Chapter 9
Molecular Geometries
and Bonding Theories
Coverage of Chapter 9

9.1 All
9.2 All
9.3 All
9.4 All
9.5 Omit Hybridization Involving d Orbitals
9.6 All
9.7 and 9.8 Omit ALL
MOLECULAR SHAPES

• The shape of a molecule plays an important role in its reactivity.

• By knowing the number of bonding and nonbonding electron pairs we can predict the shape of the molecule.
Two (2) Theories for MOLECULAR GEOMETRY

1. Valence Shell Electron Pair Repulsion (VSEPR) THEORY

2. The Valence Bond (VB) THEORY
Lewis Structures
&
Formal Charge

Formal charge is a charge assigned to each atom in a Lewis structure that helps to distinguish among competing structures.
What is the correct formula for Hypo Chlorous Acid
HClO (aq)

H – Cl – O

or

H – O – Cl
Hypo chlorite ion

$\text{ClO}^-$

\[ \left| \overline{\text{O} - \overline{\text{Cl}}} \right| \]

Number of Valence e$^-$
6 \hspace{1cm} 7

Number of Nonbonding e$^-$
-6 \hspace{1cm} -6

$\frac{1}{2}$ Number of Bonding e$^-$
-1 \hspace{1cm} -1

Formal Charge
-1 \hspace{1cm} 0
Where does the H go on HClO?

\[
\begin{array}{c}
| \overline{O} - \overline{Cl} - H \quad \text{or} \quad H - \overline{O} - \overline{Cl} | \\
\end{array}
\]

\[
\begin{array}{c|c|c|c|c}
\text{O} & \text{Cl} & \text{O} & \text{Cl} \\
\text{Valence e}^- & 6 & 7 & 6 & 7 \\
\text{Nonbonding} & -6 & -4 & -4 & -6 \\
\text{e}^- & -1 & -2 & -2 & -1 \\
\frac{1}{2} \text{ Bonding e}^- & -1 & -1 & 0 & 0 \\
\end{array}
\]
**ELECTRON DOMAINS**

- Electron pairs are referred to as electron domains.
- Single, double or triple bonds all count as one electron domain.

![Molecule Diagram]

The atom A in this molecule, has four electron domains.
The First

**MOLECULAR GEOMETRY** theory

**(VSEPR)**

Valence Shell Electron Pair Repulsion theory
VSEPR Theory

1. To predict molecular shape, assume the valence electrons repel each other

2. The electrons adopt an arrangement in space to minimize $e^-e^-$ repulsion

3. The molecule adopts whichever 3D geometry minimized this repulsion.
What Determines the Shape of a Molecule?

Four electron domains on N
3 bonding and 1 nonbonding
What Determines the Shape of a Molecule?

Electrons, whether they be bonding or non-bonding, repel each other. So electrons are placed as far as possible from each other.
Two (2) Different “Types” of Molecules

1. Molecules with NO nonBonding electrons on the central atom

2. Molecules with nonBonding electrons on the central atom
Electron Domains & NonBonding Electrons

Example 1  $\text{CO}_2$

$\big| \underline{O} = \underline{C} = \underline{O} \big|$

- How many electron domains on C: 2
- How many NonBonding electrons on C: 0
Electron Domains & NonBonding Electrons

Example 2 $\text{H}_2\text{O}$

\[
\text{H} - \underline{\text{O}} - \text{H}
\]

How many electron domains on O 4

How many NonBonding electrons on O 4
Molecular Geometries for molecules with no nonbonding electrons on central atom

There are five fundamental geometries:

1. Linear
2. Trigonal Planar
3. Tetrahedral
4. Trigonal bepyramidal
5. Octahedral
Only consider Three in detail

1. Linear
2. Trigonal Planar
3. Tetrahedral
In order to determine geometry

First Draw Lewis Dot Formula
MOLECULES IN WHICH THE CENTRAL ATOM HAS NO LONE PAIRS

ZINC CHLORIDE

\[ \text{Zn Cl}_2 \quad \text{Zn (30) [Ar] 3d}^{10} 4s^2 \]

\[ \text{Cl} - \text{Zn} - \text{Cl} \]

\[ \text{B} - \text{A} - \text{B} \]

\[ \text{AB}_2 = \text{LINEAR} \]
AB₂ Molecules Such as CO₂ are *Linear*
(Molecules With *NO* UnPaired Electrons On the Central Atom)

\[ \vdots \quad \downarrow \quad \vdots \]

\[ : O = C = O : \]

\[ B - A - B \]
Molecular Shape and Molecular Polarity

Bond dipoles

Overall dipole moment = 0
AB$_3$ Molecules Such as BF$_3$ are *Planar*

(Molecules With *NO* UnPaired Electrons On the Central Atom)

Formula \( \text{B F}_3 \)

Number of Valence e\(-\) 3 21 = 24 total

• Lewis Structure \( \overline{\text{F}} - \text{B} - \overline{\text{F}} \)
  \( \overline{\text{F}} \)
  \( \text{F} \)
$\text{AB}_3$ (Molecules With NO UnPaired Electrons On the Central Atom) Such as BF$_3$ are Planar.
$AB_4$ Molecules Such as $CH_4$ are Tetrahedral (Molecules With NO UnPaired Electrons On the Central Atom)

- Formula: $C\text{H}_4$
- Number of Valence $e^-$: $4 \times 4 = 8$ total
- Lewis Structure: $\text{H} - \text{C} - \text{H}$
$\textbf{AB}_4$ Such as $\text{CH}_4$ are Tetrahedral

(Molecules With NO UnPaired Electrons On the Central Atom)
$\text{AB}_4$ Molecules Such as $\text{CCl}_4$ are Tetrahedral

**Carbon TetraChloride**

Bond distance, 1.78 Å

109.5°
$\text{AB}_5$ Such as $\text{PCl}_5$ are Triangular bipyramidal

- Name ?
- Number of Bonds ?
- Lewis dot structure ?

```
Cl
  Cl – P – Cl
  Cl
  Cl
```
$\text{AB}_6$ Such as $\text{SF}_6$ are Octahedral

- Name ?
- Number of Bonds ?
- Lewis dot structure ?
Molecules With NO UNPaired e⁻
Molecules with NO unpaired e$^-$ on Central Atom

1. 2 Bonds ……… AB$_2$ or AX$_2$ e.g. CO$_2$
2. 3 Bonds ……… AB$_3$ or AX$_3$ e.g. BF$_3$
3. 4 Bonds ……… AB$_4$ or AX$_4$ e.g. CH$_4$
4. 5 Bonds ……… AB$_5$ or AX$_5$ e.g. PCl$_5$
5. 6 Bonds ……… AB$_6$ or AX$_6$ e.g. SF$_6$
Polarity

H Cl
Polar

Cl
Nonpolar

F
Nonpolar

N
Polar

H

Cl

H

C

H

Polar
Part 2. of VSEPR Theory

CENTRAL ATOM HAS LONE PAIRS
Molecules With UnPaired Electrons On the Central Atom

<table>
<thead>
<tr>
<th>Class</th>
<th>Example</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AB_2E$</td>
<td>$SO_2 &amp; O_3$</td>
<td>Bent</td>
</tr>
<tr>
<td>$AB_2E_2$</td>
<td>$H_2O$</td>
<td>Bent</td>
</tr>
<tr>
<td>$AB_3E$</td>
<td>$NH_3$</td>
<td>Trigonal pyramidal</td>
</tr>
</tbody>
</table>
1. $\text{AB}_2\text{E}_2$ **OZONE**

2. $\text{AB}_2\text{E}_2$ **WATER**
$AB_2E_2$ (Molecules With UnPaired Electrons On the Central Atom) Such as $H_2O$ are Bent
3. $\text{AB}_3\text{E}$  **AMMONIA**

- **NH}_3**  
  - Lewis structure
  - Electron-domain geometry (tetrahedral)
  - Molecular geometry (trigonal pyramidal)
$AB_3E$ (Molecules With UnPaired Electrons On the Central Atom) Such as $NH_3$ are NOT Planar
Predict Molecular Shapes

