**MSE 301 Integrated Computational Materials Engineering**
**Homework 1: Density Functional Theory**
**Due in class on Thursday Feb 14**

A. <u>**Conceptual Short Answer Questions:**</u> **(35 points, 5 points each)**

1. Consider the 5 broad categories of properties which can be calculated with DFT (energetics, structural, electronic, magnetic, and optical). Provide a short description of a potential research application for each.

2. Explain the uncertainty principle in terms of position and momentum in the case of a free electron.

3. Briefly describe the major approximations and assumptions made within DFT as a method solving Schrodinger's Equation. Discuss any effects these assumptions have on the exactness of DFT.

4. What are the differences between the LDA and GGA functionals?

5. What is a pseudopotential and when do we use it and when do we question its use?

6. Why do metals require more k-points for a DFT calculation?

7. Why would you expect DFT to work better for solids than for atoms or molecules?

B. <u>**Calculations:**</u> **(65 points total)**

For these problems include a clear and concise report which discusses the results obtained in each step as well as any of the requested plots. These problems are to be completed using Quantum ESPRESSO on www.nanohub.org. The purpose of this exercise is to get hands-on experience on running a density functional theory calculation and to compute values for the equilibrium lattice parameter, bulk modulus, and single-crystal elastic constants.

Questions 1-3 are to be done for pure bulk aluminum, question 4 for both aluminum and silicon. Determine the equilibrium lattice constant, elastic constants, bulk modulus for pure aluminum. Once sufficiently accurate calculation settings are determined, this is done by comparing the energy vs. volume curves for different structures. The crystal structure of pure aluminum determined experimentally is fcc with a lattice parameter of 4.05Å.

1. <u>**Calculation Precision:**</u> **(15 points)**
   This exercise will determine if the values you are calculating are numerically precise. Accuracy will be determined later upon comparing computed values with experimental results. Discuss the importance of these initial steps in your report.

a.  Initial Calculation Parameters:
    i.   Experimental FCC aluminum crystal structure data
    ii.  Functional: GGA
    iii. k-point grid: 7x7x7
    iv.  Number of Bands: 8
    v.   Wavefunction Energy Cutoff: 16 Ry
    vi.  Charge Density Energy Cutoff: 96 Ry
    vii. Occupation options: Tetrahedra
    viii. No Band Structure or DOS calculations

b.  Wavefunction Cutoff Energy (ECUT)
    Vary the ECUT in increments of ± 2 Ry and generate a plot of Energy vs ECUT to determine the minimum ECUT value to use for the remainder of the calculations. Appropriate convergence is within ± 0.0001Ry.

c.  K-point grid spacing
    Vary the k-point grid values uniformly in increments of ± 2 and generate a plot of Energy vs X-direction k-points to determine the k-point grid to use for the remainder of the calculations.

2. **Equilibrium Lattice Constant: (20 points)**
   a.  Vary the lattice parameter in increments of ± 0.05 and generate a plot of Volume (Å/atom) vs Energy.
   b.  Calculate the BCC equilibrium lattice parameter of pure Al to confirm that the stable structure is the FCC structure. Do this by constructing a plot of Energy vs Volume/atom for both the FCC and BCC structures. Recall that an FCC cell contains 4 atoms/unit cell and a BCC cell contains 2 atoms/cell. Calculate a starting BCC lattice parameter such that the starting volume/atom is approximately the same as the ideal FCC volume/atom value. Again vary the lattice parameter in increments of ±0.05.
   c.  Once a rough plot has been generated in which the minimum structure and approximate volume is identified, adjust the lattice parameter in increments of ± 0.01Å to identify the minimum energy volume to use for the remainder of the calculations.

3. **Bulk Modulus and Elastic Constants: (20 points)**
   a.  The bulk modulus can be estimated using the following approximate finite-difference expression:

   $$B \approx -V\left(\frac{\partial P}{\partial V}\right) \approx a_0^3 \left(\frac{P_1 - P_2}{a_2^3 - a_1^3}\right)$$

   Where $a_0$ is your estimated equilibrium lattice constant, $a_1$ and $a_2$ are two values of the lattice constant on either side of this equilibrium value, and $P_1$ and $P_2$ are the values of the pressure corresponding to $a_1$ and $a_2$, respectively.

   Compare your calculated value with the experimentally obtained bulk modulus of aluminum: 76 GPa.

b. Calculate the single-crystal elastic constants $C_{11}$ and $C_{12}$ by computing the stresses resulting from a homogeneous tensile strain of the Al structure along the [001] direction. Specifically, you will use the mathematical relationship:

$$\sigma_{33} = C_{11} * \varepsilon_{33} \quad \text{and} \quad \sigma_{22} = C_{12} * \varepsilon_{33}$$

Imposing a strain along the [001] direction can be done by changing the input cell geometry. Change the "input Geometry" to "Determine unitcell (free)." Change the cell vectors to:

| | | |
|---|---|---|
| -a/2 | a/2 | 0 |
| -a/2 | 0 | a(1+ε)/2 |
| 0 | a/2 | a(1+ε)/2 |

Where "a" is the equilibrium lattice constant previously determined. The values $\sigma_{22}$ and $\sigma_{33}$ can be obtained as the negative of the 22 and 33 elements of the pressure tensor recorded under the "Data" section of the "Result" menu. (Use the right half of the stress tensor (kbar) not the (Ry/bohr) for easier unit conversion.)

Compute $C_{11}$ using the formula (similarly for $C_{12}$):

$$C_{11} = \Delta\sigma_{33} / \Delta\varepsilon = [\sigma_{33}(\varepsilon=0.005) - \sigma_{33}(\varepsilon=-0.005)] / 0.01$$

Compare with experimental elastic coefficients for Al of $C_{11}=1.0675$, $C_{12} = 0.6041$ in units of $10^{11}$ N/m$^2$

c. The bulk modulus can also be calculated from the elastic coefficients. Compare this value with the value approximated from the pressure differences in question 3.

$$\text{Bulk Modulus} = K = (C_{11} + 2C_{12}) / 3$$

4. **Density of States (DOS) and Band Gap:** (10 points)

a. Using the equilibrium lattice parameter previously determined perform a density of states calculation by turning on the option on the "Band Structure/DOS" tab. Adjust the suggested values for the energy range and step to -20eV to 20eV and 0.1eV respectively.

b. Calculate the DOS and band structure of pure Si. Si has a diamond cubic structure at room temperature. For this calculation use the preloaded crystal structure (2 atom basis, FCC, 5.43Å). For these calculations use the following energy parameters: ECUT = 24, Bands=8, KPTS: 7x7x7. Accept the values for the Band structure path, but adjust the DOS energy values to -20 – 20 to match the Al calculation.

c. Compare the shape of the DOS and the position of the Fermi energy between the metallic Al and the insulating Si. Compare the calculated band gap from the band structure with the experimental band gap of Si of 1.1eV. Does changing from the GGA to LDA functional help? What are possible sources of error?