

Bond Lengths and Dissociation Energies of Diatomic Molecules

Objectives:

In this activity, you will

- 1) calculate the stable bond length of a diatomic molecule
- 2) plot the potential energy as a function of distance of separation between the atoms of a diatomic molecule
- 3) calculate the binding energy of the diatomic molecule
- 4) report the results in a write-up

Theory:

Diatomic molecules (either homonuclear or heteronuclear) such as H₂, N₂, O₂, CO, among others, play important roles in many industrial and natural processes. Determining their stable bond lengths and binding or dissociation energies in gas-phase is an essential step in understanding the catalysis of these molecules. These parameters can be easily calculated using DFT. One step is to calculate the potential energies of these molecules as a function of the distance of separation between the constituent atoms. A simple mathematical model that approximates the distance dependence of electrostatic potential (*V*) between a pair of atoms is given by the Lennard-Jones potential:

$$V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Here, ϵ , σ and r respectively, are the depth of the potential well, the finite distance at which the inter-atomic potential is zero, and the distance between the atoms. The derivative of this potential gives the net inter-atomic forces, which may be attractive, repulsive, or zero, depending on the value of r as shown in Fig. 1. In this equation, the $1/r^{12}$ term is a repulsive term that describes the short range Pauli repulsion due to overlapping electron orbitals, while the $1/r^6$ term is an attractive term that describes the long-range attractive interaction (e.g., van der Waals, or dispersion force). At the stable distance of separation

between the two atoms of the diatomic molecule, the net force is zero. Such stable distance of separation is its stable gas-phase bond length. The binding or dissociation energy can be calculated by finding the value of ϵ shown in Fig. 1.1.

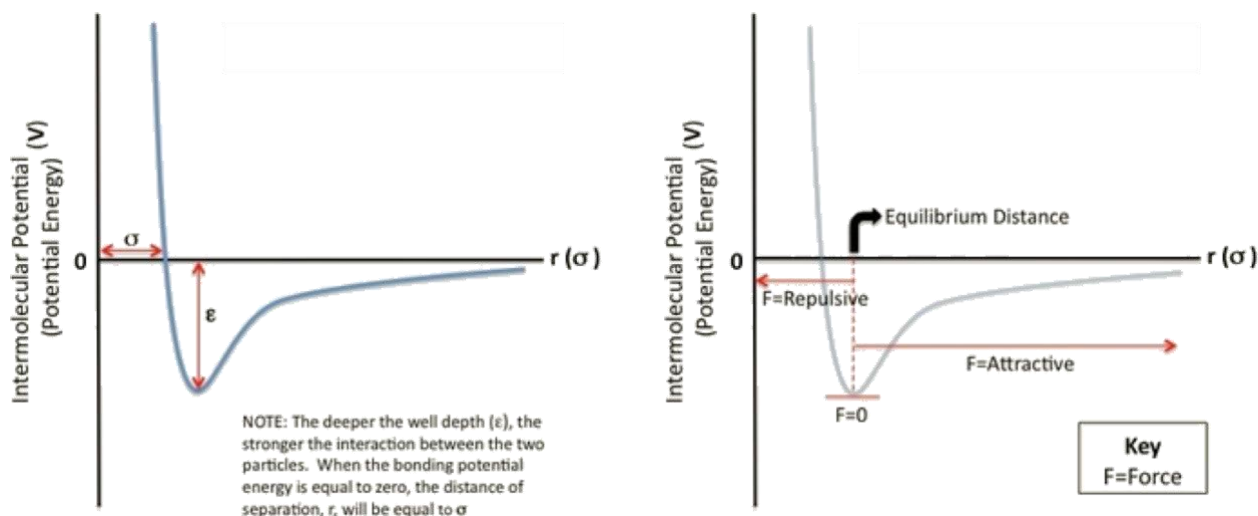


Figure 1.1: Lennard-Jones Potential (Taken from: <https://chem.libretexts.org/>)

Computational Model:

DFT calculations will be implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons will be described using the projector augmented wave (PAW) method. Plane wave basis sets will be employed with an energy cut-off of 400 eV. The surface Brillouin zone integrations will be performed on a grid of $1 \times 1 \times 1$ (gamma point only) Monkhorst-Pack k-points with Gaussian smearing.

