Chem 442: Homework for lecture L26

(only turn in **BOLD** assignment first lecture next week of classes; do all assignments)

1. Show that you cannot get both electrons in the σ (bonding) orbital AND at the same time have the same spin (e.g. α_1 *and* α_2), by constructing the determinant for the wavefunction and multiplying it out.

2. Show that $H_{12} = 0$ for the matrix element between the ground ($\sigma\sigma$) and singly excited ($\sigma\sigma^*$) state of the H_2 molecule. To do so, write it out in full, and then

a) Realize that $\hat{H}$ is independent of spin, so you can move all the $|\alpha\rangle$ and $|\beta\rangle$ functions to the left.

b) Remember that $\langle\alpha|\alpha\rangle_1 = 1$ and $\langle\alpha|\beta\rangle_1 = 0$, etc. Note that

$$(\langle\alpha_1|\langle\beta_2|)(|\alpha_2\rangle|\beta_1\rangle) = \langle\alpha|\beta\rangle_1\langle\beta|\alpha\rangle_2$$

for example.

Turn in 3. The first excited triplet state $^3\Sigma$ of H_2 (its spin is S=1, the two electron spins are parallel) has three degenerate wavefunctions, corresponding to the S_z=M_S=-1,0 and 1 components of the spin angular momentum along the z axis. One of the three determinantal wavefunctions was given as an example in class: $1/\sqrt{2}\ \{|\sigma>_1 |\sigma^*>_2 - |\sigma^*>_1 |\sigma>_2\}\ \alpha_1\alpha_2$.

a. Show that this state is antisymmetric under exchange of electrons 1 and 2.

b. Why are the three states with S=1 degenerate anyway?

c. The state in (a) has M_S=+1; write down the one with M_S=-1.

d. The third state has S=1, M_S=0. This one is a little trickier. It's not just $1/\sqrt{2}\ \{|\sigma>_1 |\sigma^*>_2 - |\sigma^*>_1 |\sigma>_2\}\ \alpha_1\beta_2$; show that that's NOT antisymmetric.

e. The correct one has to be orthogonal to the singlet (S=0, M_S=0) wavefunction $\sim\alpha_1\beta_2-\alpha_2\beta_1$ (the ground state) that we discussed in class, and have M_S=0. Using that information, calculate the S=1, M_S=0 wavefunction for the 1st excited state of H_2.