Molecular Geometry and Chemical Bonding Theory

The Valence -Shell Electron -Pair Repulsion (VSEPR) Model predicts the shapes of the molecules and ions by assuming that the valence shell electron pairs are arranged as far from one another as possible.

To predict the relative position of the atoms around a given central atom using the VESPR model you must first identify the type of arrangement of the electron pairs around the atom.

Strategy:

1. Draw the Lewis Dot structure for the molecule

2. Determine from the Lewis Dot structure the number of electron pairs around the central atom - bonding and non bonding pairs. In the case of a multiple bond - count it as one pair.

3. Determine the arrangement of the electron pairs to the central atom.

4. Obtain the molecular geometry from the direction of the bonding pairs for that arrangement.

2 Electron Pairs

Example: BeF$_2$
3 Electron Pairs
Example: BF$_3$

4 Electron Pairs
Example: CH$_4$

5 Electron Pairs
Example: PCl$_5$

6 Electron Pairs
Example: SF$_6$

Molecular geometry can be determined through your arrangement of electron pairs and how many are bonded and non bonded electron pairs.

Role of non-bonding (lone) pairs:

1. Lone pairs are structurally significant
2. Electron pair - electron pair repulsions occur
<table>
<thead>
<tr>
<th>Electron Pairs</th>
<th>Arrangement of Pairs</th>
<th>Molecular Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>Bonding</td>
<td>Lone</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Case 1: Arrangement of Pairs = Linear

$AX_2$  BeCl$_2$
Case 2: Arrangement of Pairs = Trigonal Planar

\[ AX_3 \]  Trigonal Planar  \[ BF_3 \]

\[ AX_2 \]  Bent or Angular  \[ SO_2 \]

Case 3: Arrangement of Pairs = Tetrahedral

\[ AX_4 \]  Tetrahedral  \[ CH_4 \]

\[ AX_3E \]  Trigonal Pyramidal  \[ NH_3 \]

\[ AX_2E_2 \]  Bent or Angular  \[ H_2O \]

Case 4: Arrangement of Pairs = Trigonal Bipyramidal

\[ AX_5 \]  Trigonal Bipyramidal  \[ PCl_5 \]

\[ AX_4E \]  Seesaw  \[ SF_4 \]

\[ AX_3E_2 \]  T- shaped  \[ CIF_3 \]

\[ AX_2E_3 \]  Linear  \[ I_3^- \]

Case 5: Arrangement of Pairs = Octahedral

\[ AX_6 \]  Octahedral  \[ SF_6 \]
AX₅E    Square Pyramidal    BrF₅

AX₄E₂     Square Planar     XeF₄

Note Resonance forms always have the same number of electron pairs around the central atom. Each form will have the same molecular geometry.

Example:  CO₃⁻

**Dipole Moments and Molecular Geometry**

The dipole moment is a measure of the degree of charge separation in a molecule. We can view the polarity of individual bonds within a molecule as vector quantities. Measurements of dipole moments are based on the fact that polar molecules can be oriented by an electric field.

Thus molecules that are perfectly symmetrical have a zero dipole moment and are considered nonpolar.

CO₂: 0 dipole

\[ \delta^- \quad \text{O} = \text{C} = \text{O} \quad \delta^+ \]

NH₃:

\[ \delta^- \]

\[ \delta^+ \]

[Diagram of NH₃ molecule with bond angles labeled]
Valence Bond Theory

Considered a satisfactory method of explaining the electron pair, or covalent bond from a quantum mechanics view.

According to this theory, a bond forms between two atoms when the following conditions are met.

Two atomic orbitals "overlap"

![Diagram of two atomic orbitals overlapping](image)

The theory suggests that when atoms approach a central atom, there is a modification, a “hybridizing” of the orbitals around the central atom. This theory was devised to explain the geometries that are predicted by Lewis Structures.
In a Bond:

The total number of electrons can't be more than two.

Strength of the bond depends on the orbital overlap

Hybrid orbitals - bonding that are obtained by taking combinations of atomic orbitals of the isolated atoms. The number of hybrid orbitals formed always equals the number of atomic orbitals used.

**Types of hybridization schemes**

The sp hybrid - example Be in $\text{BeF}_2$

Geometric arrangement - linear $\quad \# \text{ of orbitals} = 2$

Be ___  ___  ___  ___  atomic orbitals
2$s$  2$p$  2$p$  2$p$

Be ___  ___  ___  ___  excite an electron
2$s$  2$p$  2$p$  2$p$

Be ___  ___  ___  ___  hybridized orbital
2$s$  2$p$  2$p$  2$p$

$\text{Sp}^2$ hybrid orbitals - B in $\text{BF}_3$

B ___  ___  ___  ___  atomic orbitals
2$s$  2$p$  2$p$  2$p$

B ___  ___  ___  ___  excite an electron
2$s$  2$p$  2$p$  2$p$

B ___  ___  ___  ___  hybridized orbitals
2$s$  2$p$  2$p$  2$p$
Sp$^3$ hybrid orbitals - C in CH$_4$

C ___ ___ ___ ___ atomic orbitals
2s 2p 2p 2p

C ___ ___ ___ ___ excite an electron
2s 2p 2p 2p

C ___ ___ ___ ___ hybridize four orbitals to make a set of
2sp$^3$ 2sp$^3$ 2sp$^3$ 2sp$^3$ four equivalent orbitals

Note how the hybrid orbitals relate to the VSEPR models.

<table>
<thead>
<tr>
<th>Orbitals</th>
<th>Come in sets of:</th>
<th>Molecular Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp</td>
<td>2</td>
<td>linear</td>
</tr>
<tr>
<td>sp$^2$</td>
<td>3</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>sp$^3$</td>
<td>4</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>sp$^3$d</td>
<td>5</td>
<td>trigonal bipyramid</td>
</tr>
<tr>
<td>sp$^3$d$^2$</td>
<td>6</td>
<td>octahedral</td>
</tr>
</tbody>
</table>
Multiple Bonding

where more than one orbital from each bonding atom might overlap and will require σ and π bonding schemes.

A σ (sigma bond) has a cylindrical shape about the bond axis.

A π (pi bond) has an electron distribution above and below the bond axis.

Example: Acetylene
**Molecular Orbital Theory**

Simpler form of describing bonding in terms of electron configuration and wave functions (see Chap 7).

Constructive interference versus deconstructive interference for homonuclear diatomic molecules.

Constructive Probability Density $= [\sigma_{1s}]^2$

Deconstructive Probability Density $= [\sigma^*_{1s}]^2$

$\sigma^*_{1s}$ antibonding orbitals = against bonding orbitals

used in an excited state.

Molecular H$_2$ in the ground state $= (\sigma_{1s})^2 (\sigma^*_{1s})^2$
Example He as a diatomic molecule

He \(1s^2\) in an atomic state

Bonding Order = \(1/2 ((\# \text{ of bonding electrons}) - (\# \text{ of antibonding electrons}))\)

\(\text{He}_2 = 0 = \text{no bond}\)

Be \(1s^2 \ 2s^2\) in an atomic state

In a molecular state - as a diatomic molecule

Li \(1s^2 \ 2s^1\) in a atomic state

Correlation diagram is a little more complex, refer to Aufbau principle