

# Unit 3 Exam Review

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BONDING THEORIES, IMFS

# Exam Breakdown



22-25 Q's

100% conceptual → no calculator

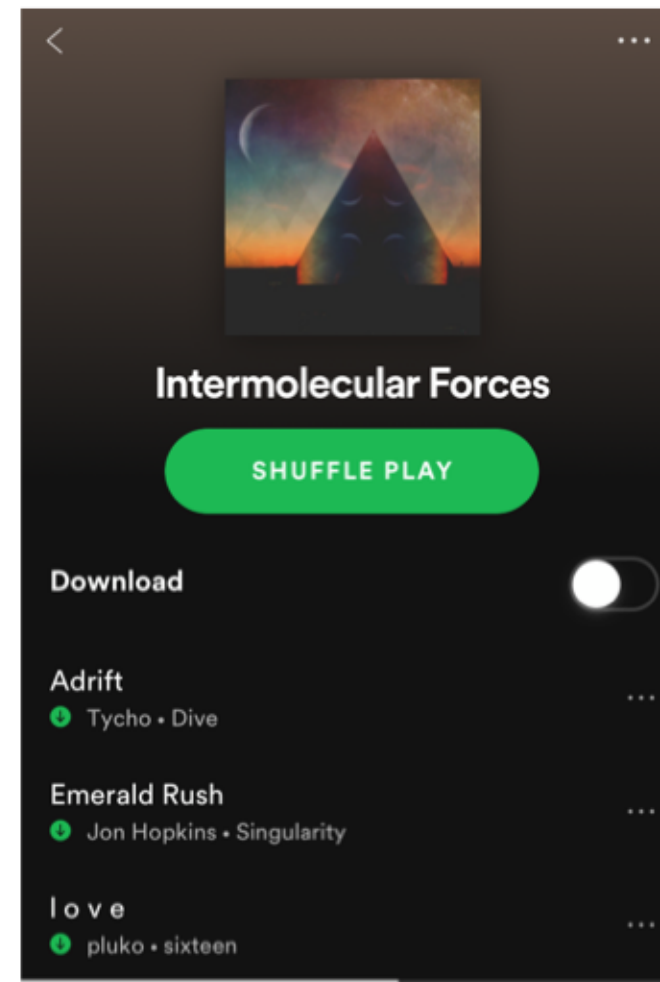
16 on bonding

VSEPR, VB, MO

9

IMFs, liquids, solids

UTC 2.102A → WCH 1.120



# Tips for a Successful Exam 3

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1. Exam 3 is 100% conceptual: be able to do draw simple conclusions using the bonding theories and put some of the more specific conclusions into your own words
2. Gchem chapters -> Helpsheets and Worksheets\*
3. VSEPR helpsheet -> <http://mccord.cm.utexas.edu/courses/vsepr/>
- \* 4. Study for a 100% because it is achievable on this exam, but only if you work really hard and leave no concepts unturned
5. Work through problems carefully.
  - For example: Don't assume that a molecule with an O and an H hydrogen bonds. Draw the structure before making conclusions.
  - Don't assume a molecule is polar because it has polar bonds
  - Don't assume a molecule is nonpolar because it has nonpolar bonds
6. Be confident with Lewis structures

# Delocalized Electrons

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- We talked about delocalized electrons in three different places this unit. It is important to understand each situation:
  1. Lewis structures, VSEPR, and VB: delocalized electrons means resonance
    - Electrons are not confined to a single bonding region, rather that electron density is distributed across a conjugated pi-system in pure p or d orbitals.
  2. MO Theory: delocalized electrons without resonance
    - For big molecules, a single molecular orbital can be shared across multiple bonding regions or the entire molecule
    - For diatomics, a fractional bond order shows that electrons can be delocalized even when there is only one bonding region
  3. Solids: electrons are delocalized between metallic nuclei in metallic bonds
    - Completely separate from our covalent bond theories, this delocalization shows how electrons swim around an entire metallic solid and conduct electricity
    - This is different from the previous two forms of delocalization (which is delocalization confined to a molecule) and this distinction is the reason why a metallic solid conducts electricity but benzene does not.



# Intermolecular Forces

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ATTRACTIONS BETWEEN MOLECULES

# Intermolecular Forces

s, l

- 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:

Strongest

1. Hydrogen bonding
2. Dipole-dipole
3. Dispersion forces

Weakest

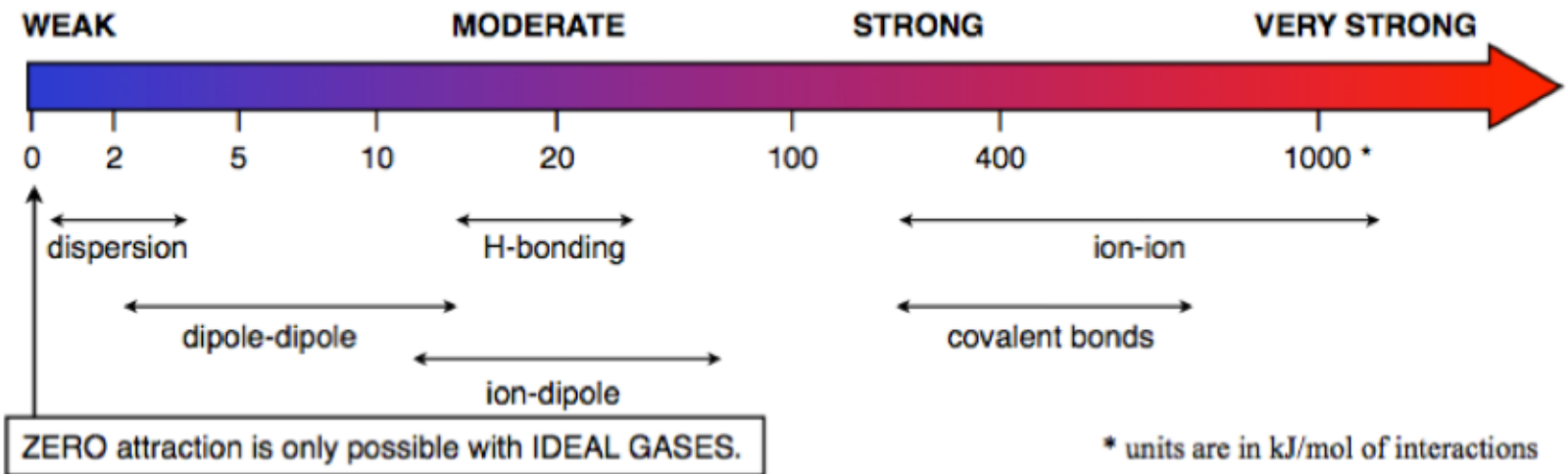
• And they depend on:

1. Shape
2. Polarizability (size)

↳ dispersion

## Intermolecular Forces (forces *between* molecules)

## Intramolecular Forces (forces *within* molecules)



# Dispersion Forces

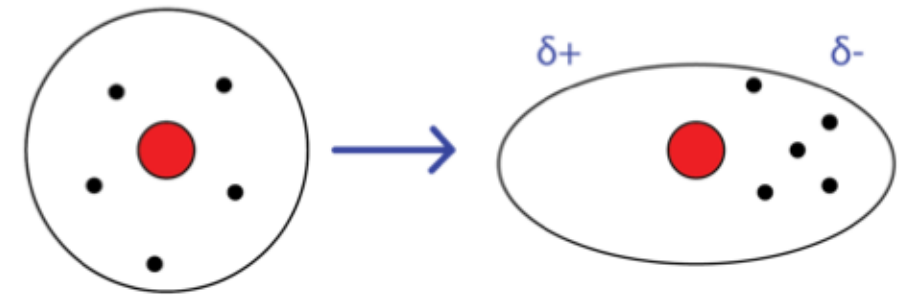
All molecules have dispersion forces

Dispersion forces depend on a molecule's ability to spontaneously induce a dipole. Its ability to do this is called its **polarizability** and is pretty consistent with the **molecular weight** of the molecule.

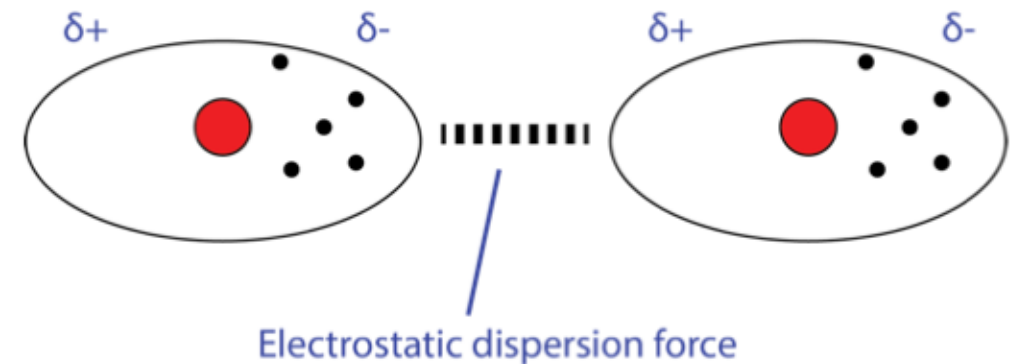
- Overall dispersion forces accumulate with
  1. More total number of interactions
  2. Size of the electron cloud

