Chem 195: Problem Set 6

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March 3, 2016

NOTE: The commented base simulation code is in the script *h2o.m*. In *ps6.m* I have a section for each problem that calls *h2o.m*. Also all of the values presented are in atomic units.
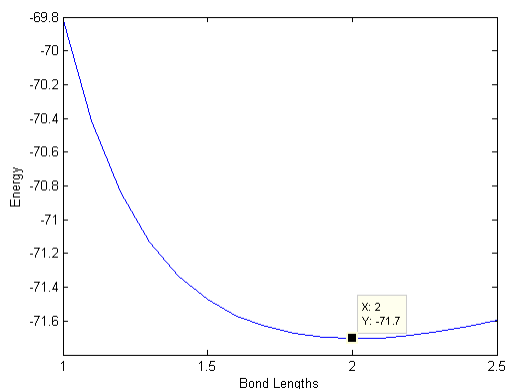
Problem 1

From the Hartree-Fock procedure, we find the energy of water in its equilibrium geometry to be -71.677 Hartrees.

Problem 2

When we perform a Mulliken population analysis, we find that for each hydyogen atom, $q_H = -0.101$, and for the oxygen atom, $q_O = 0.201$. Our answer is not consistent with the general chemical intuition that electron density should be concentrated on the much more electronegative oxygen atom (and thus the oxygen should have a negative net effective charge while the hydrogens should have a net positive charge). The results of our HF simulation are the opposite of what we would expect.
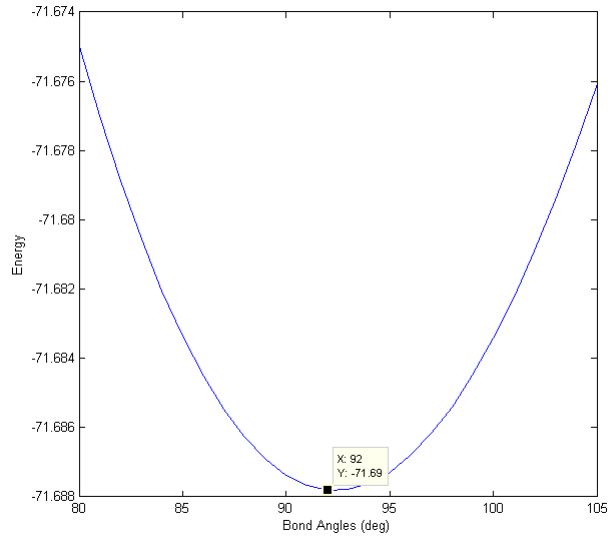
Problem 3

When we vary the OH bond length while keeping the other parameters constant we find $l_{OH} = 2.0$ at our energetic minimum with a precision of 0.1.
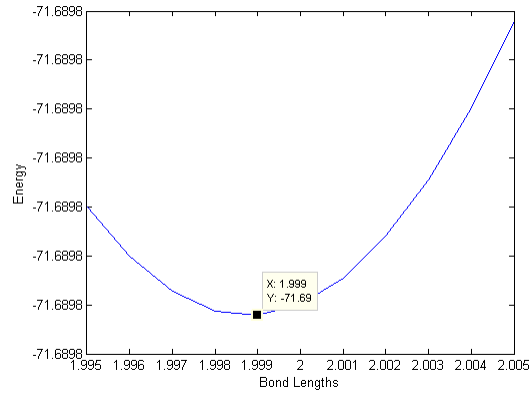

Problem 4

When we vary the HOH bond angle while keeping the other parameters consistent we find that $\theta = 92$ degrees at the energetic minimum.

Problem 5

When we on only vary one of the OH bond lengths we get the following plot of energy as a function of that one varying bond length.

Problem 6

Using our results from the previous problem we determine the curvature d^2E/dR^2 at the energy minimum. Our simulation's precision is $\delta = 0.001$ and our energy minimum was $E(R) = -71.6898$ at $R = 1.999$

$$\frac{d^2E}{dR^2} = \frac{1}{\delta^2}[E(R+\delta) - 2E(R) + E(R-\delta)] \tag{1}$$

$$= 0.624372 \tag{2}$$

Problem 7

To determine the excitation energy of for OH stretching we note that $\hbar$, and the electron mass m_e are unity in atomic units. Since we are working in atomic units, we estimate the mass of hydrogen and oxygen as,

respectively, 1 and 8 times the proton-electron mass ratio (1836.153). We also recall that the effective mass for a two body oscillator is:

$$\mu = \frac{m_1 * m_2}{m_1 + m_2}$$

Where m_1 is the mass of one H and m_2 is the mass of OH. To find the stretch energy in wavenumbers:

$$\hbar\omega_{OH} = \sqrt{m^{-1}d2E/dR^2} \times \frac{2.2 \times 10^5 cm^{-1}}{1 hartree} \tag{3}$$

$$= 4276.305 cm^{-1} \tag{4}$$

Our result is considerably larger (around 10%) than the known OH stretch energies for water ($3657 cm^{-1}$ and $3756 cm^{-1}$ for symmetric and antisymmetric water stretches)

Problem 8

From our calculations we found the eigenvalues of the Fock matrix to be

$FockEigs$
-20.0592
-1.3314
-0.5472
-0.3485
-0.1770
0.7204
0.8692

To estimate the energy of the first ionization we apply Koopman's theorem where N is the number of electrons. ϵ_μ is the highest eigenvalue of the Fock matrix corresponding to the highest energy occupied orbital, which in this case is the 5th highest energy orbital given that $N = 10$ and we can fit 2 electrons per orbital.

$$E_{HOH}(N + 1) - E_{HOH}(N) = -\epsilon_\mu = 0.1770 Hartrees$$

Generally we see that decreasing the bond angle increases the first ionization potential estimate, and vice-versa, while lowering the bond lengths decreases the ionization potentials

θ	$Ionization Potential$
95	0.1798
100	0.1785
104.52	0.1770
110	0.1747
115	0.1722

$BondLengths$	$Ionization Potential$
1.75	0.1738
1.809	0.1770
1.85	0.1796