occupied by the three valence e⁻, and the top five bands are unoccupied. Using your plot and your numerical k-point energies, state whether Al possesses a direct band gap, an indirect band gap, or neither. Justify your answer by appealing to what you know about the character and/or properties of Al.

[20 pts]

10