Induction

1. Formation of a spontaneous dipole



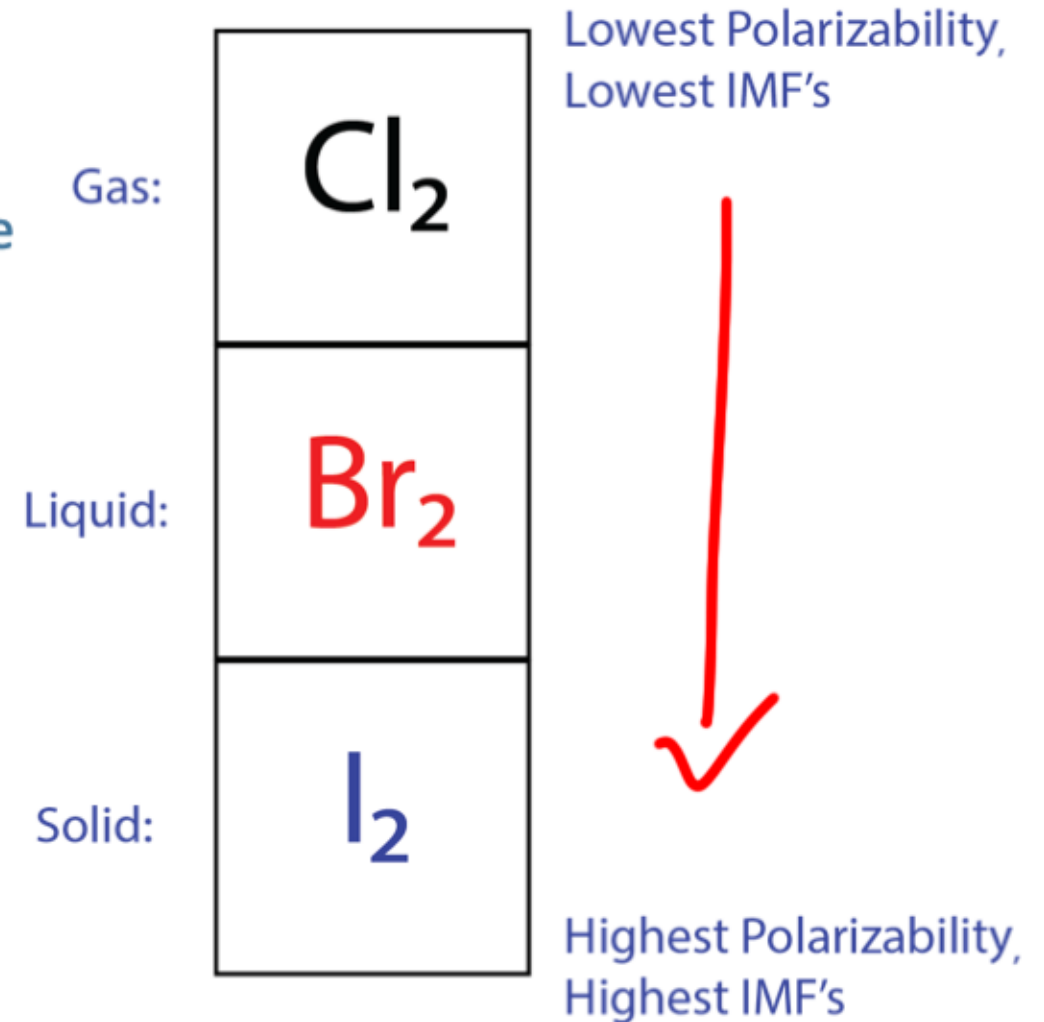
2. Induction of a second molecule



# Dispersion Forces - Polarizability

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

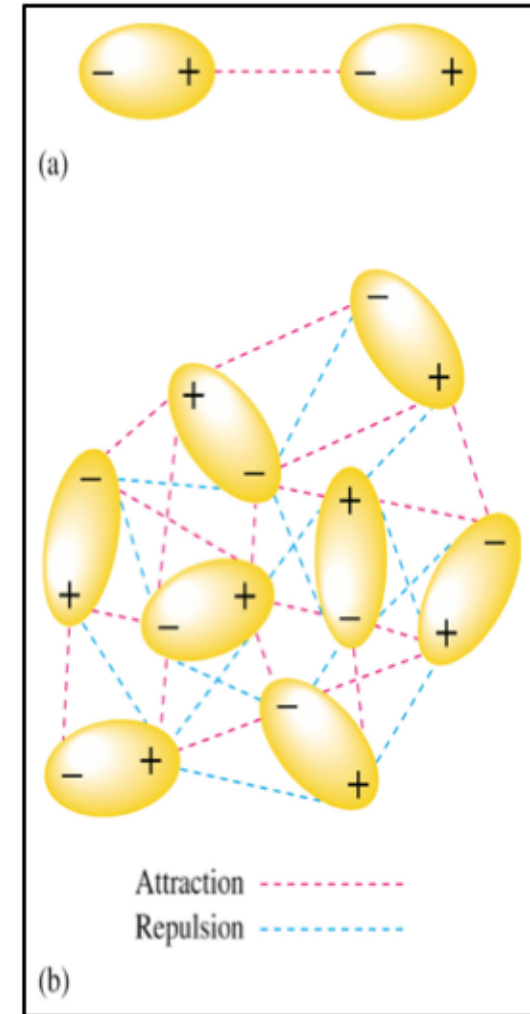
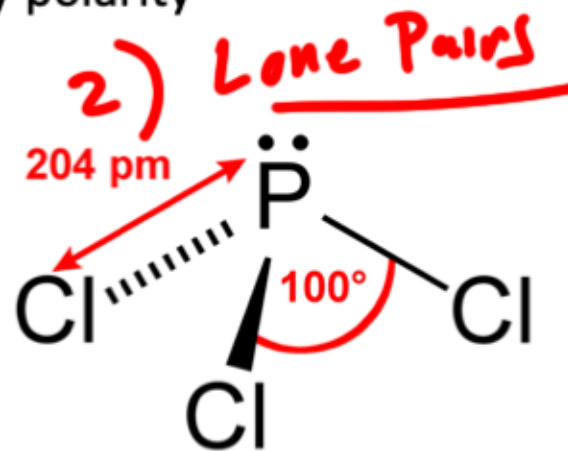
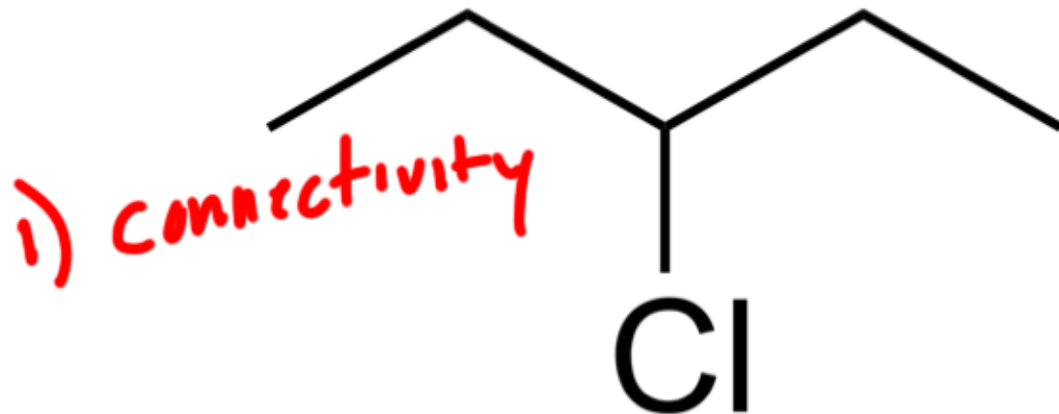
- Polarizability is the tendency for a molecule to induce an instantaneous dipole, resulting in induction and electrostatic dispersion forces
- **The larger the electron cloud, the larger the polarizability** ✓



