Nyholm and Gillespie's Valence Shell Electron Pair Repulsion Theory (V.S.E.P.R. Theory) or Electron Domain Theory¹ (E.D. Theory)

Electrons in bonded atoms occupy spatially oriented orbitals in such a way as to minimize electron-electron repulsions arising mainly from electrostatic (coulombic) forces.

- For every number of electron pairs about a central atom (2, 3, 4, 5, 6), there is a preferred arrangement that minimizes repulsions.

- The shape of a molecule is based on the preferred arrangement of electron pairs.

Basic Geometries for 2, 3, and 4 Electron Pairs

BeCl₂

Two pairs minimize repulsions if oriented 180° from one another, giving a **linear** geometry.

BCl₃

Three pairs minimize repulsions if oriented 120° from one another, giving a **trigonal planar** geometry.

CH₄

Four pairs minimize repulsions if oriented 109.5° from one another, giving a **tetrahedral** geometry.
Space-Filling Model of CH₄
Basic Geometry for 5 Electron Pairs

$\text{PCl}_5$

Five pairs minimize repulsions in a \textit{trigonal bipyramidal} geometry.
Geometry of a Trigonal Bipyramid (tbp)

Two angles:

90°  120°

Two different kinds of positions:

axial positions (2)

equatorial positions (3)
Basic Geometry for 6 Electron Pairs

$\text{SF}_6$

Six pairs minimize repulsions in an octahedral geometry.

All positions are equivalent and form $90^\circ$ or $180^\circ$ angles to each other.
Molecules with Double Bonds

Shape is determined by the number of electron domains (regions), not simply the number of electron pairs.

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

4 pairs in 3 regions
Y trigonal planar

4 pairs in 2 regions
Y linear

4 pairs in 2 regions
Y linear
Resonance Hybrid Molecules

Any individual resonance (canonical) form can be used to predict the shape, treating "multiple bonds" as if they were real.

4 pairs in 3 regions in any canonical form
\( \text{\ Y trigonal planar} \)
Molecules with Lone Pairs (Non-Bonding Pairs) On the Central Atom

1. Shape refers to the geometrical arrangement of the atoms relative to one another in a molecule, not to the idealized arrangement of electron domains.

2. Molecules with non-bonding pairs on a central atom have shapes based on the arrangement of the electron domains, but bond angles may be slightly altered by repulsions among lone pairs (l.p.) and bond pairs (b.p.), which diminish in strength in the order


3. Shapes of molecules based on a tbp geometry of electron domains (5 pairs) result from preferentially placing any lone pairs in equatorial positions.
Three Electron Domains
2 b.p + 1 l.p.

SnCl₂

Lewis model: \( \vdots \text{Cl} - \text{Sn} - \text{Cl} \vdots \)

Shape: **Bent**

L.p.-b.p. repulsions cause the Cl-Sn-Cl angle to close to less than 120°.
Four Electron Domains

NH₃

Lewis model: \[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H}
\end{array}
\]

Shape: Trigonal Pyramid

L.p.-b.p. repulsions cause the H-N-H angles to close to less than 109.5° (~107°).
Four Electron Domains

H₂O

Lewis model: \( \text{H}--\text{O}--\text{H} \)

Shape: Bent

L.p.-b.p. repulsions cause the H-O-H angle to close to less than 109.5° (104.5°).
Five Electron Domains

SF$_4$

Lewis model:

\[
\begin{align*}
\text{SF}_4 & \quad \text{Shape: Irregular Tetrahedron ("see-saw" shape)}
\end{align*}
\]

Note: Lone pair occupies an equatorial position of \textit{tbp}.

L.p.-b.p. repulsions cause both F-S-F angles to close to less than 120° and 180°, respectively.
Five Electron Domains
3 b.p. + 2 l.p.

ClF₃

Lewis model:
\[
\begin{array}{c}
\text{F} - \text{Cl} - \text{F} \\
\text{F} \\
\end{array}
\]

Shape: T-shape

Note: Lone pairs occupy equatorial positions of \textit{tbp}.

L.p.-b.p. repulsions cause both F-Cl-F angles to close to less than 90 °.
Five Electron Domains
2 b.p. + 3 l.p.

XeF₂

Lewis model:

\[
\begin{array}{c}
\text{F} & - & \text{Xe} & - & \text{F} \\
\text{F} & - & \text{Xe} & - & \text{F} \\
\end{array}
\]

Shape: **Linear**

Note: Lone pairs occupy equatorial positions of *tbp*.

L.p.-b.p. repulsions *do not* cause angle distortions in this case, but rather enforce the linearity of the molecule.
Six Electron Domains

IF$_5$

Lewis Model:

Shape: Square Pyramid

L.p.-b.p. repulsions cause the plane of the four basal F atoms to move slightly above the I atom, making the F-I-F angle between any basal F and the axial F less than 90°.
Six Electron Domains

XeF$_4$

Lewis model:

Shape: **Square Planar**

Note: Lone pairs occupy opposite positions to minimize l.p.-l.p repulsions.

