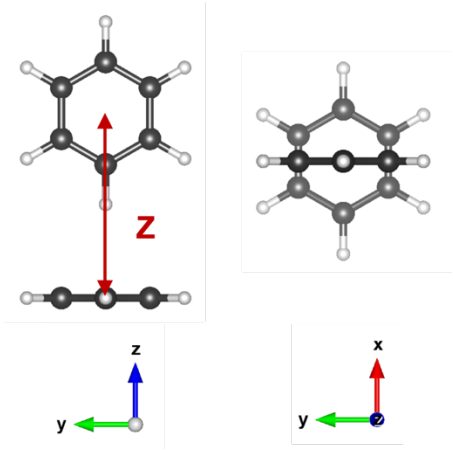
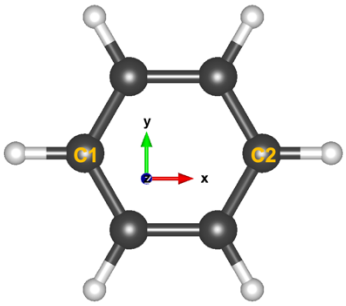
Homework #3

Electrostatic Potential and Intermolecular Interactions

1. **Benzene Dimer**. There are several important configurations of benzene dimer. Apart from the parallel-stacked one, which we investigated in the course, there is another one called T-shaped dimer (shown in Figure below). The distance Z is the distance between the center of mass (COM) of the two benzene molecules. This question set requests you to generate the E_b-Z plot (like what we did for parallel-stacked dimer) for the T-shaped dimer.

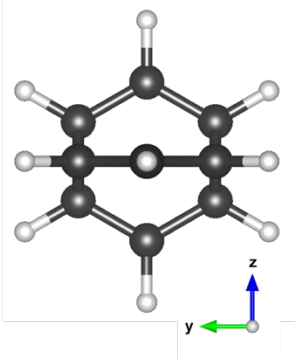


(a) Please create a benzene structure with a specified orientation: Rotate the optimized benzene structure so that (1) one of its C-C (on the opposite side, like C1-C2 in the figure below) vectors aligns with x-axis, and (2) the shortest molecular axis align with z-axis.



(b) Rotate the structure you generated from (a) along y-axis by 90 degree and append it to the original structure (a). You will get a benzene dimer

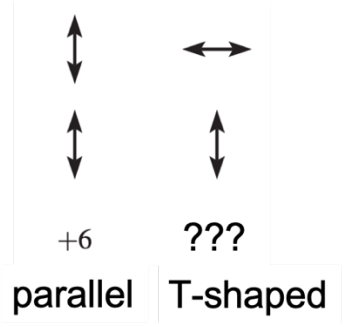
with their COMs overlapping with each other, shown in Figure below.



(c) With the first two steps, you're pretty much ready for the computations of a series of T-shaped dimers with different Z values. Please perform the computations and plot the E_b-Z plot using the bash script and python code(s) I provide in the course. You may need to modify them to suit your need.

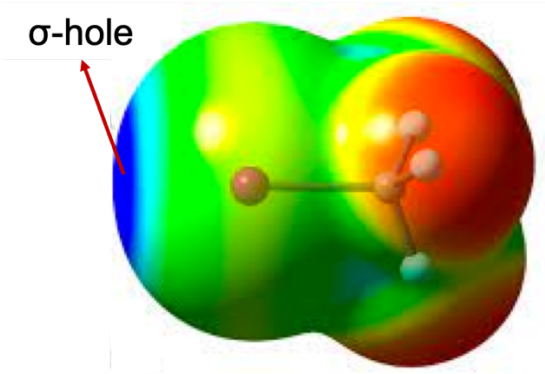
(d) What is the binding energy and equilibrium distance of the T-shaped dimer? Is it more stable than parallel-stacked one?

(e) Calculate quadrupole-quadrupole interaction energy as a function of Z for the T-shaped dimer. Generate a plot like the one in p30 of the slide. Explain your finding. Note: the U_{QQ} of T-shaped and parallel-stacked dimers are different.



2. **Halogen Bond.** When there is a net attractive interaction (D···X-R) between an electron donor (D) and a compound (X-R) with an electrophilic halogen atom (X), we call it a halogen bond. A polar region of positive electrostatic potential along the extensions of the covalent bond, or the so-called σ-hole, is often observed in X-R, see Figure below. The origin of attractive interaction of the halogen bond can thus be explained from the electrostatic perspective: the interaction between the σ-hole and the electrons from the

donor. This question requests you to plot E_b-Z curve of the HCN···ICF_3 system, which is similar to that of the H_2 case in HW1.

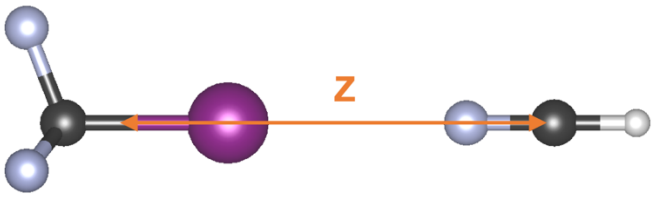


(a) HCN is a linear molecule. Please construct a HCN structure with all atoms lying on z-axis.

(b) ICF_3 is a distorted tetrahedral molecule, with the C-I bond longer than the C-F bond. Please construct a ICF_3 compound with the I and C atoms lying on the z-axis.

(c) Create a series of HCN···ICF_3 dimers with different distances (Z) between their COMs, like the figure below. Perform single-point computation for each Z value and create the E_b-Z curve. The E_b is defined as:

$$E_b(Z) = E_{dimer}(Z) - E_{ICF_3} - E_{NCH}$$



(d) What is the halogen binding energy and the equilibrium distance?

(e) Calculate dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interaction energy as a function of Z for this dimer. Generate a plot including these three terms, the E_b from (c) and the difference between them:

$$E_{diff}(Z) = E_b(Z) - [U_{DD}(Z) + U_{DQ}(Z) + U_{QD}(Z) + U_{QQ}(Z)]$$

You need to first write down the correct form for each multipole-multipole

interaction energy term ($U_{DD}(Z)$,…). How well the molecular multipole-multipole interactions describe this system? Explain your finding.

(f) Instead of using molecular multipole, now use the interactions between atomic charges (see Figure below) to describe the intermolecular electrostatic interactions. The interaction energy originated from this interatomic interactions can be written as:

$$U_{qq}(Z) = \sum_{i}^{i\in ICF_3} \sum_{j}^{j\in NCH} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{R_{ij}(Z)}$$

The q_i and q_j are Mulliken charges of atoms in ICF_3 and NCH obtained from xTB output, respectively. Please take the q_i and q_j from the isolated ICF_3 and isolated NCH computations (not from the dimer). Generate a plot including U_{qq}, the E_b from (c) and the difference between them:

$$E_{diff}(Z) = E_b(Z) - U_{qq}(Z)$$

Does this approximation gives a better description of E_b as compared to the molecular multipole-multipole interactions from (e)? Explain your finding.