Molecular Geometry and intermolecular forces

Unit 4
Chapter 9 and 11.2
Unit 4.1

Chapter 9.1-9.3
Review of bonding

• Ionic compound (metal/nonmetal) creates a lattice
  – Formula doesn’t tell the exact number of atoms, but instead the smallest whole number ratio of atoms (no Lewis structures)

• Covalent compound (nonmetal/nonmetal) creates molecules
  – Formula tells you the exact number of atoms in the molecule. (Lewis structures)
V.S.E.P.R. model

Valence-shell electron-pair repulsion theory

– Because e\(^-\) pairs repel, molecular shape adjusts so the valence e\(^-\) pairs are as far apart as possible around the central atom.

– **Electron domains:** areas of valence e\(^-\) density around the central atom; result in different molecular shapes
  - Includes bonding e\(^-\) pairs and nonbonding e\(^-\) pairs
  - A single, double, or triple bond counts as one domain

Summary of \(L_mAB_n\) (Tables 9.1 - 9.3):

- \(L\) = lone or non-bonding pairs
- \(A\) = central atom
- \(B\) = bonded atoms

**Bond angles notation used here:**

- \(< x^\circ\) means \(~2-3^\circ\) less than predicted
- \(<< x^\circ\) means \(~4-6^\circ\) less than predicted
Five basic domains

- Linear  bond angle = 180
- Trigonal planar  bond angle = 120
- Tetrahedral  bond angle = 109.5
- Trigonal bipyramidal bond angle = 120 and 90
- Octahedral  bond angle = 90
<table>
<thead>
<tr>
<th># of e-domains &amp; # and type of hybrid orbitals</th>
<th>e-domain geometry</th>
<th>Formula &amp; Molecular geometry</th>
<th>Predicted bond angle(s)</th>
<th>Example (Lewis structure with molecular shape)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Two sp hybrid orbitals</td>
<td>X A X</td>
<td>B A B AB₂</td>
<td>180º</td>
<td>BeF₂ CO₂</td>
</tr>
<tr>
<td>Hybrid Orbitals</td>
<td>Molecular Structure</td>
<td>Bond Angle</td>
<td>Compound</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>---------------------</td>
<td>------------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>Three sp²</td>
<td>AB₃</td>
<td>120°</td>
<td>BF₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trigonal planar</td>
<td></td>
<td>Cl₂CO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trigonal planar</td>
<td>&lt; 120°</td>
<td>NO₂⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bent</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Three sp² hybrid orbitals
<table>
<thead>
<tr>
<th>Four sp³ hybrid orbitals</th>
<th>4</th>
<th>109.5°</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>or Tetrahedral</td>
<td></td>
<td>&lt; 109.5°</td>
<td>NH₃</td>
</tr>
<tr>
<td>or Trigonal pyramidal</td>
<td></td>
<td>&lt; 109.5°</td>
<td></td>
</tr>
<tr>
<td>or L₂AB₂ Bent</td>
<td></td>
<td>&lt;&lt;109.5°</td>
<td>H₂O</td>
</tr>
</tbody>
</table>
Example: CH$_4$

Molecular shape = tetrahedral

Bond angle = 109.5°
Five sp$^3$d hybrid orbitals

Trigonal bipyramidal

AB$_5$

Equatorial $= 120^\circ$
Axial $= 90^\circ$

PCI$_5$

LAB$_4$

Seesaw

Equatorial $< 120^\circ$
Axial $< 90^\circ$

SF$_4$
<table>
<thead>
<tr>
<th>5</th>
<th>Five sp³d hybrid orbitals</th>
<th>L₂AB₂</th>
<th>T-shaped</th>
<th>Axial &lt;= 90º</th>
<th>CIF₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trigonal bipyramidal</td>
<td>L₃AB₂</td>
<td>Linear</td>
<td>Axial = 180º</td>
<td>XeF₂</td>
</tr>
</tbody>
</table>
PCl$_5$

Molecular shape = trigonal bipyramidal

Bond angles

- equatorial = 120º
- axial = 90º
<table>
<thead>
<tr>
<th>6</th>
<th>Octahedral</th>
<th>AB$_6$</th>
<th>Octahedral</th>
<th>SF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Six sp$^3$d$^2$ hybrid orbitals</td>
<td></td>
<td>Octahedral</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LAB$_5$</td>
<td>Square pyramidal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>90°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt; 90°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BrF$_5$</td>
</tr>
<tr>
<td>Six sp$^3$d$^2$ hybrid orbitals</td>
<td>Octahedral</td>
<td>L$_2$AB$_4$ Square planar</td>
<td>90°</td>
<td>XeF$_4$</td>
</tr>
<tr>
<td>------------------------------</td>
<td>------------</td>
<td>---------------------------</td>
<td>-----</td>
<td>--------</td>
</tr>
<tr>
<td>6</td>
<td>L$_3$AB$_3$ T-shaped</td>
<td>&lt;90°</td>
<td></td>
<td>KrCl$_3^{1-}$</td>
</tr>
</tbody>
</table>
Molecular Polarity

• A molecule is polar if its centers of (+) and (-) charge do not coincide.
  – A bond’s polarity is determined by the difference of EN between atoms in bond.
  – Partial (+) and partial (-) on atoms in a polar bond can be represented as $\delta^+$ and $\delta^-$. 

Bond polarity is most often represented by an arrow that points toward the $\delta^-$ (most EN atom), showing the shift in e- density.
The dipole moment ($\mu$) is a vector (i.e., has a specific direction) measuring the polarity of a bond which contains partial charges (Q) that are separated by a distance (r).

$$\mu = Q \cdot r$$

The sum of the bond dipole moments in a molecule determines the overall polarity of the molecule.

1. Draw the true molecular geometry.
2. Draw each bond dipole.
3. Add the vectors, and draw the overall dipole moment. If none, then $\mu = 0$. 
• If a molecule has only 2 atoms
  the molecule is polar if the atoms are different and
  nonpolar if the atoms are the same

If a molecule has more than 2 atoms, the polarity is based
on the shape

If all dipole moments cancel out when vectors are
added, the molecule is nonpolar (overall zero
dipole moment)

if the dipoles do not cancel out, the molecule is polar
Ex: Draw Lewis structures, bond dipole moments, and overall dipole moments. Also, name the e⁻ domain geometry and the molecular geometry.

\[
\begin{array}{ccc}
\text{CO}_2 & \text{BF}_3 & \text{H}_2\text{O} \\
\text{CCl}_4 & \text{NH}_3 & \text{PH}_3 \\
\end{array}
\]
Unit 4.2

Chapter 9.4-9.6
Covalent Bonding and Orbital Overlap

- **Valence-bond theory**: overlap of orbitals between atoms results in a shared valence e\(^{-}\) pair (i.e., bonding pair)

Figure 9.13: Formation of bond in H\(_2\)

- a. As 2 H atoms approach, the 2 valence e\(^{-}\) in the 1s orbitals begin to overlap, becoming more stable.
- b. As H-H distance approaches 0.74 Å, energy lowers b/c of electrostatic attraction between the nuclei & the incoming e\(^{-}\).
- c. When H-H distance = 0.74 Å, energy is at its lowest because electrostatic attractions & repulsions are balanced. (This is the actual H-H bond distance.
- d. When H-H distance < 0.74 Å, energy increases b/c of electrostatic repulsion between 2 nuclei & between the 2 e\(^{-}\).
Hybrid Orbital Theory

• Explains the relationship between overlapping orbitals (valence bond theory) and observed molecular geometries (VSEPR theory).
“sp” hybrid orbitals

• BeF$_2$ (g): observed as a linear molecule with 2 equal-length Be-F bonds. Valence bond theory predicts that each bond is an overlap of one Be 2s e$^-$ and one 2p e$^-$ of F. However, Be’s 2s e$^-$ are already paired. So...

To form 2 equal bonds with 2 F atoms:

1. In Be, one 2s e$^-$ is promoted to an empty 2p orbital.

2. The occupied s and p orbitals are hybridized (“mixed”), producing two equivalent “sp” orbitals.

3. As the two “sp” hybrid orbitals of Be overlap with two p orbitals of F, stronger bonds result than would be expected from a normal Be s and F p overlap. (This makes up for energy needed to promote the Be e$^-$ originally.)
Be (ground state) → Be (promoted) → Be (sp hybrid)

Energy

2s 1 1

2p

Orbital “shapes”
One s + one p → Two sp orbitals
(to bond with 2 F’s)

A central atom in a Lewis structure with exactly 2 e⁻ domains has sp hybrid orbitals.
“sp$^2$” hybrid orbitals

- BF$_3$ (g): observed as trigonal planar molecule with 3 equal-length B-F bonds. However, 2 valence e- in B are paired, and the s and p e- can’t make the observed 120º angle.

- One s + two p → Three sp$^2$ orbitals (to bond with 3 F’s)

- A central atom with exactly 3 e- domains has sp$^2$ hybrid orbitals.
“sp$^3$” hybrid orbitals

- CH$_4$(g): observed as tetrahedral

C (ground) → C (promoted) → C (sp$^3$ hybrid)

One s + three p → Four sp$^3$ orbitals
(to bond with 4 H’s)

A central atom with exactly 4 e- domains has sp$^3$ hybrid orbitals.
“sp\textsuperscript{3}d” hybrid orbitals (or dsp\textsuperscript{3})

- PCl\textsubscript{5} (g): observed as trigonal bipyramidal; forms 5 bonds of equal energy (* but not equal length: equatorial are slightly longer)

\[
P \text{ (ground)} \rightarrow P \text{ (promoted)} \rightarrow P \text{ (sp}\textsuperscript{3}d \text{ hybrid)}
\]

- One s + three p + one d → Five sp\textsuperscript{3}d orbitals
  (to bond with 5 Cl’s)

- A central atom with exactly 5 e- domains has sp\textsuperscript{3}d hybrid orbitals.
“sp$^3$d$^2$” hybrid orbitals (or d$^2$sp$^3$)

- SF$_6$ (g): observed as octahedral; forms 6 equal-length bonds

- One s + three p + two d → Six sp$^3$d$^2$ orbitals

- A central atom with exactly 6 e- domains has sp$^3$d$^2$ hybrids.
Non-bonding e- pairs

- Lone pairs occupy hybrid orbitals, too
  Ex: $\text{H}_2\text{O}\ (g)$: observed as bent; but e- domain is tetrahedral

$\text{O (ground)} \rightarrow \text{O (sp}^3\text{ hybrid)}$

- Four sp$^3$ orbitals (2 bonding, 2 non-bonding)

2p

\[ \begin{array}{c}
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array} \]

2 non-bonding pairs
(lone pairs)

2s

\[ \begin{array}{c}
\downarrow \\
\end{array} \]

2 bonding pairs

H H
Multiple Bonds

Draw Lewis structures. For C’s: label hybridization, molecular geometry, and unique bond angles

\[ C_2H_6 \]

\[ C_2H_4 \]

\[ C_2H_2 \]

\[ C_6H_6 \]
Practice Questions

1. In which of the following species does the central atom NOT form sp² hybrid orbitals?
   - A. SO₂
   - B. BF₃
   - C. NO₃⁻
   - D. SO₃
   - E. PCl₃

   Answer: E

2. A molecule whose central atoms as d²sp³ hybridization can have which of the following shapes?
   - I. tetrahedral
   - II. Square pyramidal
   - III. Square planar

   - A. I only
   - B. III only
   - C. I and II only
   - D. II and III only
   - E. I, II, and III

   Answer: D
Sigma and Pi bonds

Sigma (σ) bond:
• Covalent bond that results from axial overlap of orbitals between atoms in a molecule.
• Lie directly on internuclear axis.
• “Single” bonds.
  Ex: F₂

Pi (π) bond:
• Covalent bond that results from side-by-side overlap of orbitals between atoms in a molecule.
• Are “above & below” and “left & right” of the internuclear axis and therefore have less total orbital overlap, so they are weaker than σ bonds.
• Make up the 2nd and 3rd bonds in double & triple bonds.
  Ex: O₂     N₂
Sigma ($\sigma$) bonds in $C_2H_4$

Ex: ethene; C-C and C-H $\sigma$-bonds result from axial overlap of H s-orbitals and C sp$^2$-orbitals
Pi (π) bonds in C₂H₄

- Each C has 4 valence e⁻:
  - 3 e⁻ for 3 σ–bonds
  - 1 e⁻ for 1 π–bond, which results from side-by-side overlap of one non-hybridized p-orbital from each C
Sigma ($\sigma$) bonds in $\text{C}_2\text{H}_2$

Ex: ethyne (a.k.a. acetylene) C-C and C-H $\sigma$-bonds result from axial overlap of H s-orbitals and C sp-orbital
Pi ($\pi$) bonds in $\text{C}_2\text{H}_2$

- Each C has 4 valence e$^-$:
  - 2 e$^-$ for 2 $\sigma$-bonds
  - 2 e$^-$ for 2 $\pi$-bonds, which result from side-by-side overlap of two non-hybridized p-orbitals from each carbon

2p
\[ \text{sp hybrids bond} \]
C
\[ \text{orbital bonds side-by-side} = \pi \text{ bonds} \]

2s
axially = $\sigma$ bonds
Sigma (σ) bonds in C₆H₆

Ex: benzene; C-C and C-H σ-bonds result from axial overlap of H s-orbitals and C sp²-orbitals
Localized vs. Delocalized $\pi$ Bonds

Localized: Non-conjugated $\pi$ system (\(\pi\) bonds do not interact)

Delocalized: Conjugated $\pi$ system (Electron density delocalized over all four carbon atoms)
Delocalized $\pi$ bonds in $C_6H_6$

- C-C $\pi$-bonds result from overlap of one non-hybridized p-orbitals from each C
- Delocalization of $e^-$ in $\pi$-bonds results in a “double-donut” shaped $e^-$ cloud above and below the molecular carbon plane.
Unit 4.3

Chapter 11.2
Intermolecular Forces

- Forces that attract molecules to *other* molecules (van der waal forces). These include:
  - Hydrogen bonding
  - Dipole-dipole attraction
  - London dispersion forces
Melting points and boiling points reflect the strength of bonds or intermolecular forces.

Intermolecular forces are much weaker than chemical bonds

Melting/boiling points of ionic and metallic bonds reflect the strength of the bond (bonds are broken and atoms move apart)

Melting/boiling points of covalent bonds reflect the strength of intermolecular forces holding the molecules together (bonds do not break, atoms stay together, molecules are pulled apart)
Relative Magnitudes of Forces

The types of bonding forces vary in their strength as measured by average bond energy.

Strongest
- Covalent bonds (400 kcal)
- Hydrogen bonding (12-16 kcal)
- Dipole-dipole interactions (2-0.5 kcal)

Weakest
- London forces (less than 1 kcal)
A molecule, such as HF, that has a center of positive charge and a center of negative charge is said to be polar, or to have a dipole moment.
Dipole-Dipole Attraction

Attraction between oppositely charged regions of neighboring molecules.

As the polarity increases, the attraction increases.
Hydrogen Bonding

attraction between hydrogen and more electronegative neighboring atoms such as fluorine, oxygen and nitrogen. (very polar bonds)

A strong dipole-dipole attraction
Hydrogen Bonding in Water

\[ \begin{align*}
H^+ & \quad \text{H}^+ \\
\text{O} & \quad \text{H}^+ \\
H & \quad \text{H}^+ \\
\text{O} & \quad \text{H}^+ \\
\end{align*} \]
London Dispersion forces

Induced or instantaneous dipoles

Occurs in all molecules

Larger molecules (more electrons) create stronger London dispersion forces

They are said to have more polarizability
London (Dispersion) Forces

- The weakest of intermolecular forces, these forces are proportional to the total number of electrons in the molecule.
- These are the only forces of attraction between completely nonpolar molecules.
  - Large nonpolar molecules may have substantial dispersion forces, resulting in relatively high boiling points.
  - Small nonpolar molecules have weak dispersion forces and exist almost exclusively as gases.
London Forces in Hydrocarbons

Boiling points of simple hydrocarbons in degrees Kelvin

Simple hydrocarbons have only London dispersion forces as intermolecular forces
List the following in order of increasing boiling points: \( \text{BaCl}_2, \text{H}_2, \text{CO}, \text{HF}, \text{Ne} \)

Answer: \( \text{H}_2, \text{Ne}, \text{CO}, \text{HF}, \text{BaCl}_2 \)

LD, LD (larger molecule), DD, HB, ionic bond