Linear Combinations of Atomic Orbitals to make Molecular Orbitals --LCAO-MO

Rather than pursuing the exact one-electron diatomic molecule solution further, we will use the variational method to obtain approximate molecular orbitals for this problem. We will choose a trial function using a sum of one electron orbitals centered on nucleus A and one electron orbitals centered on nucleus B. Each orbital has a coefficient $c_i$ multiplying it. We determine the expectation value of energy using the $H_2^+$ Hamiltonian and this trial function. The result is a function of all of the coefficients $c_i$. We minimize this expectation value with respect to all of the $c_i$, and the result is our approximate answer.

The simplest possibility is to use one hydrogen function with the same $m$ on each of the nuclei. Thus let us take a trial $\psi$,

$$\psi = c_1 \chi_A + c_2 \chi_B$$  \hspace{1cm} (1)

The expectation value of the total energy is
\[ \langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{c_1^2 H_{AA} + 2 c_1 c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 S_{AA} + 2 c_1 c_2 S_{AB} + c_2^2 S_{BB}} \]

where \( S_{AB} = \langle \chi_A | \chi_B \rangle \), called an overlap integral. The integrals centers and the integral generally vanishes only for large R.

\( S_{BB} = \langle \chi_B | \chi_B \rangle \) etc. These terms are unity if the trial functions and \( H_{AB} = \langle \chi_A | \hat{H} | \chi_B \rangle \)

Note the matrix elements \( H_{AB} \). We take derivatives of the above expression with respect to \( c_1 \) and \( c_2 \), set them equal to zero, and find the minima.

Thus we take \( \frac{\partial E}{\partial c_1} = 0 \) and \( \frac{\partial E}{\partial c_2} = 0 \)

The easiest thing to do is to rewrite the energy expression before differentiating,
\[ E(c_1, c_2) \left[ c_1^2 S_{AA} + 2c_1c_2 S_{AB} + c_2^2 S_{BB} \right] = c_1^2 H_{AA} + 2c_1c_2 H_{AB} + c_2^2 H_{BB} \]

Remembering that \( E \) is a function of \( c_1 \) and \( c_2 \), we differentiate with respect using the chain rule. For example, \( c_1 \)

\[ E \left[ 2c_1 S_{AA} + 2c_2 S_{AB} \right] + \frac{\partial E}{\partial c_1} \left[ c_1^2 S_{AA} \right] + 2c_1c_2 S_{AB} + c_2^2 = 2c_1 H_{AA} + 2c_2 H_{AB} \]

Since the derivative is zero, we can simplify to obtain

\[ c_1 \left( H_{AA} - ES_{AA} \right) + c_2 \left( H_{AB} - ES_{AB} \right) = 0 \]

and similarly for the \( c_2 \) term,

\[ c_1 \left( H_{AB} - ES_{AB} \right) + c_2 \left( H_{BB} - ES_{BB} \right) = 0 \]

Recognize all this??
These last two equations are called **secular equations**.
Let's plot them.
In order to have a solution other than the trivial one, the slopes of the two lines must be the same. When this happens, one can show generally that the determinant of the coefficients (the secular determinant) must vanish,

$$\begin{vmatrix}
H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\
H_{AB} - ES_{AB} & H_{BB} - ES_{BB}
\end{vmatrix} = 0$$

We solve this determinantal equation for \( E \), and obtain two solutions. Let's consider the case where \( \chi_A = \chi_B \). Then \( S_{AB} = S \) and \( H_{AA} = H_{BB} \). The overlap integral \( S \) goes smoothly from 0 at \( R_{AB} = \infty \) to 1 at \( R_{AB} = 0 \). In this approximation, the above determinant simplifies to

$$\begin{vmatrix}
H_{AA} - E & H_{AB} - ES \\
H_{AB} - ES & H_{AA} - E
\end{vmatrix} = 0$$
We solve this quadratic equation for $E$, and obtain two solutions, now much simpler than we found earlier:

$$E_+ = \frac{H_{AA} + H_{AB}}{1 + S} \quad \text{and} \quad E_- = \frac{H_{AA} - H_{AB}}{1 - S}$$

These are the two energy values associated with the trial function $\psi = c_1 \chi_A + c_2 \chi_B$. Note that in this case the roots are a lot simpler than the ones that we worked out in the last homework.

