CHM 3411, Dr. Chatfield, Spring 2018
Problem Set 8
Due Monday, March 19

Suggested "warmups" (not to turn in): Discussion questions 10A.1-5, Exercises [(b)] 10A.5-3,6; Discussion question 10B.1

Problems 1-5 explore Valence Bond Theory. Problems 6 and 7 just begin to explore a few of the fundamental concepts of Molecular Orbital Theory. They are purely mathematical but will help you become comfortable with the subject.

1. (a) Write a valence bond wavefunction for HF, treating the bond as if it were perfectly covalent.
   (b) We know that HF is a polar molecule. The valence bond description can be improved by treating it as an example of ionic-covalent resonance. Write a description of the bond as a resonance hybrid, including terms the correspond to HF and H^+F^-.
   (c) An even better description of the bonding in HF can be made by including a third term in the resonance hybrid, corresponding to H^-F^+. Write a description of the resonance hybrid that includes this third term. Which term is likely to be the smallest?

2. Describe the bonding in 1,3-butadiene using hybrid orbitals.

3. Normalize these hybrid orbitals:
   (a) The sp^2 hybrid orbital $h_1 = s+2^{1/2}p$ (given that s and p are each normalized to 1).
   (b) The sp^3 hybrid orbital $h_3 = s - p_x + p_y - p_z$.

4. Describe the structures of SO_2 and SO_3 in terms of valence bond theory. Note that the bond angles in both molecules are approximately 120°. It may be helpful to begin by writing Lewis dot structures, but note that the valence bond theory description may differ a little from them. Also note that it may be helpful to use resonance structures.

5. This problem will help you understand how the orientation of hybrid orbitals in a figure is related to their mathematical form. An sp^2 hybrid orbital that lies in the xy plane and makes an angle of 60° to the x-axis has the form:

$$\psi = \frac{1}{3^{1/2}}\left(s - \frac{1}{2^{1/2}}p_x + \frac{3^{1/2}}{2^{1/2}}p_y\right)$$

   Use hydrogenic atomic orbitals to write the explicit form of the hybrid orbital. Show that the hybrid orbital has its maximum amplitude in the direction specified. Hint: look up the functional form of the orbitals in tables in the text (you may need to look up the radial function and the spherical harmonic separately), and remember that p_x and p_y are linear combinations of p_{+1} and p_{-1}. The angle with respect to the x axis is ϕ.

6. Atkins Exercise 10B.1(a). We have not discussed the overlap integral (S) in class yet, but it is discussed on p. 408 of the text. The overlap of two functions ψ_A and ψ_B is

defined as $S = \int \psi_A^* \psi_B d\tau = \int \psi_B^* \psi_A d\tau$. In this question, you are to determine the normalization constant, N, in terms of λ and S.

7. Atkins Exercise 10B.2(a). The point of this exercise is to demonstrate that you can construct 2 orthogonal MOs from any two given AOs. In this case, you are given one LCAO-MO, and you are asked to determine another LCAO-MO that is orthogonal to it (the exercise does not use the LCAO-MO language, but that is what it is talking about).