Homework H26 Solution

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.

Solution:

Writing the determinant for the wavefunction and multiplying it out we have

$$\frac{1}{\sqrt{2}}\begin{vmatrix} |\sigma\rangle_1\alpha_1 & |\sigma\rangle_1\alpha_1 \\ |\sigma\rangle_2\alpha_2 & |\sigma\rangle_2\alpha_2 \end{vmatrix} = \frac{1}{\sqrt{2}}(|\sigma\rangle_1|\sigma\rangle_2\alpha_1\alpha_2 - |\sigma\rangle_2|\sigma\rangle_1\alpha_2\alpha_1) = 0$$

Thus we see the wavefunction is zero if both electrons occupy the same orbital and have the same spin. This should come as no surprise; remember the Pauli exclusion principle! **Note** that in general if a determinant has two identical rows or two identical columns, it will be zero. This is verified here.

2. Show that $H_{12} = 0$ for the matrix element between the ground (σσ) and singly excited (σσ*) 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.

Solution:

From class, recall that

$$|1\rangle = \frac{1}{\sqrt{2}}|\sigma\rangle_1|\sigma\rangle_2\{|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle\}$$

$$|2\rangle = \frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_1\rangle|\alpha_2\rangle$$

Thus

$$H_{12} = \langle 1|\hat{H}|2\rangle$$

$$= \{\langle\beta_1|\langle\alpha_2| - \langle\beta_2|\langle\alpha_1|\}\ {}_2\langle\sigma|\ {}_1\langle\sigma|\frac{1}{\sqrt{2}}\hat{H}\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_1\rangle|\alpha_2\rangle$$

$$= \{\langle\boldsymbol{\beta_1}|\langle\boldsymbol{\alpha_2}| - \langle\boldsymbol{\beta_2}|\langle\boldsymbol{\alpha_1}|\}\{|\boldsymbol{\alpha_1}\rangle|\boldsymbol{\alpha_2}\rangle\}\ {}_2\langle\sigma|\ {}_1\langle\sigma|\frac{1}{\sqrt{2}}\hat{H}\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}$$

Dealing only with the spin portion in bold we have

$$\{\langle\beta_1|\langle\alpha_2| - \langle\beta_2|\langle\alpha_1|\}\{|\alpha_1\rangle|\alpha_2\rangle\} = \langle\alpha|\beta\rangle_1\langle\alpha|\alpha\rangle_2 - \langle\alpha|\beta\rangle_2\langle\alpha|\alpha\rangle_1 = 0 - 0 = 0$$

Because the spin portion equals zero the entire matrix element must equal zero by necessity. Thus we have shown that $H_{12} = 0$.

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.

Solution:

First, let $|\psi\rangle = \frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_1\rangle|\alpha_2\rangle$. Then,

$$\hat{P}_{12}|\psi\rangle = \frac{1}{\sqrt{2}}\{|\sigma\rangle_2|\sigma^*\rangle_1 - |\sigma^*\rangle_2|\sigma\rangle_1\}|\alpha_2\rangle|\alpha_1\rangle$$

$$= -\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_1\rangle|\alpha_2\rangle = -|\psi\rangle$$

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

Solution:

Spin does not appear in the Hamiltonian, and all three triplet states are eigenfunctions of the Hamiltonian and have the *exact same spatial wavefunction*. This directly implies that the states are degenerate; as far as the Hamiltonian is concerned, the triplet states are identical.

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

Solution:

This is accomplished by replacing the two alpha (spin up) terms in the wavefunction from part (a) with beta (spin down) terms:

$$\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\beta_1\rangle|\beta_2\rangle$$

d. The third state has S=1, M_s=0. This one is a little trickier. It's not just $1/\sqrt{2}$ $\{|\sigma>_1 |\sigma*>_2$

- $|\sigma*\rangle_1 |\sigma\rangle_2\}$ $\alpha_1\beta_2$; show that that's NOT antisymmetric.

Solution:

Let $|\psi\rangle = \frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_1\rangle|\beta_2\rangle$

$$\hat{P}_{12}|\psi\rangle = \frac{1}{\sqrt{2}}\{|\sigma\rangle_2|\sigma^*\rangle_1 - |\sigma^*\rangle_2|\sigma\rangle_1\}|\alpha_2\rangle|\beta_1\rangle$$

$$= -\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_2\rangle|\beta_1\rangle \neq -|\psi\rangle$$

e. The correct one has to be orthogonal to the singlet (S=0, M_s=0) wavefunction ~$\alpha_1\beta_2$-$\alpha_2\beta_1$ (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.

Solution:

We already know what the spatial part of the triplet wavefunction will look like (see any part of the question above) and so we need to guarantee that the spin part of the final triplet wavefunction is orthogonal to the spin part of the singlet wavefunction. That is, we need to find the unknown spin wavefunction $|X_S\rangle$ such that

$$\langle X_S|\{|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle\} = 0$$

with M_S=0. It should be clear that $|X_S\rangle$ cannot equal $|\alpha_1\rangle|\alpha_2\rangle$ or $|\beta_1\rangle|\beta_2\rangle$; both of these spin wavefunctions are orthogonal to the singlet spin wavefunction (check it!) but they have M_S values of 1 and -1, respectively. So what is left? What if instead of the negative superposition of up down spins (like in the singlet case) we try the *positive* superposition

$$|X_S\rangle = |\alpha_1\rangle|\beta_2\rangle + |\alpha_2\rangle|\beta_1\rangle$$

We see that this spin wavefunction satisfies M_S=0 since the spins are paired in both terms of the superposition, and it also satisfies the orthogonality criterion as shown below

$$\langle X_S|\{|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle\} = \{\langle\beta_1|\langle\alpha_2| + \langle\beta_2|\langle\alpha_1|\}\{|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle\}$$

$$= \langle\beta|\alpha\rangle_1\langle\alpha|\beta\rangle_2 - \langle\beta|\beta\rangle_1\langle\alpha|\alpha\rangle_2 + \langle\alpha|\alpha\rangle_1\langle\beta|\beta\rangle_2 - \langle\alpha|\beta\rangle_1\langle\beta|\alpha\rangle_2$$

$$= 0 - 1 + 1 - 0 = 0$$

Thus the S=1, M_s=0 wavefunction for the 1st excited state of H_2 is given by

$$\frac{1}{\sqrt{2}}\{|\sigma\rangle_2|\sigma^*\rangle_1 - |\sigma^*\rangle_2|\sigma\rangle_1\}\{|\alpha_1\rangle|\beta_2\rangle + |\alpha_2\rangle|\beta_1\rangle\}$$