Molecular Geometry and Chemical Bonding Theory

The arrangement of a molecule’s atoms and nonbonding valence electron pairs influences the compound's ability to react.

The valance-shell electron-pair repulsion (VSEPR) model is used to predict how the atoms and nonbonding valence electrons are arranged in molecules (and polyatomic ions).

To determine the probable geometry, we must:

(1) Determine the total number of valence electrons for the molecule (polyatomic ion).

(2) Identify the “central” atom. Usually, can be identified easily since it is usually the first atom in the formula – hydrogen is a notable exception. The central atom usually is the most “metallic” element present (elements increase in metallic character going from the upper-right to lower-left on the Periodic Table).

(3) Attach the “outer” atoms to the “central” atom using a single bond.

(4) Assign valence electrons to the outer atoms in order to complete their octet.

(5a) Any remaining valence electrons (if any) are assigned to the central atom. In some rare cases, there are an odd number of valence electrons thus the central atom may end up with an odd number of valence electrons. Atoms or ions that have an unpaired electron are called **free radicals**.

(5b) If there are not enough valence electrons available for the central atom to have a complete octet, try “sharing” an additional pair of electrons with one of the outer atoms to form a double bond. In some cases, it might be necessary to share a third pair to form a triple bond. Note: halogens cannot form double or triple bonds.

(5c) In rare instances involving metals from Period 2, compounds may be formed that do not have an octet on the central atom – especially if the outer atoms are halogens.

(6) Once the bonds and nonbonding valence electron pairs have been assigned, count the number of **electron domains**. The electron domains include the bonds (double and triple bonds are counted as if they were single bonds) and nonbonding valence electron pairs on the central atom. The number of electron domains indicates the most probable molecular geometry.
Molecular Polarity

Bonds between atoms having different electronegativities have the electrons unequally distributed – the electron density is greater around the more electronegative atom. As a result of the electron density differences along the bond, the less electronegative atom has a partial “positive” charge (+δ) while the more electronegative atom has a partial “negative” charge (−δ). The overall polarity of a molecule depends on the dipole moments, μ, and special orientation of its bonds. The dipole moment is the product of the magnitudes of the partial charges on the molecules and the distance separating them. The SI unit, coulomb-meter, is used to measure the dipole moment, but the traditional unit, the debye (D, 1 D = 3.34 x 10^-30 C·m), is often used. Depending on the spatial arrangement of the bonds, a molecule containing highly polar bonds can be non-polar … the vector addition of the dipole moments yields a net dipole moment of zero for the overall molecule.

Bond order is the number of bonding electron pairs shared by two atoms. The bond orders would be 1, 2, or 3 with fractional bond orders possible for resonance structures.

Bond length, the distance between the nuclei of two bonded atoms, depends on the size of the atoms and their bond order.

Bond dissociation energy, D, is the enthalpy change for breaking a bond in a molecule in the gaseous phase.

The formation of a bond from atoms or radicals in the gaseous phase is always exothermic (ΔE < 0). Breaking bonds is always an endothermic process (ΔE > 0).

For example the bond orders and bond length:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Order</th>
<th>Bond Length (pm)</th>
<th>“Average” Bond Energy kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–O</td>
<td>1</td>
<td>143</td>
<td>358</td>
</tr>
<tr>
<td>C=O</td>
<td>2</td>
<td>122</td>
<td>745</td>
</tr>
<tr>
<td>C≡O</td>
<td>3</td>
<td>113</td>
<td>1046</td>
</tr>
</tbody>
</table>

The actual bond energy depends on the compound. “Average” bond energy values can be used to determine a reasonably good estimate for the heat of reaction based on the bonds formed and bonds broken.

Bond energy is the amount of energy needed to break one mole of a specific type of chemical bond. Most textbooks list bond energies for selected types of bonds. For example, 436 kJ/mol is needed to break H–H bonds while 498 kJ/mol is needed to break O=O bonds.

Bond energy values can be used to approximate the “heat of reaction” for a chemical reaction. In the combustion of methane (see above), we would need to write the balanced chemical equation, then we would draw the structural formulas for each substance. Comparing the bonds present on
the reactant and produces sides of the reaction we can determine how many of each type of bond was broken or formed.

\[
\Delta H_{\text{reaction}} = \sum \Delta D_{\text{(Bonds Broken)}} - \sum \Delta D_{\text{(Bonds Formed)}}
\]

\[
\begin{align*}
\Delta D_{\text{reaction}} &= \left[ \left( 4 \text{ mol } C-H \times \frac{416 \text{ kJ}}{\text{mol } C-H} \right) + \left( 2 \text{ mol } O=O \times \frac{498 \text{ kJ}}{\text{mol } O=O} \right) \right] - \\
&\quad \left[ \left( 2 \text{ mol } C=O \times \frac{803 \text{ kJ}}{\text{mol } C=O} \right) + \left( 4 \text{ mol } O-H \times \frac{467 \text{ kJ}}{\text{mol } O-H} \right) \right] = -814 \text{ kJ}
\end{align*}
\]

As expected, the combustion reaction is exothermic.

**Orbitals and Bonding Theories**

According to the best current explanation of atomic properties, the quantum mechanical model, electrons behave as waves. The regions of space surrounding the nucleus where the probability of finding electrons is highest are atomic orbitals. The energy levels for these atomic orbitals are a function of the electrostatic forces of attraction (between the positively charged nucleus and the negatively charged electrons) and the repulsive forces (electrons acting on each other) within the atom.

Two currently accepted alternate explanations for chemical bond formation using orbitals exist: **valence bond (VB) theory** (Linus Pauling) and **molecular orbital (MO) theory** (Robert S. Mulliken). The molecular orbital theory does a better job of describing molecules in their
excited states and for molecules such as NO and O₂ whose bonding and magnetic properties cannot be explained by the valence bond theory.

According to the valence bond theory, a bond forms when two electrons (usually one from each of two atoms) with opposite spins are present in a region of higher probability formed by overlapping orbitals between the nuclei of the two atoms. For molecules involving more than two atoms, bond formation is more complex. Pauling proposed that the mixing of s, p, and d orbitals, orbital hybridization, occurs to form orbitals that are better suited for bond formation. The number of hybrid orbitals formed by this mixing is equal to the number of atomic orbitals involved. These hybrid orbitals are more directed from the central atom to the terminal atoms, have better overlap, and produce stronger bonds.

The central atom’s electron-pair geometry determines the type of hybridization. Each sigma bond or lone electron pair on the central atom requires a hybrid orbital.

Two sp hybrid orbitals (separated by 180° – linear) are formed when an s-orbital and a p-orbital on the central atom mix.

Three sp² hybrid orbitals (separated by 120° – trigonal planar) are formed when an s-orbital and two p-orbitals on the central atom mix.

Four sp³ hybrid orbitals (separated by 109.5° – tetrahedral planar) are formed when an s-orbital and three p-orbitals on the central atom mix.

Five sp³d hybrid orbitals (three coplanar hybrid orbitals separated by 120° and two hybrid orbitals perpendicular to the other plane containing – trigonal-bipyramidal) are formed when an s-orbital, three p-orbitals, and a d-orbital on the central atom mix.

Six sp³d² hybrid orbitals (four coplanar hybrid orbitals separated by 90° and two hybrid orbitals perpendicular to the other plane containing – octahedral) are formed when an s-orbital, three p-orbitals, and two d-orbitals on the central atom mix.

The molecular geometry – the geometry consisting of the central atoms and the terminal atoms – is essentially the same as the electron domain geometry – the geometry associated with the central atoms and hybrid orbitals – when a terminal atom is attached to each hybrid orbital.

Lone pairs attached to the central atom occupy a greater volume than do “bonding” hybrid orbitals and distort the bond angles between the terminal atoms and the central atom.
## Electron-Domain and Molecular Geometries

<table>
<thead>
<tr>
<th>Number of Electron Domains on the Central Atom</th>
<th>Electron Domain Geometry</th>
<th>Predicted Bond Angles</th>
<th>Number of Nonbonding Electron Pairs on the Central Atom</th>
<th>Molecular Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>180</td>
<td>0</td>
<td>Linear</td>
<td>CO₂</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td>120</td>
<td>0</td>
<td>Trigonal planar</td>
<td>BF₃</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td></td>
<td>1</td>
<td>Bent</td>
<td>SO₂</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>109.5</td>
<td>0</td>
<td>Tetrahedral</td>
<td>CH₄</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td></td>
<td>1</td>
<td>Trigonal pyramidal</td>
<td>NH₃</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td></td>
<td>2</td>
<td>Bent</td>
<td>H₂O</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>120, 90</td>
<td>0</td>
<td>Trigonal bipyramidal</td>
<td>PCl₅</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td></td>
<td>1</td>
<td>Seesaw</td>
<td>SF₄</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td></td>
<td>2</td>
<td>T-shaped</td>
<td>ClF₃</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td></td>
<td>3</td>
<td>Linear</td>
<td>XeF₂</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>90</td>
<td>0</td>
<td>Octahedral</td>
<td>SF₆</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td></td>
<td>1</td>
<td>Square pyramidal</td>
<td>BrF₅</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td></td>
<td>2</td>
<td>Square planar</td>
<td>XeF₄</td>
</tr>
</tbody>
</table>

- **Linear**
  ![Linear](image1.png)

- **Trigonal planar**
  ![Trigonal planar](image2.png)
| Bent            | Tetrahedral
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Bent Tetrahedral" /></td>
<td><img src="image2" alt="Tetrahedral" /></td>
</tr>
<tr>
<td>Trigonal pyramidal</td>
<td>Bent</td>
</tr>
<tr>
<td><img src="image3" alt="Trigonal pyramidal" /></td>
<td><img src="image4" alt="Bent" /></td>
</tr>
<tr>
<td>Trigonal bipymadial</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Trigonal bipymadial" /></td>
<td></td>
</tr>
<tr>
<td>Seesaw (disphenoidal)</td>
<td>![Seesaw Diagram]</td>
</tr>
<tr>
<td>-----------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>T-Shaped</td>
<td>![T-Shaped Diagram]</td>
</tr>
<tr>
<td>Linear</td>
<td>![Linear Diagram]</td>
</tr>
</tbody>
</table>
The above diagrams are from the following URL:

http://www.chem.purdue.edu/gchelp/vsepr/structur2.html
Multiple Bonds

According to the valence bond theory, a **double bond** between two atoms consists of a hybrid orbital along the **molecular axis** connecting the two nuclei, a sigma ($\sigma$) bond, and a pi ($\pi$) bond formed by the overlap of two unhybridized p-orbitals perpendicular to the plane containing the two bonded atoms.

A **triple bond** consists of one sigma and two bonds. It has an additional pair of overlapping unhybridized p-orbitals that are perpendicular to the molecular axis and to the first pi bond.

The presence of a pi bond drastically limits the rotation that could occur around the molecular axis. **Isomers** are compounds with the same molecular formula that have different structures.

![cis-1,2-dichloroethylene](image1)

* cis-1,2-dichloroethylene

![trans-1,2-dichloroethylene](image2)

* trans-1,2-dichloroethylene

Molecular Orbital Theory

The structure for some molecules and polyatomic ions cannot be adequately described using the valence bond theory. For example, the Lewis structure for oxygen, $O_2$, does not account for the molecule’s paramagnetic nature. Benzene and nitrate exhibit **resonance structures** – alternate Lewis structures where the double bonds are in different locations when in fact these substances have only a single structure.

Rather than assigning valence electrons to localized bonds or lone pairs between two adjacent atoms as is done in the valence bond theory, the molecular orbital theory provides for the distribution of the valence electrons throughout the entire molecule.

In the molecular orbital theory, **the total number of molecular orbitals in a molecule is always equal to the number of atomic orbitals contributed by the combined atoms**.

When two atomic orbitals overlap to form molecular orbitals, it is helpful to think of the atomic orbitals as electron waves. The constructive interference (adding the two orbitals) produces a **bonding molecular orbital** and the destructive interference (subtracting one atomic orbital from the other) produces a destabilizing **antibonding molecular orbital**. The bonding molecular orbital is essentially the same as a bond formed according to the valence bond theory.

The antibonding molecular orbital has no valence bond theory equivalent. The two **nodes** (regions of electron probability) in the antibonding molecular orbital are separated by a **nodal plane** (region of zero electron probability). Due to the reduced electron density, there is greater repulsion between the two nuclei.
Bonding molecular orbitals have lower energies than their constituent atomic orbitals. The formation of bonding molecular orbitals “stabilizes” the molecule. Since antibonding molecular orbitals have higher energies than their constituent atomic orbitals, the presence of electrons in antibonding molecular orbitals “destabilizes” the molecule – possibly to the point of preventing the formation of the molecule.

The valence electrons are assigned to molecular orbitals following the Pauli exclusion principle and Hund’s rule.

**Bond Order** = \( \frac{1}{2} \) \text{(number of electrons in bonding molecular orbitals – number of electrons in antibonding molecular orbitals)}

Fractional bond orders are possible.

Molecular orbitals form most efficiently from atomic orbitals of similar energy. Core electrons are ignored since they are assigned to bonding and antibonding orbitals that cancel out each other.

Some molecules and polyatomic ions have “left over” p-orbital valence electrons – electrons not in a bond between two adjacent atoms or assigned to a central atom – are represented (according to the valence bond theory) using **resonance structures** where one or more double bonds are located in alternate positions within the molecule/ion. Experimental evidence indicates that these molecules or polyatomic ions have only one structure thus the molecular orbital theory is needed to represent these species. The unhybridized p-orbitals in the molecule/polyatomic ion are combined to form the same number of delocalized molecular orbitals. These molecular orbitals can be bonding, nonbonding, or antibonding.