To obtain the wave function associated with each of them, we first substitute $E_+$ into eq (22) and solve for $c_1$ and $c_2$. We next substitute $E_-$ into Eq (22) and solve for $c_1$ and $c_2$. The results are $c_1 = c_2$ for $E_+$ and $c_1 = -c_2$ for $E_-$. The resulting wavefunctions are as follows:
\[
\psi_+ = c_1 \chi_A + c_1 \chi_B = \frac{1}{\sqrt{2+2S}} \left( \chi_A + \chi_B \right)
\]

and

\[
\psi_- = c_1 \chi_A - c_1 \chi_B = \frac{1}{\sqrt{2-2S}} \left( \chi_A - \chi_B \right)
\]

In the last part of each wave function, we have chosen \(c_1\) so as to normalize the function.

*Thus the two atomic functions \(\chi_A\) and \(\chi_B\) gave rise to two molecular wave functions, \(\psi_+\) and \(\psi_-\).*

We must calculate the energies \(E_+\) and \(E_-\) to see which one lies lowest in energy. Note that the energies and the matrix elements are all functions of \(R\). In general, we can expect that one of these combinations is bonding and the other is antibonding.
Notice that $H_{AA}$, $H_{AB}$ and $S$ (and hence $E_+$ and $E_-$) are all functions of the internuclear distance, $R$. Thus we must evaluate these quantities for each value of $R$.

For the ground state of $H_2^+$, we let $\chi_A = 1s_A$ and $\chi_B = 1s_B$. For the two molecular wavefunctions, one of these two states is a repulsive (dissociative) state. When we carry out the calculation, we obtain the following potential curves:
Thus for the first two $H_2^+$ states, we obtain the following Molecular Orbitals. We show a slice in the x-y, z=0 plane. The **bonding** molecular orbital is shown first, as a surface plot and as a contour plot.
And the antibonding orbitals, 

Note the nodal plane between the two atomic centers!
One of these two states is a repulsive (dissociative) state. Other excited states can be constructed using linear combinations of other orbitals. Some will be bonding and others will be repulsive. Thus for the electronic states of $H_2^+$ we obtain the molecular orbitals shown on the next figure:

**Nomenclature**

$\sigma_u^* \ 1s$

$g$ - gerade
$u$ - ungerade

* - antibonding
<table>
<thead>
<tr>
<th>LCAO Function</th>
<th>MO Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s_A + 1s_B$</td>
<td>$\sigma_g 1s$</td>
</tr>
<tr>
<td>$1s_A - 1s_B$</td>
<td>$\sigma_u^* 1s$</td>
</tr>
<tr>
<td>$2s_A + 2s_B$</td>
<td>$\sigma_g 2s$</td>
</tr>
<tr>
<td>$2s_A - 2s_B$</td>
<td>$\sigma_u^* 2s$</td>
</tr>
<tr>
<td>$2p_{z_A} - 2p_{z_B}$</td>
<td>$\sigma_g 2p$</td>
</tr>
<tr>
<td>$2p_{x_A} + 2p_{x_B}$</td>
<td>$\pi_u 2p$</td>
</tr>
<tr>
<td>$2p_{x_A} - 2p_{x_B}$</td>
<td>$\pi_g^* 2p$</td>
</tr>
<tr>
<td>$2p_{y_A} + 2p_{y_B}$</td>
<td>$\pi_u 2p$</td>
</tr>
<tr>
<td>$2p_{y_A} - 2p_{y_B}$</td>
<td>$\pi_g^* 2p$</td>
</tr>
<tr>
<td>$2p_{z_A} + 2p_{z_B}$</td>
<td>$\sigma_u^* 2p$</td>
</tr>
</tbody>
</table>
Let us look at these various combinations:
First the 1s
Next, the 2pz combinations, leading to $\sigma_u^* \, 2p$ and $\sigma_g \, 2p$ orbitals
Followed by the 2px, y combinations, leading to $\pi_u^* 2p$ and $\pi_g 2p$ orbitals