1. SiCl$_4$  
2. CH$_2$Cl$_2$  
3. GeCl$_2$  
4. OF$_2$  
5. NH$_3$  
6. PH$_3$
Give the electron domain and molecular geometries for

<table>
<thead>
<tr>
<th></th>
<th>electron domain</th>
<th>molecular geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) N₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) SO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) PCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) NH₂Cl</td>
<td></td>
<td></td>
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</tbody>
</table>
Examples of $AB_2$ molecules

- Linear $AB_2$ How many bonds
  $CO_2$
- Bent $AB_2E$ How many “bonds”
  $SO_2$ and $NO_2^-$
- Bent $AB_2E_2$ How many “bonds”
  $H_2O$
Examples of $\text{AB}_3$ molecules

- Planar $\text{AB}_3$  How many bonds  $\text{BF}_3$
- Pyramidal $\text{AB}_3\text{E}$  How many “bonds”  $\text{NH}_3$
- T shape $\text{AB}_3\text{E}_2$  How many “bonds”  $\text{ClF}_3$
Two (2) Theories for Molecular Geometry

1. Valence Shell Electron Pair Repulsion (VSEPR) Theory

Now consider

2. The Valence Bond (VB) Theory
Valence Bond Method

uses molecular orbitals
not Atomic Orbitals

What is a molecular orbital?
Orbitals used in bonding of Molecules
**CH₄ as an EXAMPLE**

**Ground State Electron Configuration**

C (6 e⁻) 1s² 2s² 2p² = (↑↓) (↑↓) (↑) (↑) ( )

*Only place for two bonds to form* ↑ ↑

*Therefore would predict CH₂ formation and not CH₄*

*But CH₂ does not exist while CH₄ does*
C (6 e⁻) 1s² 2s² 2p² = (↑↓) (↑↓) (↑) (↑) (↑)

*Only place for two bonds to form*

**Excited State Electron Configuration**

C (6 e⁻) 1s² 2s¹ 2p³ = (↑↓) (↑) (↑) (↑) (↑)

*Now a place for four bonds*

*One electron from H goes into an s orbital*

*and Three from H go into the p orbitals*
The **BONDS** in CH₄ are **ALL** the **SAME**!

One electron in an s orbital and Three in p orbitals would create different bonds.

Since All the Bonds are Equal, this cannot be correct

**INTRODUCE THE CONCEPT OF HYBRIDIZATION**
Hybridization

In order to make all bonding sites equal, we must create NEW Orbitals.

s, p, d, f are ATOMIC ORBITALS

MOLECULAR ORBITALS are formed from Atomic orbitals
VALENCE BOND THEORY

VALENCE SHELL ORBITALS

HYBRIDIZE

THE ORIENTATION OF ALL HYBRID VALENCE SHELL ORBITALS DETERMINES THE GEOMETRY OF THE MOLECULE
**Molecular Orbitals**

are formed from **Atomic Orbitals**

<table>
<thead>
<tr>
<th>Atomic Orbitals</th>
<th>Molecular Orbitals</th>
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</thead>
<tbody>
<tr>
<td>one S + one P</td>
<td>Two (2) SP</td>
</tr>
<tr>
<td>one S + two P</td>
<td>Three (3) SP²</td>
</tr>
<tr>
<td>one S + three P</td>
<td>Four (4) SP³</td>
</tr>
</tbody>
</table>
Molecular Orbitals

They are called

SP
SP²
SP³
SP³d and
SP³d²
sp³ HYBRIDIZATION

TETRAHEDRAL
Bond Angles
109½°
Methane CH₄
Four σ Bonds
on C
sp² HYBRIDIZATION
sp HYBRIDIZATION
one S orbital + one P orbital
Carbon is NOT The Only Element That Undergoes $sp^3$ HYBRIDIZATION

- Methane, $CH_4$: 4 bond pairs
- Ammonia, $NH_3$: 3 bond pairs
- Water, $H_2O$: 2 bond pairs
In CH$_3$COOH, there are three (3) hybridized atoms. Geometry is assign about each hybridized atom separately.