Chapter 8
Advanced Theories of Covalent Bonding

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Two Quantum Mechanical Theories for Chemical Bonding

Lewis VSEPR model can predict molecular geometry but cannot explain the difference between the two bonds

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{H} & \quad \text{H}
\end{align*}
\]

150.6 kJ/mol and 142 pm

436.4 kJ/mol and 74 pm

Valence Bond (VB) Theory and Molecular Orbital (MO) Theory can explain!
Covalent bond is formed when **two atomic orbitals from each of the atoms are overlapped**.

Only one pair of electrons should be shared by two overlapping orbitals and their spins should be opposite.
Now, let’s consider polyatomic molecules.
Hybridization of Atomic Orbitals

To explain the variety of molecular shapes, we often must mix two or more atomic orbitals in an atom to produce a set of hybrid orbitals.

BeH$_2$

Be

$\begin{array}{ccc}
\uparrow \downarrow & \text{2s} & \text{2p} \\
\end{array}$

$\begin{array}{cc}
\uparrow & \text{2s} \\
\uparrow & \text{2p} \\
\end{array}$

Hydrogen

$\begin{array}{cc}
\uparrow \downarrow & \text{2s} \\
\uparrow \downarrow & \text{2p} \\
\end{array}$

$\begin{array}{cc}
\uparrow & \text{unhybrid orbitals} \\
\uparrow & \text{unhybrid orbitals} \\
\end{array}$

$\begin{array}{cc}
\uparrow \downarrow & \text{sp hybrid orbitals} \\
\uparrow \downarrow & \text{sp hybrid orbitals} \\
\end{array}$

$\begin{array}{cc}
\uparrow & \text{unhybrid orbitals} \\
\uparrow & \text{unhybrid orbitals} \\
\end{array}$
Hybridization of Atomic Orbitals: \( sp: \) Linear Structure

Formation of \( sp \) hybrid orbitals

- Mixing or hybridizing an \( s \) and a \( p \) orbital of the same atom
- These two \( sp \) hybrid orbitals actually have the same center.
- Orientation of the two \( sp \) hybrid orbitals with respect to the nucleus and each other

Bonding in \( \text{BeH}_2 \)

- \( s \) and \( sp \) orbitals overlap to form a stable bond.
- The overlap creates a linear structure.
Hybridization of Atomic Orbitals: $sp^2$

Trigonal Planar

$BCl_3$

2s

2p

$sp^2$ hybrid orbitals

Unhybridized 2p orbital
**$sp^2$ Hybrid Orbitals**

- **s orbital** + **Two perpendicular p orbitals**

  ![Image of hybridization process](image)

  - **hybridization**
  - **Three $sp^2$ hybrid orbitals in central atom B**
  - **Three $p$-orbitals of Cl are overlapped with three $sp^2$ hybrid orbitals**
$sp^3$ Hybrid Orbitals

CH$_4$

C

$2s$

$2p$

$sp^3$ hybrid orbitals
$sp^3$ Hybrid Orbitals: Tetrahedral

- s orbital
- Three perpendicular $p$-orbitals

Four $sp^3$ hybrid orbitals
<table>
<thead>
<tr>
<th>Hybridization of central atom</th>
<th>Number of hybrid orbitals</th>
<th>Shape of hybrid orbitals</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp$</td>
<td>2</td>
<td>linear</td>
<td>BeCl$_2$</td>
</tr>
<tr>
<td>$sp^2$</td>
<td>3</td>
<td>Trigonal planar</td>
<td>BF$_3$</td>
</tr>
<tr>
<td>$sp^3$</td>
<td>4</td>
<td>Tetrahedral</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>$sp^3d$</td>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>PCl$_5$</td>
</tr>
<tr>
<td>Hybridization of central atom</td>
<td>Number of hybrid orbitals</td>
<td>Shape of hybrid orbitals</td>
<td>Examples</td>
</tr>
<tr>
<td>------------------------------</td>
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</tr>
<tr>
<td>$sp^3d^2$</td>
<td>6</td>
<td>Octahedral</td>
<td>SF$_6$</td>
</tr>
</tbody>
</table>
**$sp^3d$ Hybrid Orbitals: Trigonal Bipyramid**

[Diagram showing the hybridization process for $PBr_5$]

- **3s** orbitals: Hybridized to form $sp^3d$ hybrid orbitals.
- **3p** orbitals: Hybridized to form $sp^3d$ hybrid orbitals.
- **3d** orbitals: Unhybridized $d$ orbitals.
$sp^3d^2$ Hybridization Orbital: Octahedral

