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*Note: If you can rotate a molecule to have one isomer equal to another, they are both the same

*Note: For hybridization, if an SP\(^2\) is made, there is one unhybridized p orbital (because p usually has 3)

*Note: Resonance structures with pi bonds usually indicates delocalized pi bonds

*Note: Be weary of that sneaky benzene: C\(_6\)H\(_5\)CHO(OH)CHO is based off a benzene ring!

### 9.1 – Molecular Shapes

The shape of a molecule is determined by its bond angles

The Valence-Shell Electron-Pair Repulsion (VSEPR) Model can explain shapes for molecules with central representative elements

### 9.2 – VSEPR Model

A lone pair or single bond is a single electron domain (location where electrons are most likely to be found)

A double or triple bond is considered one electron domain because they occupy the same space

There are bonding and nonbonding pairs

**Electron Domain Geometries:**

<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>180°</td>
<td>Linear</td>
<td>180°</td>
</tr>
<tr>
<td>3</td>
<td>120°</td>
<td>Trigonal planar</td>
<td>120°</td>
</tr>
<tr>
<td>4</td>
<td>109.5°</td>
<td>Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>5</td>
<td>120°, 90°</td>
<td>Trigonal bipyramidal</td>
<td>120°, 90°</td>
</tr>
<tr>
<td>6</td>
<td>90°, 90°</td>
<td>Octahedral</td>
<td>90°</td>
</tr>
</tbody>
</table>

The arrangement of electron domains about the central atom or ion is the electron domain geometry

The molecular geometry is the arrangement of only the atoms in a molecule or ion (nonbonding pairs are not included)

Nonbonding pairs are larger than bonding pairs and have greater repulsions (decrease in bond angles)

Equatorial positions are less crowded and lower-energy conformations result from having nonbonding electron pairs in equatorial positions

Molecules with multiple centers can be split into separate electron/molecular domains
Electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than electron domains for single bonds (since multiple bonds are essentially enlarged electron domains).

Atoms from period 3 and beyond can have more than four electron pairs.

<table>
<thead>
<tr>
<th>Number of Electron Domains</th>
<th>Electron-Domain Geometry</th>
<th>Bonding Domains</th>
<th>Nonbonding Domains</th>
<th>Molecular Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>2</td>
<td>0</td>
<td>Linear</td>
<td>$\text{H}_2\text{C}=$ $\text{C}=$ $\text{C}=$ $\text{H}$</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td>3</td>
<td>0</td>
<td>Trigonal planar</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>4</td>
<td>0</td>
<td>Tetrahedral</td>
<td>$\text{H}_2\text{O}_2$</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal pyramidal</td>
<td>3</td>
<td>1</td>
<td>Trigonal pyramidal</td>
<td>$\text{NH}_3$</td>
</tr>
<tr>
<td>6</td>
<td>Bent</td>
<td>2</td>
<td>2</td>
<td>Bent</td>
<td>$\text{H}_2\text{O}_2$</td>
</tr>
</tbody>
</table>

Table 9.2: Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains Around the Central Atom

- $180^\circ$
- $120^\circ$
- $< 120^\circ$
- $109.5^\circ$
- $107^\circ$
- $< 109.5^\circ (104.5^\circ)$
### 9.3 – Molecular Shape and Molecular Polarity

Bond dipole is the dipole moment between two atoms in a bond (vector quantity).

Ionic compounds are the most polar compounds since they do not exist without a counter-ion.

It is incorrect to describe separate molecular ions as polar or non-polar.
9.4 – Covalent Bonding and Orbital Overlap

Valence-bond theory – bonding electron pairs are concentrated in regions between atoms and nonbonding electron pairs lie in directed regions of space and covalent bond is formed from the overlap of two valence orbitals with one unpaired electron each.

Optimized distance where attraction is maximized is the bond length.

All ionic solids turn to covalent molecules in gas phase.

9.5 – Hybrid Orbitals

Hybrid orbitals – atomic orbitals on an atom mix to form a hybrid orbital.

Hybridization – process of mixing atomic orbitals.

Hybrid orbitals are degenerate and are inbetween in energy for the two orbitals that formed it.

Eg: An sp orbital is higher in energy than the 1s orbital but less than 2p.

Hybridization and Electron-Domain Geometry:

Linear = sp hybrid

Trigonal Planar = sp$^2$ hybrid

Tetrahedral = sp$^3$ hybrid

Trigonal bipyramid = sp$^3$d hybrid

Octahedral = sp$^3$d$^2$ hybrid (etc.)

*Note: When drawing bond formation diagrams, just look at the hybridizations for each, but make sure that each pi bond also has a 2p bond.

9.6 – Multiple Bonds

Sigma Bond (σ) - Single bonds and lie on bond axis (stronger than pi bonds).

Pi Bond (π) - 2 unhybridized P orbitals overlapping parallel to the bond axis.

Pi bonds break first, and larger atoms form pi bonds less readily.

Cis isomers have same atoms on the same side and trans isomers have same atoms on opposite sides.

To rotate a cis to a trans, it is a 90 degree rotation that breaks the pi bond and produce distinct molecules.

Delocalized pi bonding occurs when resonance hybrids are created.

9.7 – Molecular Orbitals

MO theory is about the wave nature of electrons and constructive interference makes lower energy and vice versa.
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When constructive interference occurs, there is high electron density in the central of the MO. When destructive interference occurs, there is a nodal plane between the nuclei.

**Bond Order** = \( \frac{1}{2} (bonding − antibonding) \)

A bond order of zero means it is unstable.

The number of MO’s formed is equal to the number of atomic orbitals (AO) combined.

Only AO’s of similar energy can combine.

More overlap of two AO’s = More stability.

Each MO follows Hund’s rule and Pauli exclusion principle.

**9.8 – Period 2 Diatomic Molecules**

When in gas phase, metallic bonding turns to covalent bonding.

To draw energy diagrams: Have the two atoms on both sides with equal energies and then draw possible paths.

Example for Li\(_2\) (g):

The difference in energies between one bonding-antibonding pair at one quantum number increases as \( n \) increases.

Pi orbitals (for p orbitals overlapped sideways) in MO theory can hold a maximum of 4 electrons and antibonding MO’s are higher energy than bonding MO’s always.

Sigma overlap is stronger than pi overlap, so sigma is lower than pi for same quantum level.
Example for O\textsubscript{2} (g):

There are exceptions for B, C, and N due to the flipped order of \textit{sigma} 2p and \textit{pi} 2p MO's.

\begin{align*}
\text{for Li, Be, B, C, N:} & \quad (\sigma_{2s})^2 \ (\sigma_{2p}^*)^2 \ (\pi_{2p})^4 \ (\sigma_{2p})^2 \\
\text{for O, F, Ne:} & \quad (\sigma_{2s})^2 \ (\sigma_{2p}^*)^2 \ (\pi_{2p})^4 \ (\pi_{2p})^2 \ (\sigma_{2p})^2
\end{align*}

Therefore:

*Careful: If you are looking at C\textsubscript{2} \textsuperscript{-}, only \textit{one} of the carbons has an extra electron

If a heterodiatomic molecule falls into bother categories, both possible MO diagrams must be drawn (eg: CO)

Diamagnetic: \textbf{Weak repulsion from magnetic field} when all electrons are paired in MO diagram (stable) [appears to weigh less]

Paramagnetic: \textbf{Weak attraction to magnetic field} when there is at least one unpaired electron in MO diagram

Ferromagnetic: Very strong attraction to magnetic field when there are many unpaired electrons in a solid crystal

In a heteronuclear diatomic molecule that have atoms that do not differ too greatly in electronegativity, the energy of the atomic orbitals of the more electronegative atom is lower than that of the less electronegative element
Andrew Rosen

With this in mind, it is also true that in heteronuclear diatomic molecules, the atomic orbital closest in energy to the MO contributes more to it

Eg: Sigma 2s is contributed more from the 2s orbital of the O than N

If a sample doesn’t absorb visible light, it’s white, and if it absorbs all, it’s black

Color is based on a complimentary color wheel (appearance is complementary to color absorbed)

To produce light, an electron transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)

The difference in energy in the bonding and antibonding electron pairs is thus the energy of the photon emitted

High degree of conjugation (alternating double and single bonds) have small energy differences between HOMO and LUMO, so they are colored

For shorthand notations, carbons are shown as corners of lines with hydrogens not shown and all other atoms written out. All bonds are shown, functional groups may not be shown with bonds, lone electron pairs aren’t shown, and benzene ring is drawn with a hexagon with a circle in the middle or alternating double and single bonds