Chapter 10: Bonding & Molecular Structure - Hybridization & Molecular Orbitals

Chemical bonding in covalent compounds can be explained by

(VB) (1) Valence Bond Theory - bonding results from overlap of atomic orbitals

(MO) (2) Molecular Orbital Theory - a model of bonding in which pure atomic orbitals combine to produce molecular orbitals that are delocalized over 2 or more atoms.

VB Theory gives a good visual picture of molecular structure.
MO Theory gives a quantitative picture of bonding. It is more complex and is only theory that explains why Co is paramagnetic.

How does orbital overlap work to form bonds? (Figure 10-1)

But - how can we have orbital overlap with our familiar s, p and d orbitals to get the shapes we know occur with VSEPR theory? Geometries like trigonal planar? Tetrahedral? etc.

Linus Pauling proposed the theory of orbital hybridization. A new set of orbitals called hybrid orbitals can be created by mixing s, p + d orbitals to get new orbitals.
Let's look at the kind of hybridization that can occur:

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>Regions of high electron density around central atom</th>
<th>Electronic Geometry</th>
<th>s + p orbitals $\xrightarrow{\text{hybridization (mixing)}}$ 2 sp hybrid orbitals</th>
<th>s + p orbitals $\xrightarrow{\text{hybridization}}$ 3 sp$^2$ hybrid orbitals</th>
<th>s + p orbitals $\xrightarrow{\text{hybridization}}$ 4 sp$^3$ hybrid orbitals</th>
<th>s + p orbitals $\xrightarrow{\text{hybridization}}$ 5 sp$^3d$ hybrid orbitals</th>
<th>s + p orbitals $\xrightarrow{\text{hybridization}}$ 6 sp$^3d^2$ hybrid orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp</td>
<td>2</td>
<td>linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sp$^2$</td>
<td>3</td>
<td>trigonal planar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sp$^3$</td>
<td>4</td>
<td>tetrahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sp$^3d$</td>
<td>5</td>
<td>trigonal bipyramidal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sp$^3d^2$</td>
<td>6</td>
<td>octahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Examples:**

$\text{BeF}_2$

$\text{Be}$

\[
\begin{array}{c}
\text{Be} \\
\text{IIIA} \\
\text{VIIA}
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
\text{I} \\
\text{F}
\end{array}
\]

2 regions of high electron density

linear

sp hybridization

$\text{Be}$

\[
\begin{array}{c}
\text{Be} \\
\text{IIIA} \\
\text{VIIA}
\end{array}
\]

2 $\text{Be}$

\[
\begin{array}{c}
\text{Be} \\
\text{IIIA} \\
\text{VIIA}
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
\text{I} \\
\text{F}
\end{array}
\]

hybridization

$\text{F}_2$

\[
\begin{array}{c}
\text{F} \\
\text{I} \\
\text{F}
\end{array}
\]

2 $\text{F}$

\[
\begin{array}{c}
\text{F} \\
\text{I} \\
\text{F}
\end{array}
\]

p sublevel has higher energy than s sublevel

$\begin{array}{c}
\text{Be} \\
\text{IIIA} \\
\text{VIIA}
\end{array}$

$\begin{array}{c}
\text{F} \\
\text{I} \\
\text{F}
\end{array}$

$p$ orbital

sp orbital

sp orbital

$p$ orbital

single bond
BF$_3$  

IIIa VIIa 

$\text{F}^\text{3-}$  

3 regions of high electron density  
Electronic geometry is trigonal planar  
$sp^2$ hybridization

$5B$  

$\uparrow \downarrow \uparrow \uparrow \downarrow \frac{1}{2p}$  

$\downarrow$ hybridization

$5B$  

$\uparrow \downarrow \uparrow \uparrow \frac{1}{2p}$  

$\frac{1}{2p}$  

$\frac{1}{2p}$  

$\frac{1}{2p}$

$[\begin{array}{c} qF \\ \frac{1}{2s} \end{array}] + 3 \begin{array}{c} \frac{1}{2s} \\ \frac{1}{2p} \\ \frac{1}{2p} \\ \frac{1}{2p} \end{array}$

P orbital  

P orbital

sp$^2$ orbital  

sp$^2$ orbitals

p orbital

Up to now we have been concerned with **Electronic geometry**—referring to the arrangement of the valence shell electrons around the central atom. The **Molecular geometry** refers to the arrangement of atoms around the central atom—i.e., what the molecule or ion really looks like.

At the same time, we’ll talk about the polarity of the molecule or ion; whether the species is **Polar** or **Nonpolar**. A species can contain polar bonds but be nonpolar when the pulling on the electrons balances out. See Ch. 9.
Compound containing Double Bonds

Consider ethylene (ethene) \( \text{C}_2\text{H}_4 \)

\[
S = N - A \\
= [4 \times 2 (\text{fn.} \text{H}) + 2 \times 8 (\text{fn.} \text{C})] \\
\quad - (4 \times 1 (\text{fn.} \text{H}) + 2 \times 4 (\text{fn.} \text{C})) \\
= 24 - 12 = 12 \text{ shared electrons}
\]

Both carbon atoms are \( \text{sp}^2 \) hybridized (have 3 regions of high electron density), each carbon is at the center of a trigonal plane, the carbons are connected by a double bond.

But what exactly \textit{is} a double bond?

\[
\begin{align*}
6 \text{C} & \quad \uparrow \quad 1s \quad 2s \quad 2p \quad 2p, 2p \\
& \text{hybridise} \quad \uparrow \quad 1s \quad 1s \quad 1s \quad 1s \quad 1s \quad 1s \quad 1s \\
& \quad \text{sp}^2 \quad \text{sp}^2 \quad \text{sp}^2 \quad \text{sp}^2
\end{align*}
\]

Therefore, for ethene:

\* Double bond is result of
  
  16 bond and 1 TI bond

\* Ethene has a total of 56 bonds

\* TI bond

Sigma (\( \sigma \)) bond: result of head-on (end-to-end) overlap
  
  There is free rotation around \( \sigma \) bond

Pi (\( \pi \)) bond: result of side-on overlap of p orbitals
  
  There is NO free rotation around a TI bond---the side-on overlap of p orbitals locks the molecule into place at that point.
Compounds Containing Triple Bonds

Consider acetylene (ethyne) \( \text{C}_2\text{H}_2 \)

\[
\begin{align*}
S &= N - A \\
&= [2 \times 2(\text{p} \text{H}) + 2 \times 8(\text{p} \text{C})] \\
&\quad - [2 \times 1(\text{p} \text{H}) + 2 \times 4(\text{p} \text{C})] \\
&= 20 - 10 = 10
\end{align*}
\]

both \text{C} \text{ atoms are sp hybridized}
the molecule is linear
the \text{carbon atoms are connected by a triple bond.}

But what is a triple bond?

\[
\text{C} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \quad \text{hybridize} \quad \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\
1s \quad 2s \\ 2p_1 \\ 2p_2 \\ 2p_3
\]

\[
\begin{align*}
\text{one } \pi \text{ bond} \\
\text{a second } \pi \text{ bond}
\end{align*}
\]

\[
\begin{align*}
\text{a triple bond is the result of 1 } \sigma \text{ bond and 2 } \pi \text{ bonds}
\end{align*}
\]

\[
\text{ethyne } \text{H-C} \equiv \text{C-H} \text{ contains 3 } \sigma \text{ bonds and 2 } \pi \text{ bonds.}
\]

Summary:

1. all single bonds are \( \sigma \) bonds formed by the normal, head-on overlap of orbitals.
2. double bond: 1 \( \sigma \) bond, 1 \( \pi \) bond
3. triple bond: 1 \( \sigma \) bond, 2 \( \pi \) bonds
Review of hybridization using organic compounds:

1. Know organic names & structures on sheet.
2. Recall that all organic compounds (C-containing compounds) obey the octet rule. Each carbon has 4 bonds around it since there are never any lone pairs of electrons on C.

### Examples

<table>
<thead>
<tr>
<th>Example</th>
<th>Atom</th>
<th>Hybridization</th>
<th>Bond Angle (Ideal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. C₂H₅OH (ethanol)</td>
<td>C⁰</td>
<td>Sp³</td>
<td>109° 28'</td>
</tr>
<tr>
<td></td>
<td>C³</td>
<td>sp³</td>
<td>109° 28'</td>
</tr>
<tr>
<td></td>
<td>O³</td>
<td>sp²</td>
<td>109° 28'</td>
</tr>
<tr>
<td></td>
<td>lone pairs = 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 bonds = 8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TT bonds = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. CH₃COOH (acetic acid)</td>
<td>C⁰</td>
<td>sp³</td>
<td>109° 28'</td>
</tr>
<tr>
<td></td>
<td>C³</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td></td>
<td>O³</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td></td>
<td>O⁴</td>
<td>sp³</td>
<td>109° 28'</td>
</tr>
<tr>
<td></td>
<td>lone pairs = 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 bonds = 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TT bonds = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>C⁰</td>
<td>sp</td>
<td>180°</td>
</tr>
<tr>
<td></td>
<td>C³</td>
<td>sp</td>
<td>180°</td>
</tr>
<tr>
<td></td>
<td>C³</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td></td>
<td>O⁴</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td></td>
<td>O⁴</td>
<td>sp³</td>
<td>109° 28'</td>
</tr>
<tr>
<td></td>
<td>lone pairs = 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 bonds = 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TT bonds = 4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In 3-D:

- H-C≡C-C
- H-C=C-C
- H-C-H
Cis-Trans Isomerism - a consequence of π bonding in double bonds

In a double bond, the π bond “locks” the molecule into place.
(There is free rotation around single bonds - sigma bonds)

Look at
\[ \begin{align*}
\text{cis-1,2 dichloroethene} & \quad \text{vs} \quad \text{trans-1,2 dichloroethene} \\
\text{mp} & \quad -80.5^\circ C \\
\text{bp} & \quad 60.3^\circ C \\
\end{align*} \]

These compounds are isomers because they have the same chemical formula \( \text{C}_2\text{H}_2\text{Cl}_2 \) but are different compounds, with different boiling and melting points.