$\text{SF}_6$

$\uparrow \downarrow$

3s

$\uparrow \uparrow$

3p

$\uparrow \uparrow$

3d

$\uparrow \uparrow$

3s

$\uparrow \uparrow$

3p

$\uparrow \uparrow$

3d

$sp^3d^2$ hybrid orbitals

Unhybridized $d$ orbitals
Hybridization in Molecules Containing Double and Triple Bonds

**σ bonding**

(a) s orbitals

(b) p orbitals

(c) Hybrid orbitals

**π bonding**

One π bond consisting of two separate regions of electron density
Hybridization in Molecules Containing Double Bond

Double bond consists of one $\sigma$ bond and one $\pi$ bond

2s

$\uparrow \downarrow$

2p

$\uparrow$ $\uparrow$ $\uparrow$

$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$

$\pi$ bond

$s$ orbital

$p$ orbital

$sp^2$ orbital

$\sigma$ bond

$sp^2$ hybrid orbitals

$2p_z$
Hybridization in Molecules Containing Triple Bond

Triple bond consists of one $\sigma$ bond and two $\pi$ bonds

$sp$ hybrid orbital

$\sigma$ bond

$\pi$ bond

$2s$ $2p$

$2s$ $2p$

$sp$ hybrid orbitals $2p_y$ $2p_z$
Molecular Orbital (MO) Theory

\[ \text{O}_2 \text{ molecules should be diamagnetic, because there is no unpaired electron in O}_2. \]
\[ \text{Note that O atom alone is paramagnetic} \]

Valence bond theory cannot explain why \( \text{O}_2 \) molecules are paramagnetic.

Diamagnetic: all electrons are paired (\( \uparrow \downarrow \))
Paramagnetic: some electrons are unpaired (\( \uparrow \\downarrow \))
Molecular Orbital (MO) theory

Explains covalent bonds in terms of molecular orbitals, which result from interaction of the atomic orbitals of the bonding atoms and are associated with the entire molecule.
Bonding and Anti-bonding Molecular Orbitals

1s + 1s → Orbitals overlap

Anti-bonding sigma MO

Bonding sigma MO
Wave amplitudes add to give a higher amplitude.

Wave amplitudes cancel to give zero amplitude.
Bonding and Anti-bonding Molecular Orbitals

Note that x, y, and z directions of p orbitals are arbitrary.
Bonding and Anti-bonding Molecular Orbitals

$2p_y 	ext{ or } 2p_z$

$\pi_{2p_y}^* \text{ or } \pi_{2p_z}^*$

$\pi_{2p_y} \text{ or } \pi_{2p_z}$
Molecular Orbital Energy Diagram: \( \text{H}_2 \)
The number of molecular orbitals will always be **the same as the number of atomic orbitals** used to construct them.

Electrons fill the lowest energy orbitals that are available.

Each molecular orbital can hold **two electrons**, but the spins must be opposite.

As in the atomic orbitals, **Hund’s rule** should be considered.
What are the bond orders of $\text{H}_2$, $\text{H}_2^-$, and $\text{H}_2^+$?
Molecular Orbital Energy Diagram: He$_2$

What is the bond order?
What are the bond orders of Li$_2$ and Be$_2$?
Molecular Orbital Energy Diagram in Second Periodic Diatomic Molecules

Note that the energetic ordering of the molecular orbitals can be altered because of 2s-2p orbital interaction. In B₂, C₂, and N₂ molecules, π₂p orbitals are lower in energy than σ₂p orbital.
Molecular Orbital Energy Diagram in Second Periodic Diatomic Molecules

<table>
<thead>
<tr>
<th></th>
<th>B₂</th>
<th>C₂</th>
<th>N₂</th>
<th>O₂</th>
<th>F₂</th>
<th>Ne₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond order</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Bond length (pm)</td>
<td>159</td>
<td>131</td>
<td>110</td>
<td>121</td>
<td>142</td>
<td>-</td>
</tr>
<tr>
<td>Bond energy (kJ/mol)</td>
<td>288.7</td>
<td>627.6</td>
<td>941.4</td>
<td>498.7</td>
<td>156.9</td>
<td>-</td>
</tr>
<tr>
<td>Magnetic properties</td>
<td>Para-</td>
<td>Dia-</td>
<td>Dia-</td>
<td>Para-</td>
<td>Dia-</td>
<td>Dia-</td>
</tr>
</tbody>
</table>
Lewis structures use **resonance** to explain that the actual molecule appears to have several equivalent bonds, rather than different possible structures.

MO theory shows the electrons being **delocalized** in the structure.
Homework

TBA