→ VSEPR molecular polarity

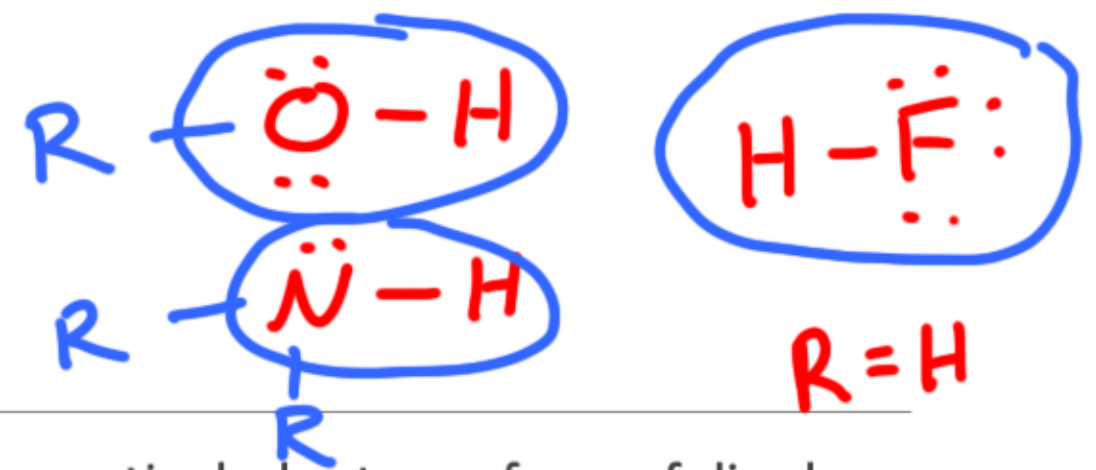
# Dipole-Dipole Forces

- Dipole-dipole forces require a permanently fixed dipole on a molecule. ↳ permanent
- **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**
- Remember the two different ways to identify polarity

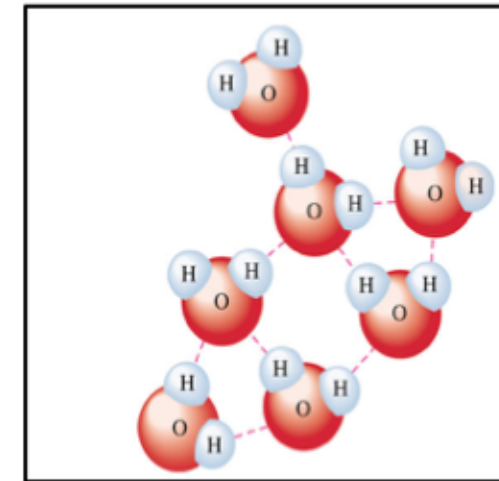
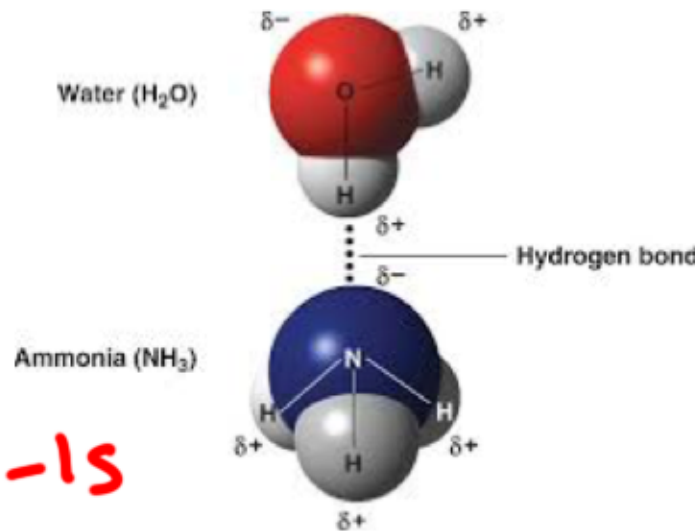
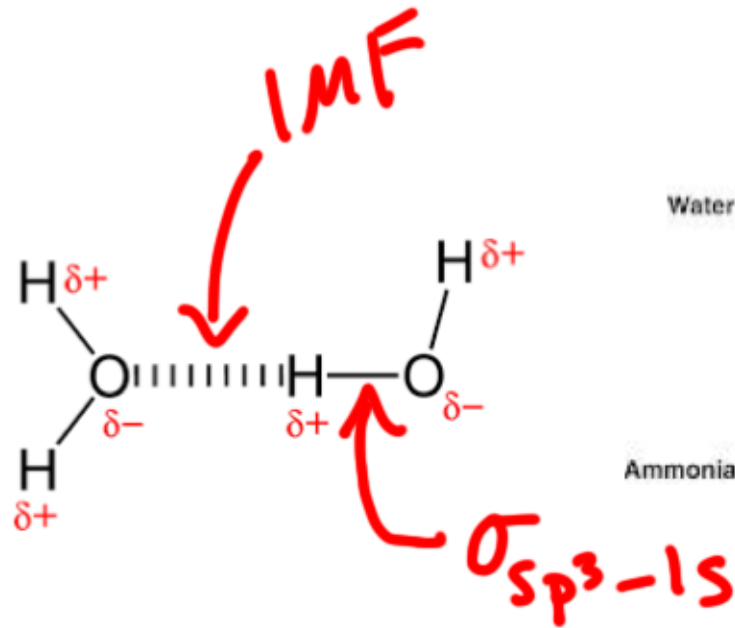


Note: the + and - in this diagram represent **partial charges**

# Hydrogen Bonds



- Hydrogen bonds (not actually bonds, still just IMFs) 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 bonded to Nitrogen, Oxygen, and Fluorine.**

