Chapter 8 Molecular Structure and Covalent Bonding Theories

In order to understand the shapes of molecules and ions, two theories work together:

1. Valence bond (VB) theory: explains that bonding results from the overlap of atomic orbitals.

2. Valence Shell Electron Pair Repulsion (VSEPR) Theory:
   - In order to attain maximum stability, each atom in a molecule or ion arranges the electron pairs in its valence shell in such a way as to minimize the repulsion of their regions of high electron density:
     (a) lone (unshared or nonbonding) pairs of electrons
     (b) single bond
     (c) double bond
     (d) triple bond
   - These four types of regions of high electron density (where the electrons are) want to be as far apart as possible. The electrons repel each other.
   - The resulting arrangement of these regions of high electron density is the ELECTRONIC geometry around the atom of interest (usually the central atom)
<table>
<thead>
<tr>
<th>Number of Regions of High Electron Density</th>
<th>Electronic Geometry</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>180°</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td>120°</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>109°28'</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>1. 90°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. 120°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. 180°</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
<td>1. 90°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. 180°</td>
</tr>
</tbody>
</table>

Lone pairs of electrons or single bonds, double bonds, triple bonds.

Bonds or lone pairs are coming out of the paper.

Bonds or lone pairs are going into the paper.

Therefore, one counts the regions of high electron density around the central atom, and one automatically knows the electronic geometry and bond angles in the molecule.

\[
\text{BeCl}_2 \quad \begin{array}{c}
\cdot \text{Cl} \\
\cdot \text{Be} \\
\cdot \text{Cl}
\end{array} \quad 2 \text{ regions of high electron density} \\
\quad \begin{array}{c}
\cdot \text{linear molecule. electronic geometry} \\
180°
\end{array}
\]

\[
\text{BF}_3 \quad \begin{array}{c}
\cdot \text{B} \\
\cdot \text{F} \\
\cdot \text{F}
\end{array} \quad 3 \text{ regions} \Rightarrow \text{trigonal planar} \\
\quad \begin{array}{c}
\cdot \text{electronic geometry} \\
120°
\end{array}
\]

\[
\text{NH}_3 \quad \begin{array}{c}
\cdot \text{H} \\
\cdot \text{N} \\
\cdot \text{H}
\end{array} \quad 4 \text{ regions} \Rightarrow \text{tetrahedral} \\
\quad \begin{array}{c}
\cdot \text{electronic geometry} \\
109°28'
\end{array}
\]

But how does this bonding occur? VB theory says that the atomic orbitals for the valence electrons around the central atom mix together (hybridize) to make new orbitals called hybrid orbitals. These new hybrid orbitals overlap with orbitals on adjacent atoms to make bonds.
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>Orbitals Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp</td>
<td>2</td>
<td>linear</td>
<td>$s + p$ orbitals $\xrightarrow{\text{hybridization (mixing)}}$ 2 sp hybrid orbitals</td>
</tr>
<tr>
<td>sp$^2$</td>
<td>3</td>
<td>trigonal planar</td>
<td>$s + p + p$ orbitals $\xrightarrow{\text{hybridization}}$ 3 sp$^2$ hybrid orbitals</td>
</tr>
<tr>
<td>sp$^3$</td>
<td>4</td>
<td>tetrahedral</td>
<td>$s + p + p + p$ orbitals $\xrightarrow{\text{hybridization}}$ 4 sp$^3$ hybrid orbitals</td>
</tr>
<tr>
<td>sp$^3$d</td>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>$s + p + p + d$ orbitals $\xrightarrow{\text{hybridization}}$ 5 sp$^3$d hybrid orbitals</td>
</tr>
<tr>
<td>sp$^3$d$^2$</td>
<td>6</td>
<td>octahedral</td>
<td>$s + p + p + d + d$ orbitals $\xrightarrow{\text{hybridization}}$ 6 sp$^3$d$^2$ hybrid orbitals</td>
</tr>
</tbody>
</table>

Examples:

\[ \text{BeF}_2 \]

\[ \text{IIA VIIA} \]

\[ :\text{F} \times :\text{Be} \times :\text{F} : \]

