CHEM 352: Homework for chapter 3.

1. a) Show that sp^2 hybrid orbital $h = \frac{1}{\sqrt{3}} \left(s + \sqrt{2}p_x \right)$ is normalized. The functions s and p_x denote normalized hydrogenlike atomic orbitals.

b) Normalize the following molecular orbital $\psi = \psi_{s,A} + \lambda \psi_{s,B}$ where $\psi_{s,A}$ and $\psi_{s,B}$ are normalized and λ is a parameter. Use the notation S for overlap integral to simplify the result.

2. Consider hydrogen molecule (H(A)-H(B)) with the LCAO-MO orbitals formed from the atomic orbitals $1s_A$ and $1s_B$:

 $1\sigma_g = N_1 (1s_A + 1s_B)$ and $1\sigma_u^* = N_2 (1s_A - 1s_B)$ a) Show that the Slater determinant corresponding to the ground state solution is antisymmetric.

b) One of the excited states of H₂ corresponds to the following Slater determinant:

$$\psi_{MO} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_u^*(1)\alpha(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_u^*(2)\alpha(2) \end{vmatrix}$$

What electron configuration does this correspond to?

3. Determine the valence electron configurations and bond orders in the following molecules: C_2^+ , C_2 , C_2^- , N_2^+ , N_2 , N_2^- , O_2^+ , O_2 , O_2^- . Which of these molecules are paramagnetic and what are their term symbols?

4. Sketch the molecular orbital diagram for B_2 molecule by using 1s, 2s and 2p atomic orbitals and all 10 electrons. What is the term symbol?

5. a) Sketch a molecular orbital diagram for XeF molecule and determine the electronic configuration. Would XeF⁺ have shorter bond length than XeF?

b) Construct a molecular orbital diagram for the double bond (4 electrons) in ethene by using the carbon sp^2 hybrid orbitals as basis set. Choose the energy order of the σ and π orbitals in such a way that a stable molecule is formed.

c) Explain why Ne_2 molecule is not stable. Why are atoms with the outmost s and p orbitals full (e.g. the octet electronic configuration) chemically inert?

6. Use the variational principle to obtain the lowest energy solution to the hydrogen atom Schrödinger equation in spherical coordinates by using the following trial wavefunctions:

a) $\psi_{trial} = e^{-kr}$ with k as a variational parameter. b) $\psi_{trial} = e^{-kr^2}$ with k as a variational parameter.

Note that both trial functions depend only on r and the angular terms disappear from the Laplacian. You may find the following integrals useful:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$
$$\int_0^\infty x^m e^{-ax^2} dx = \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}}$$
$$\Gamma[n+1] = n!, \text{ with } 0! = 1 \text{ (}n \text{ is integer)}$$
$$\Gamma[n+1] = n\Gamma[n]$$
$$\Gamma\left[\frac{1}{2}\right] = \sqrt{\pi}$$

7. Calculate the π orbitals of allyl radical (corresponding to localized structure $CH_2-C=CH_2$, however, assume delocalization in your calculation) by using the Hückel theory.

a) What is the wavelength of the LUMO \leftarrow HOMO electronic transition when $\beta = -22,000 \text{ cm}^{-1}$?

b) Calculate the charge densities and bond orders from the Hückel wavefunction. Definitions for these observables are given below:

Electron density on atom i:

$$\rho(i) = \sum_{j=1}^{N_{MO}} |c_i^j|^2 n_j$$

where n_j is the number of electrons on orbital j and c_i^j is the Hückel MO coefficient of the basis function centered on atom i for orbital j. The summation runs over the occupied orbitals.

Bond order between atoms i and j:

bond order =
$$\sum_{k=1}^{N_{MO}} c_i^k c_j^k n_k$$

where the symbols are defined as above.