Chapter 9

Bonding II:
Molecular Geometry and Bonding Theories

Molecular Orbital Theory

- **Molecular orbital theory**: Atomic orbitals (AO) combine to form new molecular orbitals (MO) which are spread out over the entire molecule.

- **Molecular** orbitals (MO) describe the properties of the entire **molecule**, and not the properties of individual atoms.

- Molecular orbitals (wave functions) result from adding and/or subtracting atomic orbitals (wave functions).
Molecular Orbital Theory

- Molecular orbitals:
  - have specific shapes and energies.
  - can have a maximum of two electrons with opposite spins.
  - are equal to the number of atomic orbitals they have been composed from “the number of orbitals is conserved”.
- Our study about MO theory is restricted to diatomic molecules.

Molecular Orbitals from s Atomic Orbitals

Hydrogen molecule: \( H + H \)

\[ 1s^1 \quad 1s^1 \]

\[ \rightarrow \quad H-H \]

\[ \sigma_{1s}^2 \]

antibonding orbital

\[ \sigma_{1s}^* \]

bonding orbital

\[ \sigma_{1s} \]

H atomic orbitals \( \rightarrow \) H\(_2\) molecular orbitals

Energy direction
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σ₁s Molecular Orbital

Hydrogen molecule

- “Bonding” molecular orbital.
- Constructive combination of "ns" AOs.
- High electron density “high probability” between the two nuclei.
- Lower energy and more stable than the AOs that were added.

σ*₁s Molecular Orbital

Hydrogen molecule

- “Antibonding” molecular orbital.
- Destructive combination of "ns" AOs.
- Very low electron density “low probability” between the two nuclei. The electron density pulls the two nuclei in opposite directions.
- Higher energy and less stable than the AOs that were subtracted.
**σ_{1s} and σ^{*}_{1s} Molecular Orbitals**

**Hydrogen molecule**

- Showing all the MOs in a molecule can result in a complicated picture.
- Energy diagrams / energy levels are often used to represent MOs in the molecule.

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**MOs in the Hydrogen Molecule**

- Energy diagrams / energy levels are often used to represent MOs in the molecule.
Bond Order

The higher the value of the bond order, the more stable the molecule and the stronger the bond.

- $\text{bond order} = \frac{1}{2} (2 - 0) = 1$
  - single bond

- $\text{bond order} = \frac{1}{2} (2 - 2) = 0$
  - no bond

The MO theory predicts Li$_2$ to be a stable molecule whereas Be$_2$ to be not.
Molecular Orbitals from $p$ Atomic Orbitals

- Some molecules, such as $B_2$, combine their $p$ AOs to generate new MOs. ($B$: $1s^22s^22p^1$).
- Recall the shape of the $2p$ orbitals.

Two pairs of parallel $p$ orbitals can overlap \textit{sideways}, and the third pair can overlap \textit{head-on}.
Head-On Overlap for $p$ MOs

The two $p$ orbitals that overlap head-on produce two $\sigma$ MOs:
- one bonding, $\sigma_{2p}$ (constructive combination), and
- one antibonding, $\sigma^*_{2p}$, (destructive combination).

Both bonding $\sigma_{2p}$ and antibonding $\sigma^*_{2p}$ MOs can be shown together in one diagram. They would look kind of complicated.
Two $p$ orbitals that lie parallel overlap to produce two $\pi$ MOs:
- one bonding, $\pi_{2p}$ (constructive combination), and
- one antibonding, $\pi^*_{2p}$ (destructive combination).

The bonding $\pi_{2p}$ and antibonding $\pi^*_{2p}$ MOs can be shown together in one diagram. They would look kind of complicated.

Remember that you have two bonding $\pi_{2p}$ MOs (along the $y$ and $z$-axes) and two antibonding, $\pi^*_{2p}$ MOs (also along the $y$ and $z$-axes), giving four $\pi$ MOs in total.
- MOs generated from the combination of \( p \) AOs are always higher in energy than MOs generated from the combination of \( s \) AOs.

- Antibonding MOs are higher in energy than bonding MOs.

- The order of MO energies assumes no interaction taking place between \( p \) and \( s \) orbitals.

- In atoms of smaller nuclear charges (Li, B, C and N) the \( s \) orbitals are held less tightly by the nucleus and some \( s-p \) interaction takes place.

