Chapter 5
Bonding in Polyatomic Molecules

Read the sections on valence bond theory/hybridization (pages 139-146) on your own.

MO Theory: the ligand group approach and application to triatomic molecules
With diatomic species, each atom's atomic orbitals were written, with the MO written in between.

But how do we devise an MO for more than two atoms? CO₂? BF₃? SF₆?

Typically we make the outer atoms act as a collective unit—the ligand group and consider the ligand group orbitals (LGO).

Consider BeH₂.
Although the H-atoms are separated, we will consider them a “basis set” of orbitals: one will be in-phase and one will be out-of-phase.

Which do you think will be higher in energy?

Constructing an MO for BeH₂
Bond order?

Notice that you can also match the symmetry of the various orbitals to determine which will “mix” (i.e., form an MO) and which will not (i.e., resulting in non-bonding orbitals). The 2s orbital as $\sigma_g$ symmetry as does the LGO(1). The 2p, has $\sigma_u$ symmetry as does LGO(2). The 2p$_x$ and 2p$_y$ orbitals have $\pi_u$ symmetry and since the LGOs don’t, there is no mixing.

A Bent Triatomic: H$_2$O

From the previous chapter, we can assign the point group $C_{2v}$ to H$_2$O. To know if the orbitals of oxygen match the LGOs in symmetry, we can use the operations found on the $C_{2v}$ character table: E, C$_2$, $\sigma_v$(xz), and $\sigma_v$´(yz).

Apply the operations for each orbital of interest:

<table>
<thead>
<tr>
<th>Orbital</th>
<th>E</th>
<th>C$_2$</th>
<th>$\sigma_v$(xz)</th>
<th>$\sigma_v$´(yz)</th>
<th>Match?</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p$_x$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p$_y$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p$_z$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When describing orbital symmetry, use lower case letters of the symmetry type.

For the LGOs, consider the hydrogens as a group and count atoms unchanged:

<table>
<thead>
<tr>
<th>E</th>
<th>C$_2$</th>
<th>$\sigma_v$(xz)</th>
<th>$\sigma_v$´(yz)</th>
</tr>
</thead>
</table>

What rows add up to be this “reducible representation”?

Those are the symmetries of the two LGOs!!

To know the contribution of H#1 and H#2 in LGO(1) and LGO(2), consider how H#1 (represented by $\Psi_1$) is transformed into the other atom ($\Psi_2$).

<table>
<thead>
<tr>
<th>E</th>
<th>C$_2$</th>
<th>$\sigma_v$(xz)</th>
<th>$\sigma_v$´(yz)</th>
</tr>
</thead>
</table>
Now multiply the characters in $A_1$ by the results above and you return...

For $b_2$, you get...

And now we can build a qualitative MO diagram for $H_2O$—paying particular attention to the symmetries of everything involved.

O   MO (H$_2$O)   LGOs
**MO for BH₃**

What is the point group for BH₃?

So based on this character table, which symmetry type corresponds to the s, pₓ, pᵧ, and pᶻ orbitals?

<table>
<thead>
<tr>
<th></th>
<th>D₃h</th>
<th>E</th>
<th>2C₃</th>
<th>3C₂</th>
<th>σₜ</th>
<th>2S₃</th>
<th>3σᵥ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁'</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂'</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>E'</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>A₁''</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
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<tr>
<td>A₂''</td>
<td>1</td>
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<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>E''</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Consider how D₃h symmetry operations affect the hydrogen basis set:

<table>
<thead>
<tr>
<th>E</th>
<th>C₃</th>
<th>C₂</th>
<th>σₜ</th>
<th>S₃</th>
<th>σᵥ</th>
</tr>
</thead>
</table>

This reduces to...?

Since there are three atoms (i.e., three atomic orbitals), there must be three LGOs. Assign hydrogen atoms as: Ψ₁, Ψ₂, Ψ₃ then follow each operation on the basis set:

<table>
<thead>
<tr>
<th>E</th>
<th>C₃</th>
<th>C₃²</th>
<th>C₂(1)</th>
<th>C₂(2)</th>
<th>C₂(3)</th>
<th>σₜ</th>
<th>S₃</th>
<th>S₃²</th>
<th>σᵥ(1)</th>
<th>σᵥ(2)</th>
<th>σᵥ(3)</th>
</tr>
</thead>
</table>

Now multiply by the characters in A₁’ and you get the first LGO as a combination of...