Method:

- 1) Construct a large cubic supercell (ca. $25 \times 25 \times 25 \text{ \AA}^3$). Place the two atoms of the diatomic molecule assigned to you at the edge of the supercell, initially at 0.80 \AA distance of separation, with one of the atoms at the $(0,0,0)$ coordinate.
- 2) Perform static calculations for different distances of separation between the atoms. Construct a table and graph of the total energy as a function of r . Start with $r = 0.80 \text{ \AA}$, then increase r at an increment of 0.1 \AA , until a "good enough" Lennard-Jones potential curve is generated.

- 3) Determine the bond length and binding/dissociation energy of the diatomic molecule assigned to you. Compare with experimental data and other DFT calculations reported in the literature.

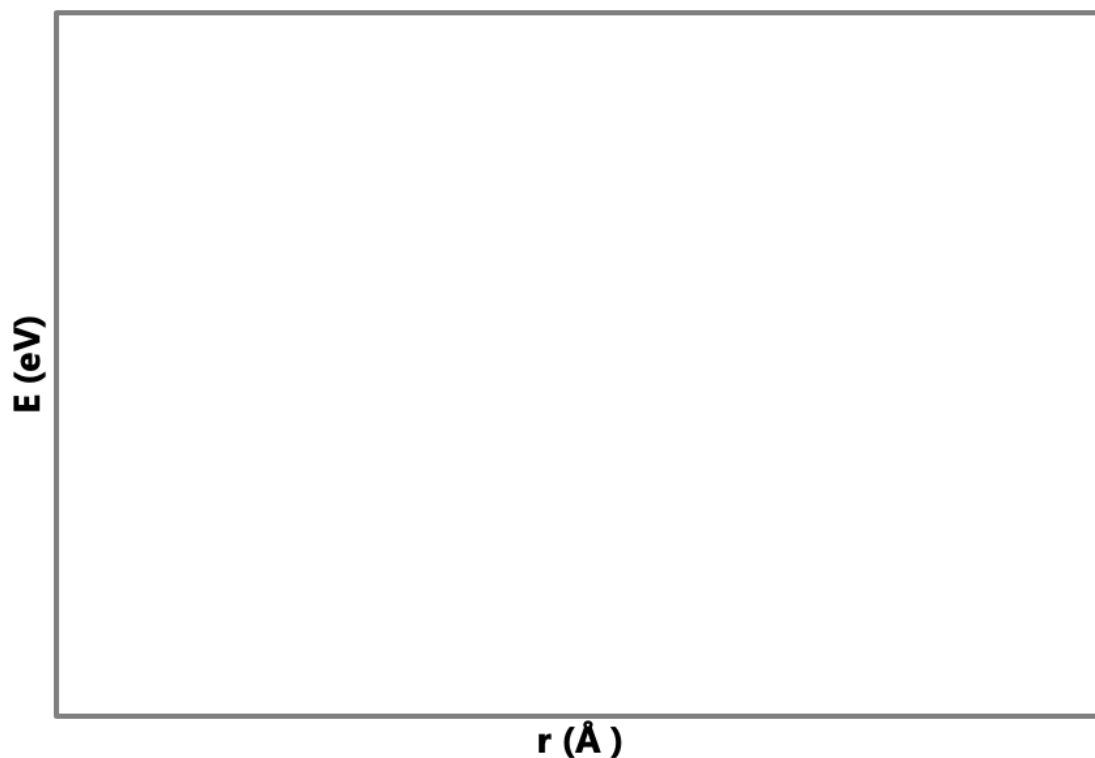
Results and Guide Questions:

Assigned Diatomic Molecule: _____

Table 1: Total Energies as a function of interatomic distances of separation.

Interatomic Distance of Separation, r (Å)	Total Energy, E_{tot} (eV)	Total Energy with Respect to Infinite r , E (eV)

Graph 1: Total energies with respect to infinite r versus the interatomic distance



1) Based on the graph, what is the most stable interatomic distance (bond length) of the diatomic molecule assigned to you?

2) Compare your calculated bond length with the reported experimental and theoretical values in the literature. Discuss the possible discrepancies in values in relation to the methods used in the literature.

3) Based on the graph, what is the dissociation energy of the diatomic molecule assigned to you?

4) Compare your calculated dissociation energy with reported experimental and theoretical values in the literature. Discuss the possible discrepancies.

Conclusion:
