5. Molecular Orbitals

5.1 Formation of Molecular Orbitals (MO’s) from Atomic Orbitals (AO’s)

\[ \Psi = c_a \Psi_a + c_b \Psi_b \]

- \( \Psi \) = molecular wave function
- \( \Psi_a \) and \( \Psi_b \) = atomic wave functions
- \( c_a \) and \( c_b \) = adjustable coefficients

For \( \text{H}_2 \):

- \( \Psi(\sigma) = N [c_a \Psi(1s_a) + c_b \Psi(1s_b)] = 1/\sqrt{2} [\Psi(1s_a) + \Psi(1s_b)] \)
- \( \Psi(\sigma^*) = N [c_a \Psi(1s_a) - c_b \Psi(1s_b)] = 1/\sqrt{2} [\Psi(1s_a) - \Psi(1s_b)] \)

\( c_a = c_b = 1 \) and \( N = 1/\sqrt{2} \) for \( \sigma \) and \( \sigma^* \)

Approximation! Remember, an anti-bonding MO is more anti-bonding than a bonding is bonding.

5. Molecular Orbitals

The significance of \( c_a \) and \( c_b \) in:

\[ \Psi_{A-B} = c_a \Psi_a \pm c_b \Psi_b \]

- **anti-bonding**
- **bonding**

- \( A-A \) = Equal energies
- \( A-B \) = Unequal energies
- \( A-B \) = Very unequal energies

...there can be non-bonding orbitals as well!
5. Molecular Orbitals

The $\sigma$, $\pi$ and $\sigma^*$, $\pi^*$ notation

...don't forget about $\delta$ and $\delta^*$ orbitals!

5.1.1 MO's from s-Orbitals

$a$ node between the nuclei!

$\sigma^* = \frac{1}{\sqrt{2}} (\psi(l_{s1}) - \psi(l_{s2}))$

$s = \frac{1}{\sqrt{2}} (\psi(l_{s1}) + \psi(l_{s2}))$

no node!
5. Molecular Orbitals

5.1.2 MO’s from p-Orbitals

However, there can be nodes in bonding MO’s from p- and d-orbitals.

5.1.3 MO’s from d-Orbitals

FIGURE 5.3: Interactions of d Orbitals. (a) Interaction of molecular orbitals. (b) Orbitals that do not form molecular orbitals.
5.2 Homonuclear Diatomic Molecules

MO Diagram for the first 10 elements:
- Works great for $O_2$ -> explains $O_2$'s paramagnetism
- But predicts $B_2$ to be diamagnetic
  -> Orbital Mixing!

Bond order = \( \frac{\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding orbitals}}{2} \)

5.2 Homonuclear Diatomic Molecules

- $B_2$ is paramagnetic! $BO = 1$, no $\sigma$-bond!
- $C_2$ is diamagnetic $BO = 2$, two $\pi$-bonds

Degenerate orbitals
- Aufbau principle
- Hund's Rule
- Pauli's Principle:
  - Effect of orbital mixing

<table>
<thead>
<tr>
<th>C—C Distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C (gas phase)</td>
</tr>
<tr>
<td>H—C=C—C—H</td>
</tr>
<tr>
<td>C≡C</td>
</tr>
</tbody>
</table>
5.2 Homonuclear Diatomic Molecules

<table>
<thead>
<tr>
<th>Bond Order</th>
<th>Internuclear Distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2^-$ (dioxygen)$^3$</td>
<td>2.5</td>
</tr>
<tr>
<td>O$_3$ (dioxogen)$^3$</td>
<td>2.0</td>
</tr>
<tr>
<td>O$_{2^-}$ (superoxide)$^9$</td>
<td>1.5</td>
</tr>
<tr>
<td>O$_{2^+}$ (peroxide)$^8$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Note: Oxygen-oxygen distances in O$_2^-$ and O$_{2^+}$ are influenced by the cation. This influence is especially strong in the case of O$_{2^+}$ and is one factor in its unusually long bond distance.

5.2 Homonuclear Diatomic Molecules

Energy of all orbitals decreases as increased nuclear charge attracts the electrons more strongly

Effect is larger for s-orbitals!
5.2 Homonuclear Diatomic Molecules

Bond Distances & Orders, Atomic Number & Radii

![Graphs showing bond distances and atomic radii.]

5.2 Homonuclear Diatomic Molecules

Photoelectron Spectroscopy:

\[ \text{O}_2 + hv \rightarrow \text{O}_2^+ + e^- \]

Ionization Energy (binding energy) =

\[ h\nu - \text{kinetic energy of expelled } e^- \]

Remember

- Morse-Potential
- Vibrational Fine Structure
5.2 Homonuclear Diatomic Molecules

A Correlation Diagram for Diatomic Molecules

note decreased spacing with decreased atomic #
5.3 Heteronuclear Diatomic Molecules

- Greater nuclear charge, lower energy AO's, more contracted orbitals
- MO has mainly oxygen character

*CO poisoning & hemoglobin architecture

5.3 Ionic Compounds & Molecular Orbitals

- MO has mainly fluorine $p_z$-character
- $\rightarrow Li^+$ and $F^-$ ($p^6$)

Electronegativity

\[
\begin{array}{cc}
2.54 & 3.61 \\
2.54 & 4.19 \\
\end{array}
\]
5.4 Molecular Orbitals for Larger Molecules

5.4.2 Carbon Dioxide’s Molecular Orbital Diagram

\[ \text{O=C=O} \]
\[ D_{\infty h} \rightarrow D_{2h} \]

<table>
<thead>
<tr>
<th>( D_{2h} )</th>
<th>( E )</th>
<th>( C_{2}(z) )</th>
<th>( C_{2}(x) )</th>
<th>( l )</th>
<th>( \sigma(xy) )</th>
<th>( \sigma(xz) )</th>
<th>( \sigma(yz) )</th>
<th>( x^2, y^2, z^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{g} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( R_{g}, xy )</td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>( R_{g}, xz )</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>( R_{g}, yz )</td>
</tr>
<tr>
<td>( A_{u} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>( z )</td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>( y )</td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>( x )</td>
</tr>
</tbody>
</table>
5.4 Molecular Orbitals for Larger Molecules

<table>
<thead>
<tr>
<th>Orbital</th>
<th>2(a_l)</th>
<th>2(b_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>-10.4 eV</td>
<td>-10.7 eV</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-32.4 eV</td>
<td>-15.9 eV</td>
</tr>
</tbody>
</table>

Diagram:

- 2\(a_l\) group orbitals
- 2\(b_1\) group orbitals
- Molecular orbitals for Carbon and Oxygen
- Energy levels for 2\(a_l\) and 2\(b_1\) orbitals
5.4 Molecular Orbitals for Larger Molecules

5 \( \sigma \) group orbitals

5

6 \( \sigma \) group orbitals

6

5.4 Molecular Orbitals for Larger Molecules

7 \( 2\pi \) group orbitals

7

8 \( 2\pi \) group orbitals

8

11
5.4 Molecular Orbitals for Larger Molecules

et voila... CO$_2$

MO Diagram

\[ O=C=O \]

$\sigma$-bonds
$\pi$-bonds

5.4 Molecular Orbitals for Larger Molecules

e.g. Water
5.4 Molecular Orbitals for Larger Molecules

e.g. Ammonia

5.4 Molecular Shapes & Hybrid Orbitals

Combination of Atomic Orbitals to form Hybrid Orbitals

Old but very useful concept!

3x localized in space & directional

Try this for NH$_3$, H$_2$O, and CO$_2$