Molecular Shapes: The VSEPR Model

AB\textsubscript{n} molecules

\textbf{AB}\textsubscript{2}  \hspace{1cm} \text{linear or bent}

\begin{align*}
\text{linear} & : \quad \begin{array}{c}
180^\circ \\
\text{B} & \text{A} & \text{B}
\end{array} \\
\text{bent} & : \quad \begin{array}{c}
\text{B} & \text{A} & \text{B}
\end{array}
\end{align*}

\textbf{AB}\textsubscript{3}  \hspace{1cm} \text{trigonal planar or trigonal pyramid (sometimes T-shaped)}

\begin{align*}
\text{120°} & : \quad \begin{array}{c}
\text{B} & \text{A} & \text{B} \\
\text{B} & \text{A} & \text{B} \\
\text{B} & \text{A} & \text{B}
\end{array} \\
\text{trigonal planar} & \quad \text{trigonal pyramid} & \quad \text{T-shaped}
\end{align*}

The VSEPR Method

**Electron domain (charge clouds)** – region in which it is most likely to find electrons.

bonding pairs – between two atoms

nonbonding pair (lone pair) – located principally on one atom.

The best arrangement of a given number of electron domains (charge clouds) is the one that minimizes the repulsions among them.
The arrangement of electron domains about the central atom of an ABₙ molecule is called its **electron-domain geometry**.

The arrangement of the atoms of a molecule in space is the **molecular geometry**.

<table>
<thead>
<tr>
<th>Number of electron domains</th>
<th>Arrangement of electron domains</th>
<th>Electron domain geometry</th>
<th>Predicted bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( \text{B--A--B} )</td>
<td>linear</td>
<td>180°</td>
</tr>
<tr>
<td>3</td>
<td>( \text{B--A--B} )</td>
<td>trigonal planar</td>
<td>120°</td>
</tr>
<tr>
<td>4</td>
<td>( \text{B--A--B} )</td>
<td>tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>5</td>
<td>( \text{B--A--B} )</td>
<td>trigonal bipyramid</td>
<td>120° 90°</td>
</tr>
<tr>
<td>6</td>
<td>( \text{B--A--B} )</td>
<td>octahedral</td>
<td>90° 180°</td>
</tr>
</tbody>
</table>

Steps to predict molecular geometries

1. Sketch the Lewis structure
2. Count the total number of electron domains around the central atom, and arrange them in a way to minimize repulsions.
3. Describe the molecular geometry in terms of the angular arrangement of the bonded atoms.
4. A double or triple bond is counted as one electron domain when predicting geometry.

\[
\text{(# of electron domains)} = \text{(# of atoms bonded to central atom)} + \text{( # of nonbonding pairs on the central atom)}
\]
The effect of nonbonding electrons and multiple bonds on bond angles.

Electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and thus tend to compress the bond angles.

Electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than do single bonds.

Molecules with expanded valence shells.

Atoms from the third period and beyond can have more than four pairs of electrons around them.

Five electron domains give rise to trigonal bipyramidal electron domain geometries.

Trigonal bipyramidal structures have three electron domains in the equatorial position and two in the axial positions. Axials have three 90° interactions while equatorial positions have only two. Put the bulkier domain in the equatorial position.

Six electron domains give rise to octahedral geometries.

All electron domains are at 90° to four other electron domains.
<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Electronic Geometry</th>
<th>Nonbonding Pairs</th>
<th>Molecular Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>0</td>
<td>linear</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td>0</td>
<td>trigonal planar</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>bent</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>0</td>
<td>tetrahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>trigonal pyramid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>bent</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramid</td>
<td>0</td>
<td>trigonal bipyramid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>see-saw</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>T-shaped</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>linear</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>0</td>
<td>octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>square pyramid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>square planar</td>
</tr>
</tbody>
</table>

- **linear**
- **trigonal**
- **tetrahedral**
- **trigonal bipyramid**
- **octahedral**
**Dipole Moments**

Dipole moment, $\mu$ $\mu = Q \times r$

$r$ - distance between charges

$Q$ - magnitude of charge

For diatomic molecules:

Polar molecules - have different elements

HCl, CO, NO

Nonpolar molecules - have the same elements

H$_2$, O$_2$, F$_2$

For polyatomic molecules, the molecular geometry will determine whether the molecule has a dipole.

CO$_2$ \qquad H$_2$O

Cis-dichloroethene   trans-dichloroethene

$\mu = 1.89$ D \qquad $\mu = 0$

\[ \begin{array}{c}
\text{Cl} & \text{C} & \text{Cl} \\
\text{H} & \text{C} & \text{H}
\end{array} \]

\[ \begin{array}{c}
\text{H} & \text{C} & \text{Cl} \\
\text{Cl} & \text{C} & \text{H}
\end{array} \]
Valence Bond Theory

Covalent Bonding and Orbital Overlap

valence-bond theory

orbital overlap

Hybridization and Hybrid Orbitals

Mathematical combination of wave functions on the same atom to form a new set of equivalent wave functions called hybrid atomic functions.

sp hybrids

sp² hybrids

sp³ hybrids
The number of hybrid orbitals is equal to the sum of the number of single (sigma, see next section) bonds and the number of lone pairs.
Multiple Bonds

internuclear axis

**sigma (σ) bonds** - electron density is concentrated between the nuclei of the bonding atoms. All single bonds are considered sigma bonds.

**pi (π) bonds** overlap of two p orbitals oriented perpendicularly to the internuclear axis.

Overlap is above and below internuclear axis, no probability of finding electron on the internuclear axis.

All multiple bonds consist of at least one sigma bond. The rest are pi bonds.

CO₂, H₂CO, CO
Molecular Orbital Theory: The Hydrogen Molecule

Molecular Orbitals

A molecular orbital is a mathematical function that describes the wave-like behavior of an electron in a molecule.

Whenever two atomic orbitals overlap, two molecular orbitals form.

- bonding molecular orbital ($\sigma$)
- antibonding molecular orbital ($\sigma^*$)

energy-level diagram (molecular orbital diagram)
Bond Order = 
\[ \frac{1}{2} (\text{#bonding electrons} - \text{#antibonding electron}) \]

Bond Order = 1 single bond

2 double bond

3 triple bond

Bond orders can be 1/2, 3/2, 5/2

If the bond order equals zero, a molecule will not form.
Second-Row Diatomic Molecules

1. The number of molecular orbitals formed equals the number of atomic orbitals combined.

2. Atomic orbitals combine most efficiently with other atomic orbitals of similar energy.

3. As the overlap increases the bonding MO lowers in energy.

4. Each molecular orbital can accommodate, at most, two electrons, with their spins paired (Pauli exclusion principle).

5. When MOs have the same energy, one electron enters each orbital (with the same spin) before spin pairing occurs (Hund’s rule).

Molecular Orbitals from 2p Atomic Orbitals

paramagnetism – some electrons unpaired

diamagnetism – all electrons paired

\[ \text{B}_2 \]
Bond Order:

Magnetic Props:

Try: O₂⁺, NO⁻

Bond Order:

Magnetic Props:
Combining Valence Bond Theory and Molecular Orbital Theory

Dealing with molecules such as ozone.

Delocalization

Delocalized molecular orbitals are not confined between two adjacent bonding atoms, but actually extend over three or more atoms.

Benzene, \( \text{C}_6\text{H}_6 \)

Carbonate, \( \text{CO}_3^{2-} \)