\( s \) and \( p \) orbitals do not interact: \( \text{O}_2, \text{F}_2, \text{Ne}_2 \)

\( s \) and \( p \) orbitals do interact: \( \text{Li}_2, \text{B}_2, \text{C}_2, \text{N}_2 \)
When filling the MO levels, you have to:

- Count the number of valence electrons,
- Start with the lower energy orbitals first,
- Follow Hund’s rule, and
- Put not more than two electrons in one MO.

**Molecular Orbital Diagram of O₂**

<table>
<thead>
<tr>
<th>MO</th>
<th>Count</th>
<th>Energy Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{2p_z}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi_{2p_y}$, $\pi_{2p_z}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi_{2p_y}$, $\pi_{2p_z}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{2p_x}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{2s}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{2s}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Molecular Orbital Diagram of N₂**

The order of these two MOs are switched.
Paramagnetism and Diamagnetism

- **Paramagnetism** causes the substance to be attracted to a magnetic field.

- **Diamagnetism** causes the substance to be repelled from a magnetic field.

- **Paramagnetism** is associated with **unpaired** electrons.

- **Diamagnetism** is associated with **paired** electrons.

Liquid oxygen, O$_2$(l), is attracted to the poles of a magnet because O$_2$ is paramagnetic.

Molecular Orbital Diagram

- Molecular orbital theory helps you predict several important properties of the substance.
  - Bond order (bond length and bond strength).
  - Bond enthalpy (bond energy)
  - Magnetic properties.

MO diagram of O$_2$
Molecular Orbital Diagrams

| Bond order | 1 | 1 | 2 | 3 | 2 | 1 | 0 |
| Bond length (pm) | 267 | 159 | 131 | 110 | 121 | 142 | – |
| Bond enthalpy (kJ/mol) | 104.6 | 288.7 | 627.6 | 941.4 | 408.7 | 156.9 | – |

| Magnetic properties | Diamagnetic | Paramagnetic | Diamagnetic | Diamagnetic | Paramagnetic | Diamagnetic | – |

Exercises

- **Predict the bond order and magnetism of Ne₂.**

  - **Bond order**
    
    \( \frac{(8 - 8)}{2} = 0 \)

    According to the MO theory, Ne₂ doesn’t exist.
Exercises

Give the electron configurations and bond orders for $O_2$, $O_2^+$, and $O_2^-$. 

<table>
<thead>
<tr>
<th></th>
<th>$O_2$</th>
<th>$O_2^+$</th>
<th>$O_2^-$</th>
<th>Bond Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{2p}^*$</td>
<td>↑↑</td>
<td>↑↑</td>
<td>↑↓↓↓</td>
<td>2</td>
</tr>
<tr>
<td>$\pi_{2p}^*$</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↓↓↑↑</td>
<td>2.5</td>
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<tr>
<td>$\pi_{2p}$</td>
<td>↑↑</td>
<td>↑↑</td>
<td>↑↑↑↑</td>
<td>1.5</td>
</tr>
<tr>
<td>$\sigma_{2s}$</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓↓↓</td>
<td>2</td>
</tr>
</tbody>
</table>

$O_2$: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

$O_2^+$: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

$O_2^-$: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$

Exercises

Predict the bond order and magnetism of $P_2$. 

Bond order $= \frac{8 - 2}{2} = 3$

According to the MO theory, $P_2$ exists and it is diamagnetic.
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Bonding in Heteronuclear Diatomic Molecules

- MO model can be expanded to diatomic molecules with two different nuclei whose electronic natures are not so different.
- Carbon monoxide (CO) is expected from MO theory to be diamagnetic and to have a bond order of: 
  \[(8 - 2) / 2 = 3\]

The MO energy-level diagram of the CO molecule

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Descriptions of Molecules with Delocalized Bonding

- Localized electron model assumes that the bonding electron pair is being shared between two atoms (localized).
- In several cases, such as O₃ and NO₃⁻, the π-electron bonding pairs are delocalized and are not present at a specific location in the molecule.
Descriptions of Molecules with Delocalized Bonding

- In molecules with resonance structures,
  - $\sigma$ bonds can be viewed to be localized, and
  - $\pi$ bonds can be considered to be delocalized.

Example: Benzene ($C_6H_6$)

Each C atom has 3 electron domains

Hybridization: $sp^2$