# Homework #1

Geometry Optimization

1. The particle in a box is probably the most classic and analytically solvable system in quantum mechanics. By solving the Schrödinger equation of this system, we can understand the "weird" behavior of quantum effect. The particle in a box basically describes the translational motion of a single particle confined inside an infinitely deep well (0 to L) from which it cannot escape, as shown in the figure below. Please answer the question set below.
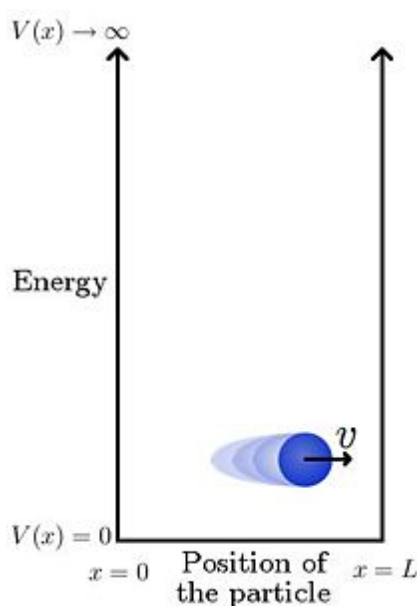
(a) The general form of the time-independent Schrödinger equation is:

$$\hat{H}\Psi = E\Psi$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is the wavefunction (eigen function) of the total system and E is the energy (eigen value) of the system. Please write down the Schrödinger equation of this 1-dimensional particle in a box system.

(b) Following Q1(a), please solve this equation. (*Hint: non-trivial solution of a 2nd order homogenous ODE*)

(c) Is the number of states between E and $E + \delta E$ (density of states) higher in high energy region or low energy region?

(d) How do the differences between energy levels change when we

increase the box size (increase L)?

2. Following similar steps showing in the hands-on session, please perform the ground-state geometry optimization for the following molecules. Specify all the non-redundant internal coordinates (bond lengths, angles and dihedrals) according to symmetry. In addition, identify all possible conformational isomers for all compounds and specify their relative energies.

(a) O_2, (b) H_2O, (c) C_2H_6, (d) [structure] and (e) [structure]
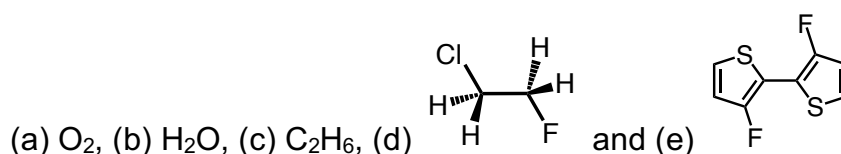
3. Following Q2, please specify their molecular dipole moment. Note that, the molecular long axis should be aligned with the z-axis.

   (a) Write down the definition of moment of inertia matrix.

   (b) How to define the molecular long axis? (*Hint: moment of inertia matrix*)

   (c) How to align the molecule? (*Hint: you may need to write/find a code to rotate the molecules*)

4. Compute the binding energy-distance curve of H_2 shown in the p7 of the slide (xTB_Geometry Optimization_W1_08072022.pptx). To do this, please follow the instructions below:

   (a) Generate a series of folders, named 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 250, 300, 400, and 500.

   (b) In each folder, create a xyz file of H_2. The distance (D) between two hydrogen atoms should be:

   $$D = 0.74 \frac{folder\ name}{100}\ Å$$

   where 0.74 Å is the equilibrium bond length of H_2. This is to create the H_2 structures with H···H distance of 0.8, 0.9, 1.0,…5.0 times the equilibrium bond length.

   (c) Copy the running script to each folder and perform a **single-point** computation for each H_2 structure. Single-point means that we don't want to optimize the structure. Instead, we want to know the energy of H_2 at different H···H distances. Hence, you need to remove the --opt

normal keyword in the script:

xtb -c 0 -u 0 filename.xyz > xtb.out

(d) Extract the "total energy" in the **SUMMARY** section from each folder. Plot the "total energy" vs "D".

(e) Compute the energy of an isolated H atom: create a folder called H. Generate an xyz file with only one H atom. Perform a single-point computation.

(f) Compute the binding energy (E_{bind}) for H_2 structure of different H⋯H distance. The binding energy is defined as:

$$E_{bind}(D) = E_{H_2}(D) - 2 * E_H$$

where $E_{H_2}(D)$ is the total energy of H_2 as a function of D, E_H is the total energy of isolated H atom. Plot the $E_{bind}(D)$ vs D. Does it goes to zero when it reached infinity?