2 regions of high electron density
Linear
sp hybridization

\[ 4\text{Be} \]

\[ \begin{cases} \downarrow 1s \\
\uparrow \downarrow 2s \\
\uparrow \downarrow 2p \ \downarrow \downarrow 2p \\
\end{cases} \]

\[ \xrightarrow{\text{hybridization}} \]

\[ 4\text{Be} \]

\[ \begin{cases} \downarrow 1s \\
\uparrow \uparrow \downarrow \downarrow 2p \ \downarrow \downarrow 2p \\
\end{cases} \]

\[ 2 \left[ 9\text{F} \right] \]

\[ \begin{cases} \downarrow 1s \\
\uparrow \downarrow 2s \\
\end{cases} \]

p orbital
sp orbital
sp orbital
p orbital

p sublevel has higher energy than s sublevel
BF₃

III A VII A

3 regions of high electron density
Electronic geometry is trigonal planar
sp² hybridization

5B

$\frac{1s}{ls} \quad \frac{2s}{2s} \quad \frac{2p}{2p} \quad \frac{2p}{2p}$

↓ hybridization

5B

$\frac{1s}{ls} \quad \frac{2p}{2p} \quad \frac{2p}{2p} \quad \frac{2p}{2p}$

$3 \left[ \frac{1s}{ls} \quad \frac{2s}{2s} \quad \frac{2p}{2p} \quad \frac{2p}{2p} \quad \frac{2p}{2p} \right]$

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 - ie what the the molecule or ion really looks like.

At the same time, we will 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.
I Two (2) regions of high electron density around central atom.
  sp hybridization (180°)
  electronic geometry: linear

example: $\text{BeCl}_2$

$\text{Cl}^{-}\text{Be}\rightarrow\text{Cl}^{+}$

Be-Cl bond is polar
but the bond polarities
CANCER!

molecular geometry: linear

II Three (3) regions of high electron density around central atom.
  sp$^2$ hybridization (120° ideal)
  electronic geometry: trigonal planar

example: $\text{BF}_3$

$\text{F}^{-}\text{B}\rightarrow\text{F}^{+}$

B-F bond is polar but
the bond polarities
CANCER!

molecular geometry: trigonal planar.

$\text{NO}_2^-$

molecular geometry: angular

Bond polarities do NOT
cancel
III Four (4) regions of high electron density

$sp^{3}$ hybridization

electronic geometry: tetrahedral (09° 28' ideal)

Examples: CH$_4$ and CF$_4$

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

C-H bonds are polar but CH$_4$ is nonpolar since polarities cancel

C-F bond is polar but CF$_4$ is nonpolar.

molecular geometry = electronic geometry = tetrahedral for CH$_4$, CF$_4$

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

molecular geometry = tetrahedral for CH$_3$Cl

Examples: NH$_3$

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

electronic geometry: tetrahedral

molecular geometry: pyramidal

SO$_3^{2-}$

\[
\begin{align*}
& \text{O} \quad \text{S} \quad \text{O} \\
& \text{O} \quad \text{O} \quad \text{O} \\
& \text{O} \quad \text{O} \\
\end{align*}
\]

electronic geometry: tetrahedral

molecular geometry: pyramidal

POLAR

POLAR
Examples: \( \text{H}_2\text{O} \)

\[
\begin{array}{c}
\text{H} \quad \text{O} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

electronic geometry: tetrahedral
molecular geometry: angular

POLAR

IV Five (5) regions of high electron density (does not obey octet rule)
sp\(^3\)d hybridization

Example:

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{P} \\
\text{X}
\end{array}
\]

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

\(
\begin{array}{c}
\text{F}\\
\text{F}
\end{array}
\)

molecular geometry = electronic geometry = trigonal bipyramidal

Example: \( \text{SF}_4 \) (1 lone pair of electrons on central atom)

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

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

or

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

"see saw"

electronic geometry: trigonal bipyramidal
molecular geometry: see saw
molecule is polar
Example: 2 lone pairs of electrons on central atom

\[ \text{BrF}_3 \]

electronic geometry: trigonal bipyramidal
molecular geometry: T-shaped and molecule is polar

