CHM 3411, Dr. Chatfield, Spring 2018
Problem Set 10

Suggested "warmups" (not to turn in): Discussion Questions 10D.1,2,4, 10E.1,2; Exercises from 10D and 10E not included below

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This problem set explores Molecular Orbital Theory applied to polyatomc molecules.

1. Atkins Exercise 10D.2(a). Note ionization energies: F: I=17.4 eV; Xe: I= 12.1 eV.

2. Atkins Exercise 10D.4(a)

3. Atkins Exercise 10E.2(a)

4. Atkins Exercise 10E.3(a)

5. Atkins Exercise 10E.4(a)

6. Apply the method we discussed in class to determine the energies (in terms of a and b) and the coefficients in the LCAO-MO expansion for the MOs of the allyl radical (CH_2CHCH_2). Make a diagram of the energy levels and determine the ground state energy of the molecule. Draw schematic pictures of the molecular orbitals and describe them as bonding, antibonding, or nonbonding. What relevance does your calculation have for the understanding the stability of the allyl radical?

7. Spartan problem.

(A) In Spartan, sketch ethene ($H_2C=CH_2$) and do an equilibrium geometry calculation using the HF/6-31G* method. View the molecular orbitals, identify the HOMO and LUMO, and characterize them as bonding or antibonding. Also measure the C-C distance. Next, form the cation and anion by removing or adding an electron. Optimize the geometry in each case, and measure the C-C distance. Can you understand your results on the basis of the nature of the HOMO and LUMO? How? Hint: to form the cation an anion, change the charge AND the number of unpaired electrons in the Spartan calculations window. Also note that the other orbitals may be confusing to interpret. That is because they may be linear combinations of degenerate orbitals. The HOMO and LUMO, though, should be simple to interpret.

(B) You may need to reoptimize neutral ethene at the HF/6-31G* level. Follow this with an energy calculation at the HF/3-21G level. Does the energy increase or decrease (note the negative sign)? Can you understand why on the basis of the variational principle?