Week 2 – Homework Assignment 3

Density functional theory calculations of bonding and band diagrams

**Problem 1. Bonding and electronic structure in O2.** You will use DFT to explore bonding and electronic structure of the oxygen molecule. Follow the tutorial to perform calculations on O2 and answer the following questions. Perform calculations for both spin 0 and spin 1 (two unpaired electrons). Remember in the code we specify the difference in the number of electrons between majority and minority populations (for spin 1, you have 2 extra electrons in the majority population).

**Question 1.1:** Do you find the oxygen molecule to have zero spin or spin 1?
- a) Spin 0
- b) Spin 1

**Question 1.2:** What is the predicted energy difference between the spin 1 and spin 0 configurations?
- a) ~0.1 eV
- b) ~1.2 eV
- c) ~12 eV
**Problem 2. Electronic structure of Si.** In this problem you will perform DFT calculations of crystalline silicon. Follow the instructions in the tutorial “Binding and electronic structure of Si” to perform the calculations.

**Question 2.1.** Starting with a large lattice parameter and reducing it to observe the formation of the band structure, at what lattice parameter do you first observe the bonding/anti-bonding splitting to lead to the overlap (in energy) between the s and p bands?

a) a~10 Å  
b) a~7 Å  
c) a~5.5 Å

**Question 2.2. Role of strain on bandgap.** Starting with Si in its equilibrium lattice parameter: what effect does increasing the lattice parameter have on the band gap?

a) It increases the band gap  
b) It reduces the band gap

**Equation of state and equilibrium lattice parameter.** Perform several DFT calculations for lattice parameter between 5 and 6 Å. Plot energy as a function of lattice parameter and fit the data to a parabola (\(E(a) = E_0 + \alpha(a - a_0)^2\)) to obtain the equilibrium lattice parameter (\(a_0\)).

**Question 2.3.** The predicted equilibrium lattice parameter deviates from the experimental value (5.43 Å) by:

a) 2%  
b) 10%  
c) 50%

**Question 2.4.** The predicted energy-lattice parameter curve deviates from a parabola in the following way:

a) Actual energy increases less steeply in compression and more steeply in tension  
b) Actual energy increases more steeply both in compression and tension  
c) Actual energy increases less steeply both in compression and tension  
d) Actual energy increases more steeply in compression and less steeply in tension

This phenomena is the origin of thermal expansion.