MS 131, Problem Set #4

assigned 10/19/05
due 10/26/05

1. Consider the diatomic AB molecule with one bonding electron.

   (a) Starting with the Schroedinger equation, show that the energy of the molecular orbital, if written as a LCAO, must satisfy the following:

$$\begin{bmatrix} -\frac{1}{2}\Delta E-(E-\overline{E}) & h-(E-\overline{E})S \\ h-(E-\overline{E})S & \frac{1}{2}\Delta E-(E-\overline{E}) \end{bmatrix} \cdot \begin{bmatrix} c_A \\ c_B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

   (b) Define all the terms and list any approximations made.

2. Show that for the bonding state of the AB molecule, the constants c_A and c_B are given as:

$$c_A = \frac{1}{\sqrt{2}}\left(1+\frac{\delta - S}{\sqrt{1+\delta^2}}\right)^{1/2}$$

$$c_B = \frac{1}{\sqrt{2}}\left(1-\frac{\delta + S}{\sqrt{1+\delta^2}}\right)^{1/2}$$

   where $\delta = \frac{\Delta E}{2\,|\,h\,|}$

   hint: solve for c_A/c_B first, then normalize ψ^{MO}.

3. Write out the electronic charge density of the AB molecule. Show that it leads to the quantities the degree of ionicity, α_i, and the degree of covalency, α_c. Provide the definitions of these terms.

4. Compare the bonding and antibonding wave functions for homonuclear molecules ($E_A = E_B$) and heteronuclear molecules ($E_A < E_B$). Examine the ratios $(c_A/c_B)^+$ and $(c_A/c_B)^-$, and plot the total wave functions (use 1s atomic orbitals).

5. The equilibrium internuclear distance of the hydrogen molecule is 1.4 Bohr radii. Calculate S for the hydrogen molecule.

6. If a molecule exhibits a certain symmetry, *O*, this implies that that $|\psi|^2$ is unchanged upon operation by $\hat{O}$ on ψ. In turn, this implies $|\hat{O}\psi|^2 = |\psi|^2 \Rightarrow \hat{O}\psi = \pm\psi$. Thus, the eigenvalues for the symmetry operater are +1 (symmetric) or -1(antisymmetric). Using this analysis, fill in the information in the table below

LCAO	I (eigenvalue)	σ_{xz} (eigenvalue)	σ_{yz} (eigenvalue)	Bond type (σ, π or δ; g or u)	Bond/Anti
$s_A + s_B$	1	1	1	σ_g	bonding
$s_A - s_B$					
$p_{z,A} + p_{z,B}$					
$p_{z,A} - p_{z,B}$					
$p_{x,A} + p_{x,B}$					
$p_{x,A} - p_{x,B}$					
$p_{y,A} + p_{y,B}$					
$p_{y,A} - p_{y,B}$					
$d_{z^2,A} + d_{z^2,B}$					
$d_{z^2,A} - d_{z^2,B}$					
$d_{xy,A} + d_{xy,B}$					
$d_{xy,A} - d_{xy,B}$					
$d_{yz,A} + d_{yz,B}$					
$d_{yz,A} - d_{yz,B}$					
$d_{zx,A} + d_{zx,B}$					
$d_{zx,A} - d_{zx,B}$					
$d_{x^2-y^2,A} + d_{x^2-y^2,B}$					
$d_{x^2-y^2,A} - d_{x^2-y^2,B}$					

7. Show graphically that the overlap integral between the $d_{x^2-y^2}$ and the d_{yz} orbitals is zero.