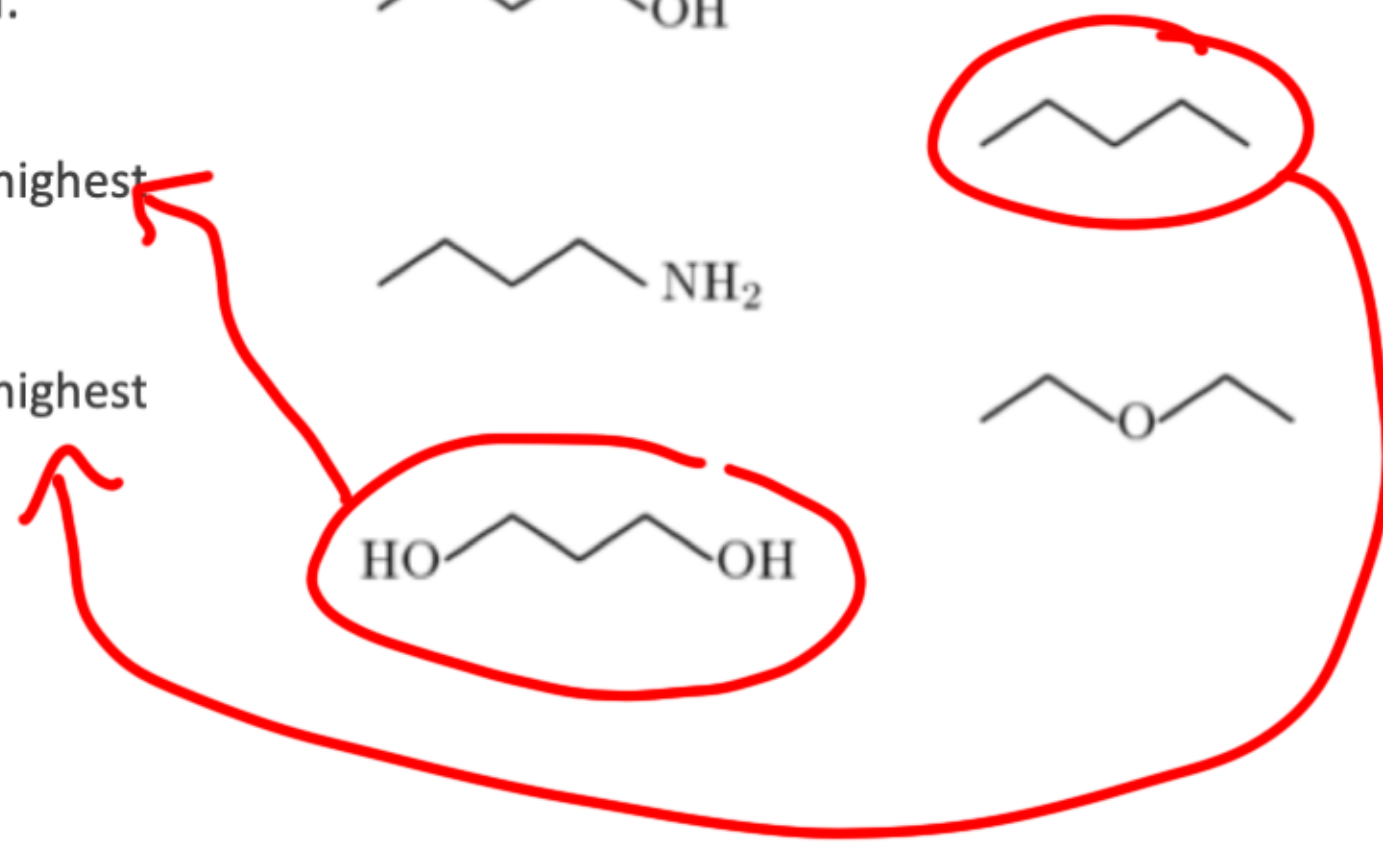
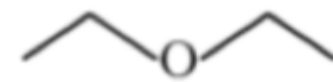




# Comparing IMFs I

You can use the strengths in IMFs to determine physical properties, such as boiling point, vapor pressure, viscosity, and surface tension.

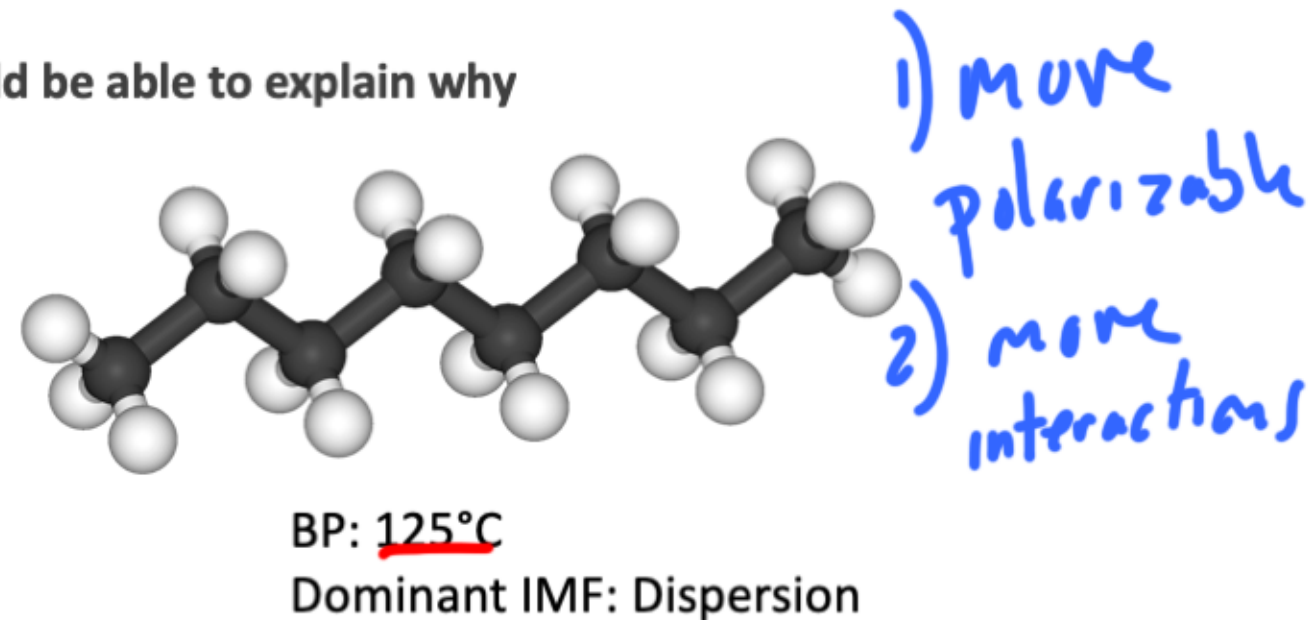
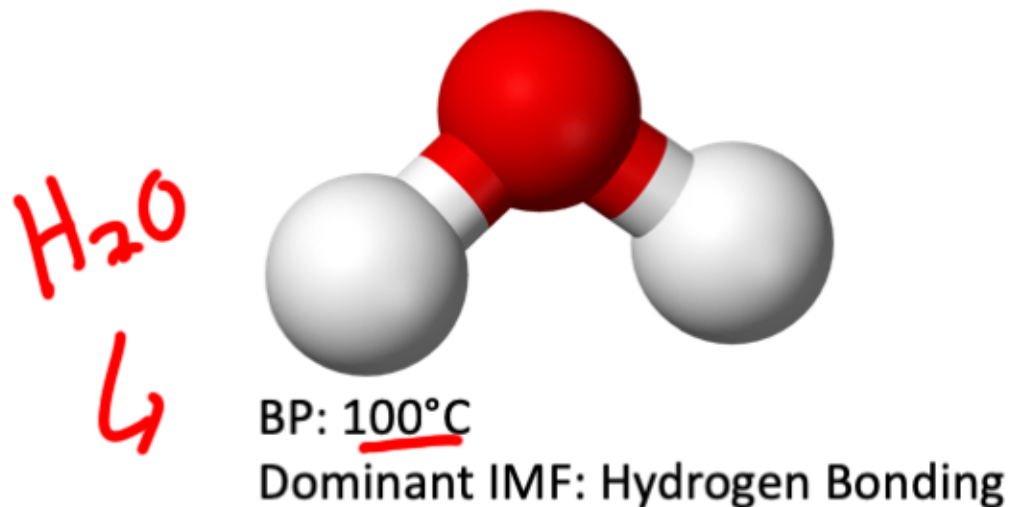
1. Which of these molecules has the highest IMFs?
2. Which of these molecules has the highest vapor pressure?





