Exercise 1 Molecular Mechanics

a) Why is it not valid in all cases to obtain the relative energies of isomers by comparing their MM strain energies?

b) Why is it not valid to calculate a geometry by a fast method, then use that geometry for a frequency calculation at a much higher level of theory (more accurate)?

Exercise 2 TIPS: water model

Together with this exercise you'll find the first two pages of the paper that introduces the TIPS force field. Part of this force field is a model for water interactions and the TIPS model is the most simple form of the famous TIPnP-family for water potentials which is often used

a) Read sections I and IIA.

b) Determine the dipole of the water molecule in eÅ for this model.

c) Determine the optimum O–O distance for a water dimer ignoring the Coulomb interaction. How does this compare to the distance given in the paper and why?

d) Instead of calculating the nine charge-charge coulomb contributions for the water dimer, we can approximate this by a multipole expansion which results in a dipole-dipole interaction:

$$U_{\mathrm{dip-dip}} = -\frac{1}{4\pi\epsilon_0}\frac{p_A p_B}{R^3}\left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi\right)$$

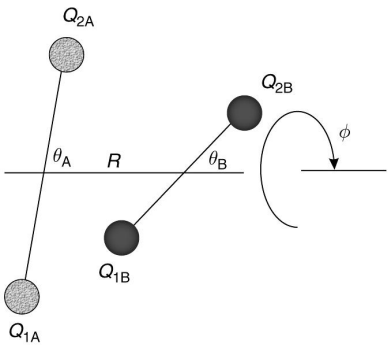
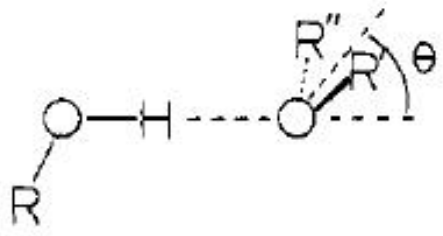


Figure 2.4 *Multipole expansion for a pair of diatomics*

Table III gives the optimal dimer configuration using the following conventions:



Calculate the C_{d} in

$$U_{\mathrm{dip-dip}} = -\frac{C_{\mathrm{d}}}{r^3}$$

using $\frac{1}{4\pi\epsilon_0} = 332$ Åkcal/(mol·e^2).

e) Determine again the optimum O–O distance including the dipole-dipole interaction use:

$$ax^2 + bx^3 - c = 0$$

$$x = \frac{p}{6b} + \frac{2a^2}{3bp} - \frac{a}{3b}$$

with

$$p = \left(108cb^2 - 8a^3 + 12b\sqrt{3c(27cb^2 - 4a^3)}\right)^{\frac{1}{3}}$$

Exercise 3 Optimizing a H_2O dimer

In the previous exercise we have worked with the TIPS potential for water. In the paper which introduced the force field, this was done numerically. In this exercise we will work on how to set up such a problem.

(a) Draw a water dimer. What are the degrees of freedom with and without rigid molecules?

(b) If we would use Cartesian coordinates what would be the dimensions of the force/gradient vector?

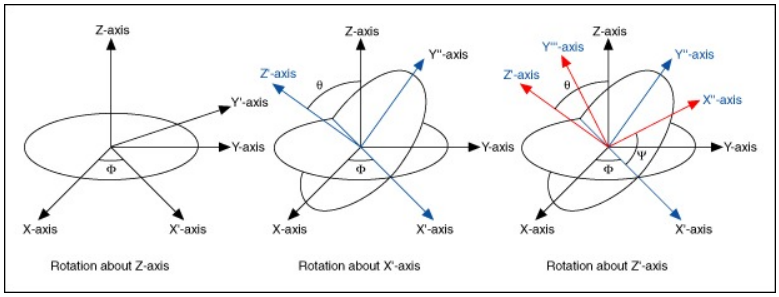
(c) What would be the contributions to the forces on the H atoms? What on the O atoms?

(d) Determine their r dependence.

(e) What would happen if you would optimize the dimer configuration using gradients with respect to Cartesian coordinates?

A common solution is to represent rigid molecules in terms of Euler angles ϕ, θ and ψ. These angles describe the rotation of an axes-frame X'', Y'', Z'' with respect to the original reference frame X, Y, Z. The following three steps describe the rotation (see figure):

1. Rotate about the $Z-$axis by ϕ $(-\pi \leq \phi \leq \pi)$, resulting in the X'-, Y'-, and Z-axes.
2. Rotate about the X'-axis by θ $(0 \leq \theta \leq \pi)$, resulting in the X'-, Y''-, and Z'-axes.
3. Rotate about the Z'-axis by ψ $(-\pi \leq \psi \leq \pi)$, resulting in the X''-, Y'''-, and Z'-axes.



Rotation matrix $\mathbf{A}$

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \mathbf{A} \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

can be obtained by multiplying the three individual rotation matrices

$$\begin{aligned} \mathbf{A} &= \begin{bmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix} \cdot \begin{bmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ &= \begin{bmatrix} \cos\varphi\cos\psi - \sin\varphi\cos\theta\sin\psi & -\sin\varphi\cos\psi - \cos\varphi\cos\theta\sin\psi & \sin\theta\sin\psi \\ \cos\varphi\sin\psi + \sin\varphi\cos\theta\cos\psi & -\sin\varphi\sin\psi + \cos\varphi\cos\theta\cos\psi & -\sin\theta\cos\psi \\ \sin\varphi\sin\theta & \cos\varphi\sin\theta & \cos\theta \end{bmatrix} \end{aligned}$$

In this way, we can express a water dimer by two sets of Euler-angles, $\omega_\mathbf{1} = \{\phi_1, \theta_1, \psi_1\}$ and $\omega_\mathbf{2} = \{\phi_2, \theta_2, \psi_2\}$, and distance R.

(a) Let's define the reference frame of a water molecule with the origin at the centre of mass, the z-axis along the dipole vector and the H-atoms in the xz-plane. Now draw the configuration with $\omega_\mathbf{1} = \{0, \pi/2, \pi\}$ and $\omega_\mathbf{2} = \{\pi/2, \pi, 0\}$

(b) How many degrees of freedom are now available? Is this a problem when one performs a geometry optimization?