Study Guide for Lecture 5: Consequences of Spin in Bonding

Dan Fisher
Oct 5, 2005

1 Summary

- We have discussed inversion and transposition symmetry for the H$_2$ molecule. Since inversion and transposition do not change the energy of the molecule, the spatial wavefunctions must be either symmetric or antisymmetric with respect to the operations.

- Spin is an additional coordinate that describes how electrons behave in a magnetic field.

- The Pauli Principle states that wavefunctions must be antisymmetric with respect to interchanging the spatial and spin coordinates of any two electrons. Therefore, a symmetric spatial combination must go with an antisymmetric spin combination, and vice versa.

- The antisymmetrizer is an operator that generates an antisymmetric wavefunction from a product of orbitals.

- Overlap of same spin orbitals explains the lack of bonding in He$_2$.

2 H$_2$ Symmetry

The Hamiltonian operator for H$_2$ is $\hat{H} = h(1) + h(2) + \frac{1}{r_{12}}$.

The Hamiltonian commutes with the inversion operator, $\hat{I}$, because all interparticle distances are preserved under inversion.

Consider the eigenstates of the Hamiltonian in the MO picture. For the H$_2^+$ molecule, our single electron orbitals are $\phi_g = l + r$ and $\phi_u = l - r$. We can make the H$_2$ molecule by putting two electrons in the $\phi_g$ orbital. This state is bonding and is symmetric under inversion and transposition.

There are two possibilities for the first excited state. We can put electron 1 in $\phi_g$ and electron 2 in $\phi_u$, giving $\phi_g \phi_u$. We can also have $\phi_u \phi_g$. These states are not eigenstates of the transposition operator.

We can take linear combinations of these two states to get eigenstates of the transposition operator. The symmetric combination is $\phi_u \phi_g + \phi_g \phi_u$ and the antisymmetric combination is $\phi_u \phi_g - \phi_g \phi_u$. The state $\phi_u \phi_g - \phi_g \phi_u$ is antibonding and is antisymmetric under inversion and transposition.

In the VB picture, our ground state is $LR + RL$, which is bonding and symmetric under inversion and transposition. The first excited state is $LR - RL$, which is antibonding and antisymmetric under inversion and transposition.

3 Spin

In addition to its spatial coordinates, each electron has a spin coordinate, which describes how it behaves in a magnetic field. Possible spin values are up, or $\alpha$, and down, or $\beta$.

Some possible spin combinations for two electrons are $\alpha \alpha$, $\alpha \beta$, $\beta \alpha$, and $\beta \beta$. Of these, $\alpha \beta$ and $\beta \alpha$ are not eigenfunctions of the transposition operator. In order to make eigenfunctions, we take symmetric and antisymmetric linear combinations to get $\alpha \beta + \beta \alpha$ and $\alpha \beta - \beta \alpha$. 

1
\( \alpha \beta + \beta \alpha, \alpha \alpha, \) and \( \beta \beta \) all have \( S = 1 \). Since there are three of them, they are called a \textbf{triplet state}. \( \alpha \beta - \beta \alpha \) has \( S = 0 \) and is called the \textbf{singlet state}.

The \textbf{Pauli principle} states that all wavefunctions must be antisymmetric with respect to interchanging the spatial and spin coordinates of any two electrons. Therefore, a symmetric spatial combination must be accompanied by an antisymmetric spin combination, and an antisymmetric spatial combination must have a symmetric spin combination.

As we saw in the previous section, bonding states are symmetric with respect to transposition, so they must have a singlet spin combination. Antibonding states are antisymmetric in space, so they have triplet spin.

Consider two nonorthogonal orbitals, \( \langle a|b \rangle = s \). If these orbitals have a triplet spin combination, the spatial parts will have to get orthogonal to each other. Let \( \overline{b} = b - sa \). Then \( \langle a|\overline{b} \rangle = \langle a|b \rangle - s \langle a|a \rangle = 0 \). As we bring the orbitals closer together, their overlap increases, and the negative contribution to \( b \) increases. The orbital \( \overline{b} \) becomes steeper, which results in unfavorable kinetic energy and repulsion. Therefore, overlapping orbitals of the same spin will always be repulsive.

If the orbitals have a singlet spin combination, on the other hand, the spatial orbitals don’t have to change. They can combine to form a new orbital with a decreased gradient and more favorable KE.

4 \textbf{He}_2

Consider bringing two Helium atoms together to form a molecule analogous to \textbf{H}_2. Our VB ground state wavefunction would be \( L^2 R^2 + R^2 L^2 \).

We can see why this molecule doesn’t form when we use the antisymmetrizer to make a wavefunction to describe it. In the expression \( \forall (La)(L\beta)(Ra)(R\beta) \), we see that the orbitals \( L \) and \( R \) have triplet spin combinations. Therefore, the spatial orbitals will have to get orthogonal to each other as the atoms approach, which will lead to a repulsive interaction.

In the MO picture, we can consider adding two electrons to the \textbf{H}_2 molecule. These two electrons will have to go into the antibonding \( gu - ug \) orbital, leaving us with no net bonding.

The \textbf{He}_2\textsuperscript{+} molecule, however, will have only one electron in the antibonding orbital, so we will have a bond order of 1/2. This molecule will have a greater bond distance and less bond energy than \textbf{H}_2.

Some HF/6311G**++ results: \textbf{He}_2\textsuperscript{+} is unbound because it dissociates into two \textbf{He} ions, which would repel each other. There is a barrier and a local minimum at 0.69 \, \text{Å}, but it is unlikely that this molecule would ever form.

5 \textbf{Suggested Reading}

- Spin - 4.1, 4.2, 4.3, 4-A in the Goddard Book

- Spin Angular Momentum, Pauli Principle, Slater Determinants - McQuarrie p. 298-307