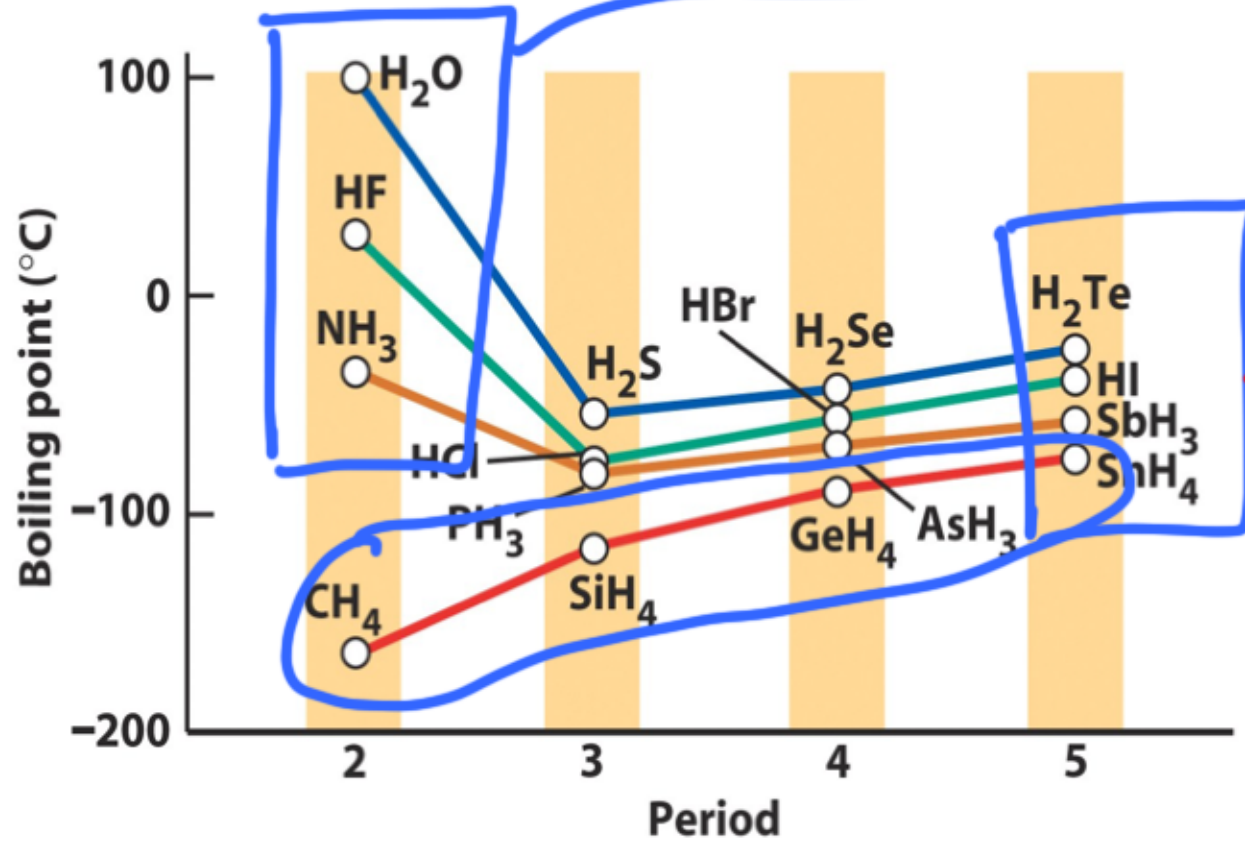
# Comparing IMFs II

- Even 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.
- Consider water vs. octane. You can't predict which of these two samples will have a higher boiling point without knowing the physical data.
  - If we tell you that octane has higher IMFs, you should be able to explain why



