

March 1, 2017

Due Tue, Mar. 7 by 5 pm.

1. (a) How many nodal surfaces of each type will an 11k orbital with $|m| = 3$ have.

(b) Using the scheme covered in lecture and handout 514_8, draw pictures of an 11k orbital with $|m| = 3$ that collectively account for all nodal surfaces.

2. For the following matrix,
$$\begin{pmatrix} 3. & 0.2 & 0 & -0.2 \\ 0.2 & 0 & 0 & 0 \\ 0 & 0 & 100. & -2. \\ -0.2 & 0 & -2. & 3. \end{pmatrix}$$
 find the approximate eigenvalues and

eigenvectors. Do this by considering separate 2×2 parts. First diagonalize the 2×2 matrix for which there is strong mixing. Then use the eigenvectors of that result as new basis vectors whose linear combinations with the remaining two states can be estimated by the perturbation approximations. You are free to use a matrix diagonalizing program as a check, but you must write out the results as instructed above, including all equations used.

3. At an atom separation of 1.40 a.u (not Angstroms), a Hartree-Fock calculation with a certain basis set on the H₂ molecule gives the following MO energies:

$\sigma_g = -0.623$ a.u. , $\sigma_u = +0.401$ a.u., where σ_g and σ_u are the HOMO and LUMO respectively.

The pertinent two-electron integrals of these MOs are given below:

$$\iint \sigma_g(1)\sigma_g(2)(1/r_{12})\sigma_g(1)\sigma_g(2) dv(1) dv(2) = 0.566 \text{ a.u.}$$

$$\iint \sigma_g(1)\sigma_u(2)(1/r_{12})\sigma_g(1)\sigma_u(2) dv(1) dv(2) = 0.558 \text{ a.u.}$$

$$\iint \sigma_g(1)\sigma_u(2)(1/r_{12})\sigma_g(2)\sigma_u(1) dv(1) dv(2) = 0.140 \text{ a.u.}$$

$$\iint \sigma_u(1)\sigma_u(2)(1/r_{12})\sigma_u(1)\sigma_u(2) dv(1) dv(2) = 0.582 \text{ a.u.}$$

(a) Write the two Slater determinants for the $\sigma_g\sigma_u$ configuration in which one electron has $m_s = +1/2$ and the other has $m_s = -1/2$.

(b) Calculate the energy of these two configurations with the information given above.
(obviously the two energies must be equal)

(c) Determine the Hamiltonian matrix element of interaction between these two configurations, and calculate the energy eigenvalues and eigenvectors from a linear variation calculation using

these two Slater determinants as a basis? The resulting two states are the singlet and triplet states associated with these configurations with $M_S = 0$ (i.e., $m_{s1} + m_{s2} = 0$).

- (d) For the two-electron case only, it is possible to factor these two linear combinations into a product of space and spin wavefunctions. Each linear combination is antisymmetric with respect to interchange of the two electrons. Write the two linear combinations in this way.
- (e) The one for which the space part is symmetric is the singlet state. The other is one wavefunction of the triplet (3-fold degenerate). Write the functions for the other two members of the triplet (they are single Slater determinants), and show that they have the same energy as the triplet $M_S = 0$ function.
- (f) Calculate the energy required to remove the σ_u electron. in both states. Koopman's theorem does not apply to the open shell case here.

4. Perform a Gaussian 09 calculation on the ground state of the formaldehyde molecule in which you optimized the geometry using the hf/3-21g method/basis and pop=full , and from the output (.out or .log file, answer the following questions:

- a) In kJ/mol, how much did the energy decrease from your initial geometry to the final minimum energy geometry.
- b) Which direction does the dipole point. Does this conform to your chemical intuition regarding electronegativity?
- c) Make rough drawings of each occupied MO. You should try to do this without using GaussView to display the MOs. Do that to check if your drawings are more or less correct, but on the midterm exam, you will be asked to sketch the MOs without GaussView.
- d) Classify each of the molecular orbitals as to being pi or sigma, and indicate whether each is bonding, antibonding, or non-bonding regarding each bond and overall. This will be somewhat subjective, and will be considered in evaluating your answers.
- e) What is the lowest ionization potential and the electron affinity in eV according the Koopman's Theorem.