Example: 3 lone pairs of electrons on central atom

\[ \text{ICl}_2^- \]

electronic geometry: trigonal bipyramidal
ionic geometry (since this is an ion): linear + NONPOLAR

IV Six (6) Regions of High Electron Density (does not obey octet rule)
sp\(^3d^2\) hybridization
electronic geometry: octahedral (90°, 180° bond angle)

Example: No (0) lone pairs of electrons on central atom

\[ \text{SF}_6 \]
molecular geometry = electronic geometry = octahedral
molecule is non-polar
Example: 1 lone pair of electrons on central atom

\[
\begin{align*}
\text{IF}_5 & \quad \text{VIIA VIIA} \\
& \quad \text{electronic geometry: octahedral} \\
& \quad \text{molecular geometry: square pyramidal; molecule is polar.}
\end{align*}
\]

Example: 2 lone pairs of electrons on central atom

\[
\begin{align*}
\text{XeF}_4 & \\
& \quad \text{electronic geometry: octahedral} \\
& \quad \text{molecular geometry: square planar; molecule is nonpolar}
\end{align*}
\]

Note: In discussing bond angles, we have only considered ideal bond angles. Eg. in a molecule with tetrahedral electronic geometry, the bond angle is 109°28' ideally.

In reality, lone pairs of electrons occupy more space than bonding pairs with the following result: a decrease in the angles between bonding pairs.

\[
\begin{align*}
\text{H} & \quad \text{N} & \quad \text{H} \\
107° & \quad \text{H} \\
\text{F} & \quad \text{O} & \quad \text{F} \\
102° & \quad \text{F} \\
\end{align*}
\]
<table>
<thead>
<tr>
<th>Regions of High Electrom Density Around Central Atom</th>
<th>Hybridization</th>
<th>Electronic Geometry</th>
<th>No. of Lone Pairs of Electrons Around Central Atom</th>
<th>Molecular (Ionic) Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>sp</td>
<td>linear</td>
<td>0</td>
<td>linear</td>
<td>BeCl₂, CO₂</td>
</tr>
<tr>
<td>3</td>
<td>sp²</td>
<td>trigonal planar</td>
<td>0</td>
<td>bent or angular</td>
<td>BF₃, CO₂²⁻, NO₂⁻</td>
</tr>
<tr>
<td>4</td>
<td>sp³</td>
<td>tetrahedral</td>
<td>0</td>
<td>tetrahedral</td>
<td>HClO₄, CH₄, CH₃Cl, NH₄⁺, NH₃, SO₄²⁻, H₃O⁺, H₂O</td>
</tr>
<tr>
<td>5</td>
<td>sp³d&lt;sub&gt;2&lt;/sub&gt; or dsp³&lt;sub&gt;3&lt;/sub&gt;</td>
<td>trigonal</td>
<td>0</td>
<td>trig. bipyrm. see saw T-shaped linear</td>
<td>PF₅, SF₄, BrF₃, ClF₃, I₃⁻, XeF₂</td>
</tr>
<tr>
<td>6</td>
<td>sp³d&lt;sub&gt;2&lt;/sub&gt; or d&lt;sub&gt;2&lt;/sub&gt;sp³&lt;sub&gt;3&lt;/sub&gt;</td>
<td>octahedral</td>
<td>0</td>
<td>octahedral square planar</td>
<td>SF₆, IF₅, BrF₅, IF₄⁻, XeF₄</td>
</tr>
</tbody>
</table>
Review

Polarity of Bonds:

Bonds are polar if $\Delta EN$ between atoms $\neq 0$

eg $\text{C} = \text{O}$ in $\text{CO}_2$ creating a bond dipole.

EN 2.5 3.5
$\Delta EN = 1.0$

Polarity of Molecules

Molecules are nonpolar if bond dipoles cancel each other out.

eg $\text{CO}_2$ $\text{O} \leftrightarrow \text{C} \leftrightarrow \text{O}$ Nonpolar

Notes:

If the dot structure contains lone pairs of $\text{e}^-$ on central atom, the molecule is polar (only a few exceptions) – lone pairs have a dipole, too.

