Chemical Bonding and Molecular Structure (Chapter 10)

Molecular Structure

1. General Summary -- Structure and Bonding Concepts

2. VSEPR Theory -- simple prediction of molecular shapes
**Valence Shell Electron Pair Repulsion Theory**

Hypothesis -- The structure of a molecule is that which minimizes the repulsions between pairs of electrons on the central atom.

"Steric Number" (SN) = # of atoms attached to central atom
(aka "electron groups") + # of lone pairs on central atom

<table>
<thead>
<tr>
<th>SN</th>
<th>Electron Pair Arrangement (aka &quot;electron geometry&quot;)</th>
<th>Molecular Shape</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear 180°</td>
<td>AX₂ linear</td>
<td>BeCl₂, CO₂</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar 120°</td>
<td>AX₃ trigonal planar, AEX₂ bent</td>
<td>BCl₃, CH₃⁺, SnCl₂, NO₂⁻</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral 109.5°</td>
<td>AX₄ tetrahedral, AEX₃ pyramidal, AE₂X₂ bent</td>
<td>CH₄, PO₄³⁻, NH₃, ClO₃⁻, H₂O, SeF₂</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal 120° &amp; 90°</td>
<td>AX₅ trig bipyramid, &quot;see saw&quot;, AE₂X₃ T-shaped, AE₃X₂ linear</td>
<td>PF₅, SeCl₅⁺, SF₄, BrF₄⁺, ClF₃, XeO₃²⁻, XeF₂, ICl₂⁻</td>
</tr>
<tr>
<td>6</td>
<td>octahedral 90°</td>
<td>AX₆ octahedral, AEX₅ square pyramid, AE₂X₄ square planar</td>
<td>SF₆, PCl₆⁻, BrF₅, SF₅⁻, XeF₄, IF₄⁻</td>
</tr>
</tbody>
</table>

(A = central atom, X = terminal atom, E = lone pair)

Related aspects:
- In trigonal bipyramid structures, lone e⁻ pairs adopt equatorial positions (e)
- Order of repulsions: Lp - Lp > Lp - Bp > Bp - Bp
  (Predicts distortions from ideal geometries)
3. Polarity of Molecules -- can predict from molecular shape

Polar or Non-Polar?

In very symmetrical structures (e.g., CO₂ or CF₄), the individual bond dipoles effectively cancel each other and the molecule is non-polar.

In less symmetrical structures (e.g., SO₂ and SF₄), the bond dipoles do not cancel and there is a net dipole moment which makes the molecule polar.

Other examples for practice:

Polar: H₂O, SnCl₂, NH₃, SeF₂, PF₃, BrF₅, XeO₃
Non-Polar: BeCl₂, CH₄, PF₅, XeF₂, XeF₄, SO₃
Valence Bond Theory

1. Basic Concept

Covalent Bonds result from *overlap of atomic orbitals*

for example, consider the H$_2$ and HF molecules:

Two types of covalent bonds:

- **σ** *(sigma) bond*  
  "head-to-head" overlap along the bond axis

- **π** *(pi) bond*  
  "side-to-side" overlap of p orbitals:

single bond  --  always a **σ** bond

double bond  --  combination of one **σ** bond and one **π** bond

triple bond  --  combination of one **σ** bond and two **π** bonds
2. Hybrid Atomic Orbitals

**Question:** Description of bonding in CH\(_4\) molecule?

- **Experimental fact:** CH\(_4\) is tetrahedral (H-C-H angle = 109.5°)
- **VSEPR theory** "explains" this -- 4 e\(^-\) pairs, \(\therefore\) tetrahedral
- **However,** if only \(s\) and \(p\) orbitals are used, the angles ought to be 90° since the \(p\) orbitals are mutually perpendicular!

**Solution:** modify the theory of atomic orbitals and use:

| Hybridization: combination of 2 or more atomic orbitals on the same atom to form a new set of "Hybrid Atomic Orbitals" used in bonding. |

**Types of Hybrid Orbitals**

<table>
<thead>
<tr>
<th>Atomic Orbitals</th>
<th>Hybrid Orbitals</th>
<th>Geometry</th>
<th>Unhybridized (p) Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>one (s) + one (p)</td>
<td>two (sp)</td>
<td>Linear (180°)</td>
<td>2</td>
</tr>
<tr>
<td>one (s) + two (p)</td>
<td>three (sp^2)</td>
<td>Trigonal planar (120°)</td>
<td>1</td>
</tr>
<tr>
<td>one (s) + three (p)</td>
<td>four (sp^3)</td>
<td>Tetrahedral (109.5°)</td>
<td>0</td>
</tr>
</tbody>
</table>

\{ **Note:** combination of \(n\) \(AO\)'s yields \(n\) Hybrid Orbitals \}

Example: in CH\(_4\), C is \(sp^3\) hybridized:

- \(\text{ground state}\) - valence shell orbital diagram (predicts 90° angles -- wrong!)

- \(\text{hybridized state}\) (predicts 109.5° angles -- right!)
3. Examples

Use valence bond theory to describe the bonding in the following.

(Draw clear 3-D pictures showing orbital overlap, etc.)

H₂O, NH₃, CH₄, PF₃ (simple σ bonds and lone pairs)
H₂CNH double bond like H₂CCH₂ (ethene) and H₂CO (formaldehyde)
HCN triple bond like HCCH (ethyne) and N₂ (nitrogen)

Molecular Orbital Theory

1. Comparison of VB and MO Theory

Valence Bond Theory ("simple" but somewhat limited)

e⁻ pair bonds between two atoms using overlap of atomic orbitals on two atoms

Molecular Orbital Theory (more general but "complex")

all e⁻'s in molecule fill up a set of molecular orbitals that are made up of linear combinations of atomic orbitals on two or more atoms

MO's can be:

"localized" -- combination of AO's on two atoms, as in the diatomic molecules

"delocalized" -- combination of AO's on three or more atoms as in benzene (C₆H₆)
2. Molecular Orbitals for simple diatomic molecules (H\textsubscript{2} and He\textsubscript{2})

In H\textsubscript{2} the 1\textit{s} atomic orbitals on the two H atoms are combined into:

- a \textit{bonding MO} -- \( \sigma_{1s} \)
- an \textit{antibonding MO} -- \( \sigma^*_{1s} \)

MO energy level diagram for H\textsubscript{2} (only the bonding MO is filled):

\begin{center}
\begin{tikzpicture}
  \node (H) at (0,0) {H};
  \node (He) at (3,0) {He};
  \node (H2) at (1.5,0) {H\textsubscript{2}};
  \draw (H) -- (He); \draw (H2) -- (He);
  \draw (H) -- (H2); \draw (He) -- (H2);
  \fill (H2) circle (0.1cm);
\end{tikzpicture}
\end{center}

In contrast, the MO diagram for the nonexistent molecule, He\textsubscript{2} shows that both bonding and antibonding MO's are filled:

\begin{center}
\begin{tikzpicture}
  \node (He) at (0,0) {He};
  \node (H2) at (3,0) {He};
  \node (He2) at (1.5,0) {He\textsubscript{2}};
  \draw (He) -- (He2); \draw (H2) -- (He2);
  \draw (He) -- (H2); \draw (He2) -- (H2);
  \fill (H2) circle (0.1cm);
\end{tikzpicture}
\end{center}

\begin{center}
\textbf{Bond Order} = \frac{1}{2} \left[(\# \text{ bonding e}^\text{-}\text{s}) - (\# \text{ antibonding e}^\text{-}\text{s})\right]
\end{center}

- for H\textsubscript{2} = \frac{1}{2} \left[2 - 0\right] = 1 \quad \text{(a single bond)}
- for He\textsubscript{2} = \frac{1}{2} \left[2 - 2\right] = 0 \quad \text{(no net bonding interaction)}
3. MO's for 2nd Row Diatomic Molecules (e.g., N₂, O₂, F₂, etc.)

AO combinations -- from s orbitals and from p orbitals

MO energy level diagram -- Page 467

e.g., Fill in MO diagram for C₂, N₂, O₂, F₂, and Ne₂ and determine bond order for each:

<table>
<thead>
<tr>
<th>molecule</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>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

General "rules"

- electrons fill the lowest energy orbitals that are available
- maximum of 2 electrons, spins paired, per orbital
- Hund’s rule of maximum unpaired spins applies*

*accounts for paramagnetism of O₂ (VB theory fails here!)

4. Delocalized Molecular Orbitals

By combining AO's from three or more atoms, it is possible to generate MO's that are "delocalized" over three or more atoms

Examples:

**Resonance** in species like formate ion HCO₂⁻ and benzene (C₆H₆) can be "explained" with a single MO description containing delocalized π bonds.