October 9, 2003 - Lecture 11: Molecular Orbitals II.

Bonding in heteronuclear dimers: (Example is CO - important ligand in organometallic chemistry)

- atomic electron configuration: C 1s² 2s² 2p² and O 1s² 2s² 2p⁴ - big difference in the \( Z_{\text{eff}} \) ⇒ O orbitals are more stabilized than C, larger 2s/2p splitting in O₂ (compare the MO levels in homodimeric structures)

- VB theory requires formal negative charge on the C and positive charge on the O - triple bond between ⇒ need to form 1 \( \sigma \) and 2 \( \pi \) bonds and 2 lone pairs

- Molecular orbital levels:
  - 1s orbitals: asymmetric orbital picture ⇒ higher orbital has more C character (all antibonding orbitals) ⇒ general wavefunction form \( \Psi_{\text{bnd}} = \alpha \phi_C + \sqrt{1 - \alpha^2} \phi_O \) and \( \Psi_{\text{antibnd}} = \sqrt{1 - \alpha^2} \phi_C - \alpha \phi_O \)
  - 2s, 2p orbitals: asymmetry remains ⇒ O based orbitals are lower in energy than C based ⇒ allow for mixing of 2s and 2p orbitals along the C-O bond
    \[
    \Psi(h_1) = \frac{1}{\sqrt{1 + c^2}} [\phi_s + c \phi_p] \quad \Psi(h_2) = \frac{1}{\sqrt{c^2 + 1}} [c \phi_s - \phi_p] + 2 \text{ atomic orbitals with 1 electron}
    \]
  - draw the orbital energy diagrams: \( (1\sigma_C)^2 \) \( (1\sigma_C^*)^2 \) \( (2\sigma_{\text{nb, O}})^2 \) \( (3\sigma_{\text{O,C}})^2 \) \( (1\pi_{\text{C, O}})^4 \) \( (4\pi_{\text{C}})^2 \) \( (1\pi_{\text{C, O}})^0 \) \( (3\sigma_{\text{C, O}})^0 \)
  - shape of the orbitals: bonding more on the O, antibonding more on the C

Bonding in trinuclear molecules:

Linear molecules: (Example is CO₂ - we already did CO - and focus only on valence orbitals)

- use character table \( (D_{\infty h}) \) to organize the atomic orbitals and aid their combination to form LCAOs:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O + O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s is</td>
<td>( a_{1g} ) (totally symmetric)</td>
<td>2s+2s is ( a_{1g} )</td>
</tr>
<tr>
<td>2p₂ is</td>
<td>( a_{1u} ) (antisymmetric to inversion)</td>
<td>2s-2s is ( a_{1u} )</td>
</tr>
<tr>
<td>2pₓ, 2pᵧ are</td>
<td>( e_{1u} ) (degerate)</td>
<td>2pₓ+2pᵧ is ( a_{1u} )</td>
</tr>
<tr>
<td>2pₓ, 2pᵧ are</td>
<td>( e_{1u} ) (degerate)</td>
<td>2pₓ-2pᵧ is ( a_{1g} )</td>
</tr>
<tr>
<td>(2pₓ, 2pᵧ) + (2pₓ, 2pᵧ) are</td>
<td>( e_{1u} )</td>
<td></td>
</tr>
<tr>
<td>(2pₓ, 2pᵧ) - (2pₓ, 2pᵧ) are</td>
<td>( e_{1g} )</td>
<td></td>
</tr>
</tbody>
</table>

- Orbitals within the same irred.rep. can be combined! Order the orbitals based on the extent of overlap:

<table>
<thead>
<tr>
<th></th>
<th>1a₁g (O s(pₓ) + O s(pᵧ))</th>
<th>1a₁u(O s(pₓ) - O s(pᵧ)): non-bonding electron pairs (lone pairs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a₁g (C s + O p₂ - O p₂)</td>
<td>2a₁u (C p₂ - O p₂ - O p₂): ( \sigma ) bonds</td>
<td></td>
</tr>
<tr>
<td>1e₁u (C pₓ/pᵧ + O pₓ/pᵧ + O pₓ/pᵧ): 3 center ( \pi ) bonds</td>
<td>1e₁g (O pₓ/pᵧ - O pₓ/pᵧ): non-bonding electron pair (lone pair)</td>
<td></td>
</tr>
<tr>
<td>2a₁g* (C 2pₓ/pᵧ - O pₓ/pᵧ - O pₓ/pᵧ): ( \pi^* ) orbitals</td>
<td>1e₁u* (C 2pₓ/pᵧ - O pₓ/pᵧ - O pₓ/pᵧ): ( \pi^* ) orbitals</td>
<td></td>
</tr>
<tr>
<td>2a₁g* (C 2s - O p₂ + O p₂)</td>
<td>3a₁u* (C p₂ + O p₂ + O p₂): ( \sigma^* ) orbitals</td>
<td></td>
</tr>
</tbody>
</table>
Angular molecules: (Example is H$_2$O)

- symmetry is C$_{2v}$, character table gives A$_1$, A$_2$, B$_1$, B$_2$ irreducible representations. (molecule is in the yz plane)

\[
\begin{align*}
\text{O} & \quad 2s \text{ is } a_1 \quad \text{(totally symmetric)} \\
& \quad 2p_z \text{ is } a_1 \quad \text{(totally symmetric)} \\
& \quad 2p_x \text{ is } b_1 \quad \text{(C}_2\text{ inverts sign, in } \sigma_v) \\
& \quad 2p_y \text{ is } b_2 \quad \text{(C}_2\text{ and } \sigma_v\text{ invert sign)} \\
\text{H + H} & \quad 1s+1s \text{ is } a_{1g} \\
& \quad 1s-1s \text{ is } b_2
\end{align*}
\]

- Orbitals within the same irreducible representation can be combined! Order the orbitals based on the extent of overlap:

\[
\begin{align*}
2a_1 \ (\text{O } s(p_z)) &: \text{ non-bonding (lone pair)} \\
1b_2 \ (\text{O } p_y + H s - H s) & \ 3a_1 \ (\text{O } p_x(s) + H s + H s): \sigma \text{ bonding} \\
1b_1 \ (\text{O } p_x) &: \text{ non-bonding} \\
3a_1^* \ (\text{O } p_x(s) - H s - H s) & \ 1b_2^* \ (\text{O } p_y - H s + H s): \sigma^* \text{ orbitals}
\end{align*}
\]

- Start opening up the bond angle from 104.5° to 180° (going back to linear trinuclear system):

\[
\begin{align*}
2a_1 &: \text{ slightly increases in energy } \Rightarrow 2a_{1g} \\
1b_2 &: \text{ slightly decreases in energy } \Rightarrow 1a_{1u} \\
3a_1 &: \text{ sharply increases in energy } \Rightarrow 1e_{1u} \\
b_1 &: \text{ remain constant } \Rightarrow 1e_{1u}
\end{align*}
\]

The correlation of orbital energies upon geometry change give the Walsh diagrams.