L.p.-b.p. repulsions *do not* cause angle distortions in this case, but rather enforce the planarity of the molecule.
A single, double, or triple bond constitutes one domain of electron density. Therefore, count bond domains around the central atom (i.e., the number of atom-pair linkages), not numbers of electron pairs. For this reason, the co-author of V.S.E.P.R. theory has renamed it the Electron Domain theory. [R. J. Gillespie. *J. Chem. Educ.* 1992, 69, 116.]

Listed polarity is for binary compounds (MXₙ) only. Composition of ternary (MXₙYₘ) and higher compounds may result in polarity for a shape that might be nonpolar if the compound were binary.

<table>
<thead>
<tr>
<th>Electron Regions</th>
<th>Arrangement of Regions</th>
<th>Bond Domains</th>
<th>Lone Pairs</th>
<th>Molecular Shape</th>
<th>Polar?</th>
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</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>2</td>
<td>0</td>
<td>linear [MX₂]</td>
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<td>3</td>
<td>trigonal planar</td>
<td>3</td>
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<td>trigonal planar [MX₃]</td>
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<tr>
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<td>2</td>
<td>1</td>
<td>bent (&lt;120°) [MX₂]</td>
<td>Yes</td>
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<tr>
<td>4</td>
<td>tetrahedral</td>
<td>4</td>
<td>0</td>
<td>tetrahedral [MX₄]</td>
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<tr>
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<td>trigonal pyramidal [MX₃]</td>
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<tr>
<td></td>
<td></td>
<td>2</td>
<td>2</td>
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<tr>
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<td>trigonal bipyramidal</td>
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<tr>
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<td>irregular tetrahedron [MX₄]</td>
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<td>T-shaped [MX₃]</td>
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<td>square pyramid [MX₅]</td>
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</tr>
<tr>
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<td></td>
<td>4</td>
<td>2</td>
<td>square planar [MX₄]</td>
<td>No</td>
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</tbody>
</table>
VSEPR-Predicted Shapes for MXₙ Molecules (n = 2, 3, 4, 5, 6)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Case</th>
<th>Shape</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX₂</td>
<td>2 bonds + 0 lone pairs</td>
<td>linear</td>
<td>BeF₂</td>
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<tr>
<td></td>
<td>2 bonds + 1 lone pair</td>
<td>bent (&lt;120°)</td>
<td>SnCl₂</td>
</tr>
<tr>
<td></td>
<td>2 bonds + 2 lone pairs</td>
<td>bent (&lt;109.5°)</td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td>2 bonds + 3 lone pairs</td>
<td>linear</td>
<td>XeF₂</td>
</tr>
<tr>
<td>MX₃</td>
<td>3 bonds + 0 lone pairs</td>
<td>trigonal planar</td>
<td>BF₃</td>
</tr>
<tr>
<td></td>
<td>3 bonds + 1 lone pair</td>
<td>trigonal pyramidal</td>
<td>NH₃</td>
</tr>
<tr>
<td></td>
<td>3 bonds + 2 lone pairs</td>
<td>T-shape</td>
<td>ClF₃</td>
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<tr>
<td>MX₄</td>
<td>4 bonds + 0 lone pairs</td>
<td>tetrahedral</td>
<td>CH₄</td>
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<tr>
<td></td>
<td>4 bonds + 1 lone pair</td>
<td>irregular tetrahedron</td>
<td>SF₄</td>
</tr>
<tr>
<td></td>
<td>4 bonds + 2 lone pairs</td>
<td>square planar</td>
<td>XeF₄</td>
</tr>
<tr>
<td>MX₅</td>
<td>5 bonds + 0 lone pairs</td>
<td>trigonal bipyramid (tbp)</td>
<td>PF₅</td>
</tr>
<tr>
<td></td>
<td>5 bonds + 1 lone pair</td>
<td>square pyramid</td>
<td>IF₅</td>
</tr>
<tr>
<td>MX₆</td>
<td>6 bonds + 0 lone pairs</td>
<td>octahedral</td>
<td>SF₆</td>
</tr>
</tbody>
</table>

Note: In this table, “bond” means a linkage between two atoms in a molecule. Thus a single-, double-, or triple-bond constitutes only one bond.
Relationship Between Lewis Structures and Actual Molecular Geometry

Lewis structures are inherently two dimensional and do not attempt to represent the true three-dimensional shape and angular relationships that exist in the actual molecule.

V.S.E.P.R. theory can be used to estimate the actual bond angles in a molecule from the Lewis structure and the number of electron domains about each atom.