Unit 3 Review 2

BONDING RECAP, MO THEORY, INTRO TO IMF’S
Bonding Learning Outcomes

1. Apply the VSEPR model to determine a molecule’s electronic and molecular geometry based on its Lewis dot structure.

   \[ \text{NH}_3 \rightarrow \text{N} \cdot \cdot \cdot \text{H} \rightarrow \text{tetrahedral} \rightarrow \text{trigonal pyramidal} \rightarrow \text{Full description} \]

2. Assess if a molecule is polar based on polar bonds and its molecular geometry.

3. Identify the orbital hybridization for any atom in a given molecule using the VB model.

4. Describe the type of bond (e.g. sigma, pi) and the atomic orbitals that are associated with the bond using the VB model.

   \[ \text{O}_2 \rightarrow \sigma_{\text{sp}-\text{sp}} \rightarrow \pi_{\text{2p}-\text{2p}} \]

5. Differentiate between localized and delocalized electrons within a structure.


7. Recognize that Molecular Orbital (MO) theory is used to determine the energy of the electron in a molecule as well as its geometry.

8. Differentiate between constructive interference and destructive interference of atomic orbitals.

9. Construct and fully interpret a MO diagram, including identifying the bond order, the lowest energy electronic excitation energy (HOMO-LUMO gap), and the magnetism (paramagnetic or diamagnetic) for a compound.

   For \( \text{H}_2, \text{He}_2 \), \( \text{Li}_2 \rightarrow \text{Fe} \) plus their ions.
Bonding Theories Compared

- **VSEPR Theory:**
  - Shapes: molecular and electronic geometries
  - Explains bond angles
  - Focuses on the electron “regions”
  - Depends on the number of electron-dense regions (bonding and lone-pair regions)

- **Valence Bond Theory**
  - Hybrid Orbitals: $sp$, $sp^2$, $sp^3$, $sp^3d$, $sp^3d^2$
  - Sigma and pi bonds
  - Identifies the overlapping orbitals to “name” the bonds
  - Focuses on the electron “clouds”
  - Depends on the number of electron-dense regions
  - Easy navigation of central atoms

- **Molecular Orbital Theory**
  - Diagrams
  - Answers three fundamental questions regarding your molecule: bond order, magnetism, HOMO-LUMO gap
  - Sigma and pi bonds and **anti-bonds**
  - Focuses on the electrons as “waves”
  - Depends on the number of electrons
  - Whole molecule geometry with computers (Hard, good information but a disadvantageous process)
All red shapes are polar

Basic rules for molecular polarity:
1. Look for asymmetry in connectivity. (example: CH₃Cl)
2. Look for lone pair asymmetry. EVERYTHING with lone pairs is polar, except for the linear and square planar geometries

Molecular geometries can be any of the shapes on the whole page. The electronic geometries are only those in the box (and orbital hybridizations). The molecular geometry will be different from the electronic when there is at least one or more lone pairs on the central atom. Look at the top of the table and go DOWN a column. As you change from bonding electrons to lone pair electrons, the molecular shape is now different from the electronic because some of the positions are missing atoms. The new shape is then renamed based on the shape of the atoms.

Remember, once you have established the correct electronic geometry, the molecular geometry MUST be either the same as the electronic or one of the shapes listed directly under the electronic geometry. In other words, each shape in a given column here has the same electronic geometry given at the top of the column.

Polarity
If all the positions on the electronic geometry are the same (have the same atoms surrounding the central atom), the molecule is NOT polar because of the symmetry. Any of the other molecular geometries (except square planar and linear) under the box will be polar.
Shape and Molecular Polarity

- $\text{SF}_4$
- $\text{ClF}_3$
- $\text{BeF}_2$
- $\text{CH}_2\text{O}$

...then what is the hybridization? Dominant IMF?
Valence Bond Summary

<table>
<thead>
<tr>
<th># of Electron-Dense Regions</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>sp</td>
</tr>
<tr>
<td>3</td>
<td>sp²</td>
</tr>
<tr>
<td>4</td>
<td>sp³</td>
</tr>
<tr>
<td>5</td>
<td>sp³d</td>
</tr>
<tr>
<td>6</td>
<td>sp³d²</td>
</tr>
</tbody>
</table>

**Advanced**: the more your practice, you will see that:
1. Sigma bonds are almost always overlapping hybrid orbitals (with the exception of hydrogen’s pure 1s)
2. Pi bonds are always overlapping valence p-orbitals.

**Types of Bonds**

**Single Bonds**: 1 sigma bond

**Double Bonds**: 1 pi bond and 1 sigma bond

**Triple Bonds**: 2 pi bonds and 1 sigma bond
Bonding Names Overview

Name bonds by identifying the “overlapping” orbitals:

1. Identify the bond(s) present
2. Identify the hybridization of each bonding atom
3. Name the bond based on the type of bond and overlapping orbitals

Sigma bonds are the **end-on-end (on axis)** overlap between hybrid orbitals (or pure 1s in the case of hydrogen because hydrogen doesn’t hybridize)
- Sigma bonds form on the inter-nuclear axis

Pi bonds are the **side-by-side (off axis)** overlap between p orbitals
- Pi bonds form above and below the inter-nuclear axis (two regions of overlap)
Consider the VB electron configuration for the valence of a central atom:

\[ \text{sp}^2 \]

This configuration could be the central atom of which of the following molecules (more than one can be correct):

- HCN
- NO$_3^-$
- CO$_3^{2-}$
- CO$_2$

Consider the compound ethene, C$_2$H$_4$. The bond between the two carbons that is formed above and below the internuclear axis is a \_\_ bond. The atomic orbitals that combine to form this bond are \_\_ orbitals.

1. \( \pi; \text{sp}^2 \)
2. \( \pi; 1p \)
3. \( \pi; 2p \)
4. \( \sigma; \text{sp}^2 \)
5. \( \sigma; \text{sp}^3 \)
Organic Molecules

1. Print this page
2. Write the formula for this compound
3. Identify the shape and bond angles around various central atoms
4. Count the sigma and pi bonds
5. Identify the hybridization of each central atom until you identify a common thread
   • Don’t forget lone pairs
6. Name the bonds until you identify a common thread
Molecular Orbital Theory

Atomic orbitals combine to form molecular orbitals.
Valence Bond vs. Molecular Orbital Theory

- **Valence Bond Theory**
  - Hybrid Orbitals: $sp$, $sp^2$, $sp^3$, $sp^3d$, $sp^3d^2$
  - Sigma and pi bonds
  - Focuses on the electron “clouds”
  - Depends on the number of electron-dense regions
  - **Justifies VSEPR by creating hybrid orbitals from pure atomic orbitals**
  - Practical for big molecules, but falls short when it comes to physical properties and delocalized electrons

- **Molecular Orbital Theory**
  - Diagrams
  - Answers three fundamental questions regarding your molecule: bond order, magnetism, HOMO-LUMO gap
  - Sigma and pi orbitals
  - Focuses on the electrons as “waves”
  - Depends on the number of electrons
  - **Accurate, but very complex for polyatomic molecules; important for physical properties and delocalization of electrons, but not ideal for quickly navigating big organic molecules**
Molecular Orbital Theory

- Molecular Orbital Theory is a quantum mechanical approach to bonding.

- **This theory looks at bonds as regions with a high probability of electron density according to the Schrödinger Equation.**

- **Constructive interference** results in a high electron density (bond):
  - Low Energy
  - More stable than atomic orbital

- **Destructive interference** results in repulsion (zero electron density; anti-bond):
  - High Energy
  - Less stable than atomic orbital
Molecular Orbital Theory

- Molecular Orbital Theory looks at electrons as mathematical “waves.”
- MO theory looks at bonds as regions with a high probability of electron density
- **Constructive interference** results in a high electron density (bond)
  - Low Energy
  - More stable than atomic orbital
- **Destructive interference** results in repulsion (zero electron density; anti-bond)
  - High Energy
  - Less stable than atomic orbital

MO Diagram for H₂

For every analogous bonding orbital, there is a higher energy anti-bonding orbital

Note: our focus in this class will be on Hydrogen, Helium, row 2 diatomics, and their ions
Molecular Orbital Theory

$O_2$ and $F_2$

$M_{\text{IO}}$

$B_2$, $N_2$, and $C_2$
Molecular Orbital Theory: Conclusions

- Molecular Orbital Theory provides three conclusions that Valence Bond and VSEPR are unable to explain:
  1. MO Theory can describe fractional bond orders ascribed to charged molecules and resonance structures using anti-bonding and bonding orbitals
  2. MO Theory can identify the magnetic properties of a given molecule (diamagnetic, paramagnetic)
  3. MO Theory can predict the photon emission energy of excited electrons (HOMO-LUMO)
MO Theory Question

What is the molecular orbital electron configuration for O$_2^-$? What is the bond order? Are the electrons delocalized? Is O$_2^-$ paramagnetic or diamagnetic? Identify the HOMO-LUMO gap.

\[ \text{weakly attract} \]

\[ \text{O}_2^- \]

\[ 2(6) + 1 = 13 \text{ e}^- \]

\[ \text{B.O.} = \frac{8 - 5}{2} = 1.5 \rightarrow \text{delocalized} \]
MO Theory Question

Does F$_2^{2-}$ exist? How does molecular orbital theory prove this?

\[ \text{No} \]

\[ \begin{align*}
\text{F}_2^{2-} & \quad \downarrow \\
7(2) + 2 & \quad = 16 \\
8 - 8 & \quad = \emptyset
\end{align*} \]
Molecular Orbital Theory: HOMO-LUMO

- One of the most important conclusions in molecular orbital theory is the energy difference between the **Highest Occupied Molecular Orbital (HOMO)** and the **Lowest Unoccupied Molecular Orbital (LUMO)**.

- This energy gap is important because it corresponds to energy of the photon emitted when an excited electron falls back down to ground state. **This can be applied to far more complicated molecules/materials**

- Because light is important here,

  Remember:

  **IR....R.O.Y.G.B.I.V. ...UV**

  (---increasing energy, decreasing wavelength--->)
MO Theory – HOMO-LUMO Application

\[ E_{\text{light in}} = E_{\text{gap}} \]

A company is trying to make a UV-blocking sunscreen. Their current prospect molecule absorbs in the x-ray range. This company should look for a better molecule with a _______ HOMO-LUMO gap.
Intermolecular Forces

Attractions Between Molecules
Intermolecular Forces

Dispersion Forces
ex: $\text{H}_2$

Dipole-Dipole
ex: $\text{HCl}$

Hydrogen Bond
ex: $\text{HF}$

In everything!

Polar molecule

Hydrogen bonded to $\text{N, O, or F}$
Intermolecular Forces

- Intermolecular forces (IMF’s) are **electrostatic** interactions between molecules.
  - IMF’s vary in strength, but are weaker than **intramolecular** forces (bonds)
  - Intermolecular forces are the electrostatic “glue” that hold molecules in **condensed phases**

- The three types of IMF’s (in decreasing strength) are:
  1. Hydrogen bonding
  2. Dipole-dipole
  3. Dispersion forces

- And they depend on:
  1. Shape
  2. Polarizability (size)
  3. Temperature

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Intermolecular Forces (forces *between* molecules) vs Intramolecular Forces (forces *within* molecules)

- **Weak**
  - Dispersion
  - Dipole-dipole
- **Moderate**
  - H-bonding
- **Strong**
  - Ion-ion
- **Very Strong**
  - Covalent bonds

* units are in kJ/mol of interactions

ZERO attraction is only possible with IDEAL GASES.
Dispersion Forces

All molecules have dispersion forces

Dispersion forces depend on a molecule's ability to spontaneously induce a dipole. Its ability to do this is called its polarizability and is directly influenced by the molecular weight of the molecule.

1. Dispersion forces depend on “stackability”
2. Overall dispersion forces accumulate with more total number of interactions
Dispersion Forces - Polarizability

Dispersion forces scale with the size of a molecule, which correlates directly to polarizability.

- The larger the electron cloud, the larger the polarizability
- The larger the surface area (overlap), the larger the polarizability
- "Stackability" is important here

\[
\text{Saturated Fatty Acid} \\
\text{Unsaturated Fatty Acid}
\]

- Gas: \( \text{Cl}_2 \) (Lowest Polarizability, Lowest IMF’s)
- Liquid: \( \text{Br}_2 \)
- Solid: \( \text{I}_2 \) (Highest Polarizability, Highest IMF’s)
Size - Comparing IMF’s

• Dispersion forces can become extremely significant with an increase in size (number of interactions)

• We can conclude that weaker intermolecular forces can become more substantial when there are more of them, resulting in overall stronger forces of attraction.

• You can’t predict which of these two samples will have a higher boiling point without knowing the physical data.
  • However, you should be able to explain why octane has a higher BP if you are given the physical data!
Dipole-Dipole Forces

- Dipole-dipole forces require a permanently fixed dipole on a molecule.
- Because the dipole moment is permanent, dipole-dipole forces are stronger than dispersion forces.
- Dipole-Dipole forces can be easily identified if you can spot out a polar molecule.

Note: the + and − in this diagram represent partial charges.
Hydrogen Bonds

- Hydrogen bonds (not actually bonds) are a particularly strong form of dipole-dipole interaction that deserve their own class of intermolecular force.

- Hydrogen bonds only occur in compounds that contain hydrogen directly bound to Nitrogen, Oxygen, and Fluorine.
IMF Comparisons

- The key features of this graph are as follows:
  - Polarizability increases down a group (left to right on this chart)
  - Shape changes across a period, leading to different polarity across a group (down up on this chart)
  - Ammonia, hydrofluoric acid, and water break the trend in polarizability because they form hydrogen bonds. The red line follows the trend the best (no hydrogen bond)