Now multiply by the characters in E’ and you get

<table>
<thead>
<tr>
<th>E</th>
<th>C₃</th>
<th>C₃²</th>
<th>C₂(1)</th>
<th>C₂(2)</th>
<th>C₂(3)</th>
<th>σₜ</th>
<th>S₃</th>
<th>S₃²</th>
<th>σᵥ(1)</th>
<th>σᵥ(2)</th>
<th>σᵥ(3)</th>
</tr>
</thead>
</table>

So the result is:

Since one orbital of e’ has a node, the other, degenerate orbital will also have a node:
Now construct the MO for BH₃:

**MO for NH₃**
For ammonia, the point group is C₃ᵥ. The symmetry of the LGOs will develop into the same shapes (a₁ and e) and the atomic orbitals will be...?
What’s so strange about nitrogen in ammonia? Nitrogen inversion!

**MO for CH₄.**
This molecule obviously has Tₐ symmetry and looking at the character table, the atomic orbitals on carbon fall into a₁ and t₂ symmetries. A basis set of the four hydrogen atoms also leads to a₁ and t₂ symmetries, so there is good overlap between atomic orbitals and the LGOs.
MO theory: bonding analyses soon become complicated
Up to now, believe it or not, the bonding has been pretty simple. Our LGOs have consisted of only what type of orbitals?

Consider BF₃, which has D₃h symmetry (same as BH₃)
The atomic orbitals on boron have the same symmetry as before (a₁, e, a₂), but what about fluorine(s)? We must make LGOs out of the atomic orbitals there. First define the axes: (x, y are in the plane of the atoms, z is perpendicular to the plane of the atoms).

What would the LGO symmetries be for the fluorine s-orbitals?

To determine the p-orbitals, consider the D₃h operations on pₓ (or pᵧ) and on pₜ.

For pₓ:

\[
\begin{array}{c|c|c|c|c|c}
E & C₃ & C₂ & σₕ & S₃ & σᵥ \\
\end{array}
\]

What does this equal in the D₃h character table?

For pᵧ:

\[
\begin{array}{c|c|c|c|c|c}
E & C₃ & C₂ & σₕ & S₃ & σᵥ \\
\end{array}
\]

What does this equal in the D₃h character table?

For pₜ:

\[
\begin{array}{c|c|c|c|c|c}
E & C₃ & C₂ & σₕ & S₃ & σᵥ \\
\end{array}
\]

What does this equal in the D₃h character table?

By assigning Ψ₁, Ψ₂, Ψ₃ values to each fluorine orbital, we can find how they transform into each other—multiply by the characters in the character table (for the appropriate row), and you can find what the LGOs look like.
NOTE: see page 157 of your textbook for a “disclaimer” (in the figure caption) and 158 (1st paragraph)

B.O. calc for BF₃?
**π-bonding with CO₂**

With $D_{\text{ch}}$ symmetry, we will use the oxygens to form a basis set (LGO). Looking at the character table, we see that the symmetry labels look quite different ($\Sigma$, $\Pi$, instead of $A$, $B$, $E$, $T$).

![Energy levels and MO diagrams for CO₂](image)

**Bond order calculation?**

**Similarly for nitrate ion (NO₃⁻)**

![Energy levels and MO diagrams for NO₃⁻](image)

**Bond order calc?**
Skip the section on SF₆

Lastly... **Three center two electron bonds (3c, 2e)**
Most covalent bonds we deal with (or like to deal with) are two center two electron bonds (2c,2e)

EX. H₂O

But some molecules appear to be “electron deficient”. We saw earlier that BF₃ actually has some multibond character (1½ bond), but that can’t be true for BH₃. (Why?)

Is boron really “happy” with only 6 electrons (according to a valence bond sense)?