# IMF Comparisons

H-bonding

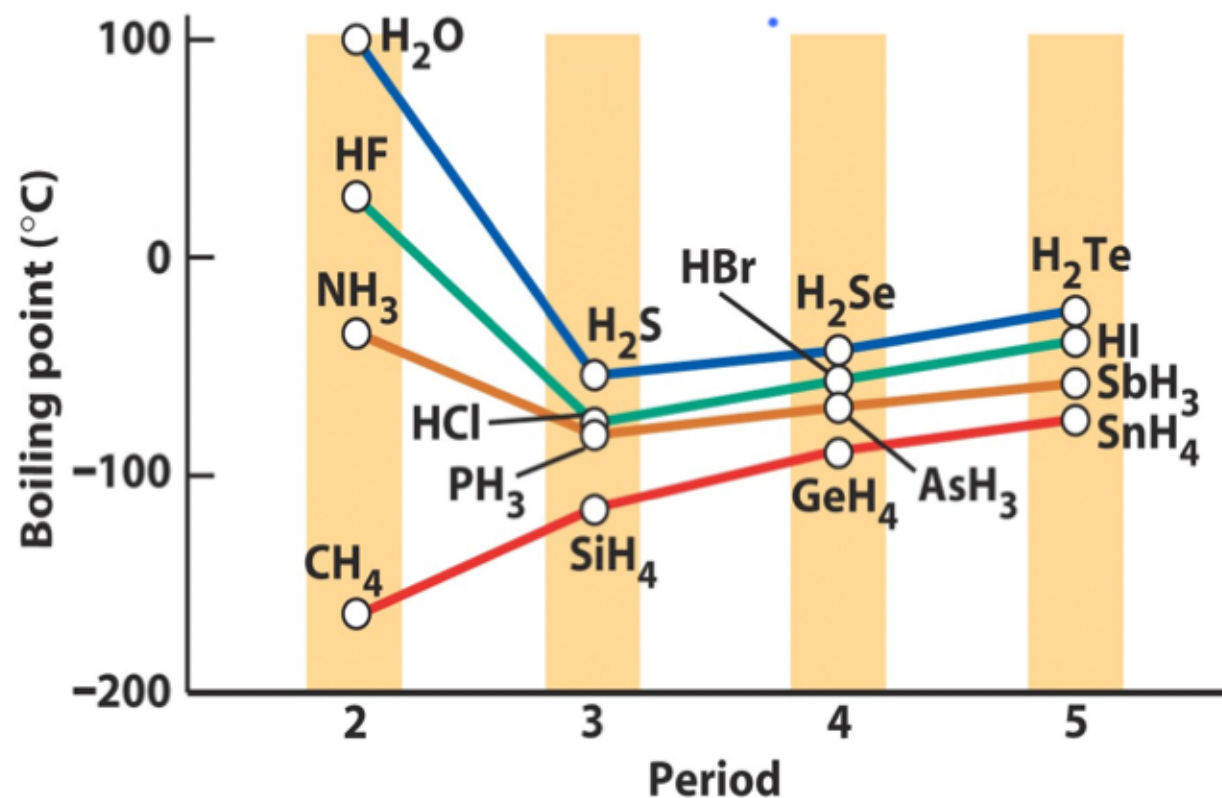


down a group  
↳ increasing polarizability

across a period  
↳ changing shape  
↳ dipole-dipole forces

# IMF Comparisons

- The key features of this graph are as follows:
  - **Comparing central atoms in the same group: use polarizability**
    - Shape is constant, but the size of the electron cloud is increasing as you go down in a group
    - Polarizability (and therefore dispersion force strength) increases with the size of the electron cloud
  - Comparing central atoms in the same period: use shape/polarity
    - Shape changes across a period, leading to different polarity across a group (down up on this chart)
    - A more polar shape will have higher IMFs based on dipole-dipole forces
  - Ammonia, hydrofluoric acid, and water break the trend in polarizability because they form hydrogen bonds.
    - Water is the strongest here because it can make 2 hydrogen bonds per oxygen atom and stacks very well



# Liquid and Solid Properties

# Liquid Properties Summary

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Strong IMF -> High Viscosity, High BP, High Surface Tension, Lower Energy  
(more stable in the liquid phase)

Weak IMF -> High vapor pressure, High volatility

High Temperature -> Overcomes IMFs, Viscosity, and Surface Tension

High Temperature -> Raises vapor pressure

(no effect on properties like boiling point, melting point, etc.)

# Viscosity

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- Boiling point can indicate if a molecule is a liquid at a given temperature, but it does not do a good job of qualitatively describing of that liquid (think water versus syrup. Both are liquids, but very different).
- **Viscosity is defined as a liquid's resistance to flow.** You can think of viscous fluids as being “thick” liquids, like ketchup or syrup.
- The viscosity of a liquid is directly related to IMF's. ↴



Strong IMF -> High Viscosity

Weak IMF -> Low Viscosity



# Surface Tension

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- Surface Tension is the boundary formed between a liquid and another phase (either the gas above the liquid or a solid on the surface).
- **Surface tension is defined as measure of the inward forces that must be overcome in order to expand the surface area of a liquid**

Strong IMF - > High Surface Tension

Weak IMF -> Low Surface Tension

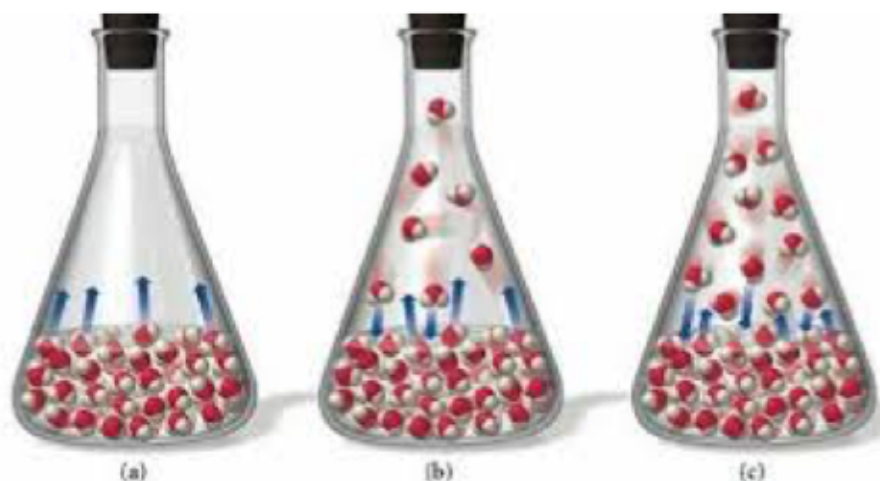




# Vapor Pressure

→ The one that is opposite

- For any given condensed-phase (solid or liquid) sample in a closed container, a certain amount of that sample exists in the gas phase. This is what is known as the **vapor pressure**.
- **These molecules have enough kinetic energy to “escape” the attractions of other molecules on the surface.**



- The Vapor Pressure is a function of the IMF's of the liquid and the temperature.
  - **We are currently focused on the relationship between vapor pressure and IMFs.**

# Vapor Pressure and IMF's

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- If Vapor Pressure is the pressure of gas above a liquid in a closed container at a given temperature, we can easily determine that a sample with High IMF's will have a Low VP (less molecules able to overcome the IMFs and be "lifted into the gas phase).

