Chem. 3430 Homework # 1

Assigned Aug 28, due Sept. 6.

1. Optimize the geometry of H_2, N_2, and F_2 at the HF/6-31G(d) level of theory.
    a) How do your optimized geometries compare with experiment?
    b) Calculate the dissociation energies using DE = $E(X_2) - 2E(X)$. Be sure to use the correct state for the atomic fragments. How do your results compare with experiment? It should be clear from your results that the HF method works better for some molecules than others. Discuss the factors impacting the suitability of the HF method for these three molecules.

2. Calculate the potential energy curve of H_2 at the HF/6-31G level. Choose bond lengths of 0.6, 0.7, 0.8, 1.0, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2 Å. (Note: You might find it difficult to converge the HF calculations at the longer distances. In that case, you might find it useful to use guess=read, starting from the checkpoint file at a short distance, or to use the scan option.) Plot the resulting potential energy curve. Extrapolate your results to obtain a DE value. How does it compare with that obtained in part b)? Discuss your result.

Beyond some critical distance you can find more than one solution to the Hartree Fock equations, the so-called restricted HF (RHF) and spin-unrestricted HF (UHF). To find the latter, you will have to choose the UHF option, and you might need to break symmetry in the initial guess.

3. Which molecule – benzene or ethylene – has the smaller HOMO/LUMO gap at the HF/3-21G level of theory? Is this consistent with your expectation? (Note the degeneracy of the π and π^* orbitals of benzene.)

4. Using the geometry that you optimized in problem 1, calculate the dissociation energy of N_2 at the HF and MP2 levels of theory (Note that MP2 automatically does HF as a first step) using each of the following basis sets: 6-31G, 6-31G(d,p), 6-311G(2d,2p), 6-311G(2d), and 6-311G(2df,2pd). Discuss the importance of various basis functions for the dissociation energy.

5. Calculate the dipole moment of water at using the HF and B3LYP methods using the 6-31G(d) and aug-cc-pVDZ basis sets.