Which of following are polar?

$\text{CBr}_4$  $\text{CBr}_3\text{H}$  $\text{CBr}_2\text{H}_2$  $\text{CBrH}_3$  $\text{CH}_4$
**Compounds Containing Double Bonds**

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

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

Both carbon atoms are \( sp^2 \) 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 is a double bond?

\[
\begin{align*}
\text{C} & \quad \text{hybridize} \quad \text{N} \\
1s & \quad 2s \quad 2p \quad 2p_1 \quad 2p_2
\end{align*}
\]

Therefore, for ethene:

\[
\begin{align*}
\text{sigma (}\sigma\text{) bond: result of head-on (end-to-end) overlap} \\
\text{there is free rotation around } \sigma \text{ bond}
\end{align*}
\]

\[
\begin{align*}
\text{pi (}\pi\text{) bond: result of side-on overlap of p orbitals} \\
\text{there is NO free rotation around } \pi \text{ bond - the side-on overlap of p orbitals locks the molecule into place at that point}
\end{align*}
\]
Compounds Containing Triple Bonds

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

$\text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H}$

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

But what is a triple bond?

$S = N - A$

$= [2 \times 2(\text{fn} \text{H}) + 2 \times 8(\text{fn} \text{C})]$

$- (2 \times 1(\text{fn} \text{H}) + 2 \times 4(\text{fn} \text{C})]$

$= 20 - 10 = 10$

:: a triple bond is the result of 1 σ bond and 2 π bonds

:: ethyne $\text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H}$ contains 3 σ bonds and 2 π bonds.

Summary:
(1) all single bonds are sigma (σ) bonds formed by the normal, head-on overlap of orbitals.
(2) double bond: 1 σ bond, 1 π bond
(3) triple bond: 1 σ bond, 2 π 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. $\text{C}_2\text{H}_5\text{OH}$ (ethanol)</td>
<td>$\text{C}^{1}$</td>
<td>$\text{sp}^{3}$</td>
<td>109° 28'</td>
</tr>
<tr>
<td>$S = N - A$</td>
<td>$= 36 - 20$</td>
<td>$= 16$</td>
<td></td>
</tr>
<tr>
<td>lone pairs - 2</td>
<td>6 bonds - 8</td>
<td>11 bonds - 0</td>
<td></td>
</tr>
<tr>
<td>2. $\text{CH}_3\text{COOH}$ (acetic acid)</td>
<td>$\text{C}^{0}$</td>
<td>$\text{sp}^{3}$</td>
<td>109° 28'</td>
</tr>
<tr>
<td>$S = N - A$</td>
<td>$= 40 - 24$</td>
<td>$= 16$</td>
<td></td>
</tr>
<tr>
<td>lone pairs - 4</td>
<td>6 bonds - 7</td>
<td>11 bonds - 1</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>$\text{C}^{1}$</td>
<td>$\text{sp}$</td>
<td>180°</td>
</tr>
<tr>
<td>$\text{C}^{2}$</td>
<td>$\text{sp}$</td>
<td>180°</td>
<td></td>
</tr>
<tr>
<td>$\text{C}^{3}$</td>
<td>$\text{sp}^{2}$</td>
<td>120°</td>
<td></td>
</tr>
<tr>
<td>$\text{O}^{4}$</td>
<td>$\text{sp}^{2}$</td>
<td>120°</td>
<td></td>
</tr>
<tr>
<td>$\text{O}^{5}$</td>
<td>$\text{sp}^{3}$</td>
<td>109° 28'</td>
<td></td>
</tr>
<tr>
<td>$\text{C}^{6}$</td>
<td>$\text{sp}^{2}$</td>
<td>120°</td>
<td></td>
</tr>
<tr>
<td>$\text{C}^{7}$</td>
<td>$\text{sp}^{2}$</td>
<td>120°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{sp}^{3}$</td>
<td>109° 28'</td>
<td></td>
</tr>
</tbody>
</table>

In 3-D: