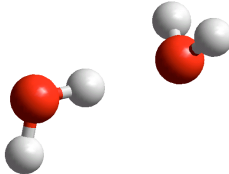


CBE 422 Problem Set # 6
Due @ 11:59 pm Fri. 5/3 by electronic submission on BlackBoard

1. Hydrogen chloride (HCl) is a strongly polar gas. Compute the bond length and dipole moment of the isolated molecule, and compare your results to experimental data (list your data sources). Use three different basis sets in your calculations: (a) a small, fast one (b) a “medium” one and (c) the most accurate basis set you can think of (which could be one of the “Other Basis Sets” of HyperChem). Describe the number and type of orbitals included in each basis set that you use, and compare their relative accuracy and speed of calculations.
2. a. Compute the molecular geometry (specifically, C=C bond length and C=C-H bond angles) for ethylene, using the large 6-31G** basis set, and compare your calculations to experimental data (list your data sources). Also obtain the electrostatic potential around the molecule and illustrate regions of high negative potential associated with the π electrons.
b. Compute the bond stretching potential between 1.2 and 4 Å, using both RHF and UHF calculations and the same basis set as in part a. Do you think that the resulting plots are physically realistic over the complete range of distances? What would be a rough estimate of the C=C double bond strength based on your results?
3. The geometry of the linear water dimer is shown to the right in a “ball-and-stick” representation (see also[†]). Setup two H₂O molecules in approximately this geometry and optimize it using the 6-31G* basis set. Obtain the O-O distance, O-H-O angle for the H-bond, and H-bond energy, and compare your values to experimental data.[‡]
4. Use the 6-31G* basis sets for a single Ar atom to obtain the energy (a) without electron correlations, (b) with CI corrections using both singly and doubly excited states and 3+3 levels for the orbital criterion, and (c) with MP2 corrections (no CI). Now repeat with *two* Ar atoms at a distance of approximately 6 Å. Obtain the energy of interaction implied by your calculations, and compare it to the Lennard-Jones (LJ) interaction energy at the same distance. Use Ar parameters $\epsilon = 120$ K and $\sigma = 3.4$ Å for the LJ calculations.[‡]
5. Protonation energy of a water molecule is defined as the energy difference between H₃O⁺ and H₂O. (a) Perform geometry optimization for H₂O and H₃O⁺ at two different levels of theory, Hartree-Fock and B3LYP using 6-31G* basis set. Compare the optimized geometries (bond lengths and angles) obtained at two different levels of theory. Also, report the optimized energies. (b) Use the B3LYP optimized geometries as initial configuration and compute the protonation energy of a water molecule by employing the following basis sets (PBE96 exchange-correlation potential): STO-3G, 3-21G, 6-31G, 6-31G* and 6-31G**. Report the energies of individual species in tabular form. Explain your observation and comment on the performance of basis sets used. Remember, you have to perform single point energy calculation for this part, no need to do geometry optimization.

Please submit your results, graphs, and snapshots electronically, as a single PDF file. We will assign 20% of the grade to the “aesthetics” of your solution: how easy it is to follow, quality and proper labeling of graphs and snapshots, etc.

[†] http://en.wikipedia.org/wiki/Water_dimer

[‡] If you encounter errors related to the “two-electron integral files,” you need to close HyperChem and issue the command “C:\Hyper80\Program\NewUser80.exe” at a command-line (DOS) window.