**Strong IMF - > low VP (and high boiling point)**

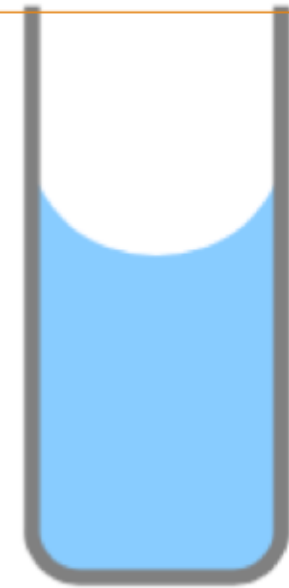
**Weak IMF -> high VP (and low boiling point)**

- **Therefore, while IMF's correlate directly with boiling point and viscosity, they correlate inversely with Vapor Pressure.**

# Adhesion and Cohesion

- An important phenomenon that arises as a result of surface tension, liquid stability, and gravity is the formation of a meniscus in a container
  1. Cohesion: the forces between a liquid and itself (think cohesion...cooperate, community, company etc.)
  2. Adhesion: the forces between two different molecules (think adhesion..."add" another molecule). **Adhesion in this context refers to the forces between a liquid and the walls of the container.**

Adhesion Dominates



concave



convex

Cohesion Dominates

# Comparing Solids

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Class	Examples	Characteristics
Ionic	NaCl, KNO <sub>3</sub> , CuSO <sub>4</sub>	Hard, rigid, brittle; high melting/boiling points; conduct electricity in liquid and aqueous phases
Covalent Network	Carbon (graphite, graphene, diamond) and *SiO <sub>2</sub>	Hard, rigid, brittle; very high melting points (highest); insoluble in water; do not conduct electricity
Metallic	<i>s</i> - and <i>d</i> - block solids and alloys	Malleable, ductile, lustrous; electrically and thermally conducting
Molecular	BeCl <sub>2</sub> , I <sub>2</sub> , ice, glucose, etc.	Relatively low melting/boiling points; brittle if pure; do not conduct electricity

# Comparing Solids

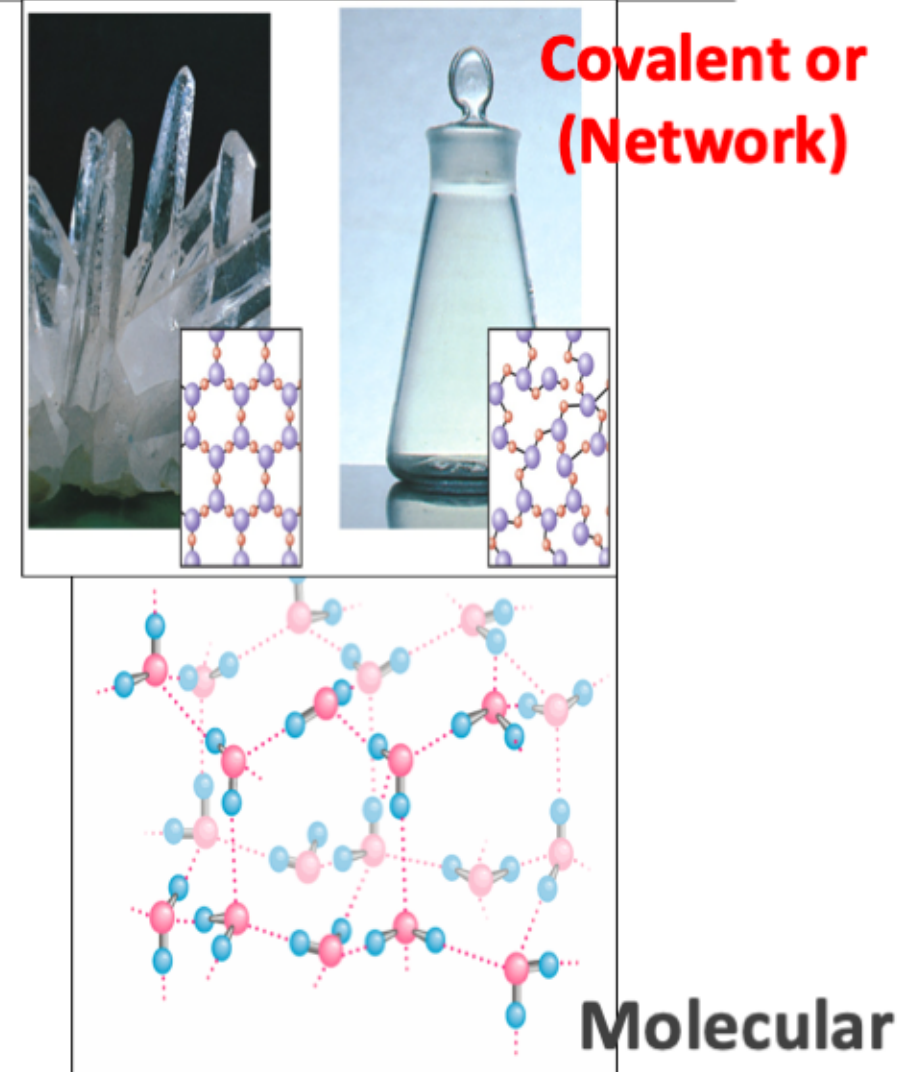
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<b>Class</b>	<b>Electrons</b>	<b>Conductivity</b>
Ionic	Localized	Not a good conductor (only conducts electricity in aqueous solutions or when molten)
Network	Localized	Not a good conductor
Metallic	Delocalized	Good conductor
Molecular	Localized	Not a good conductor



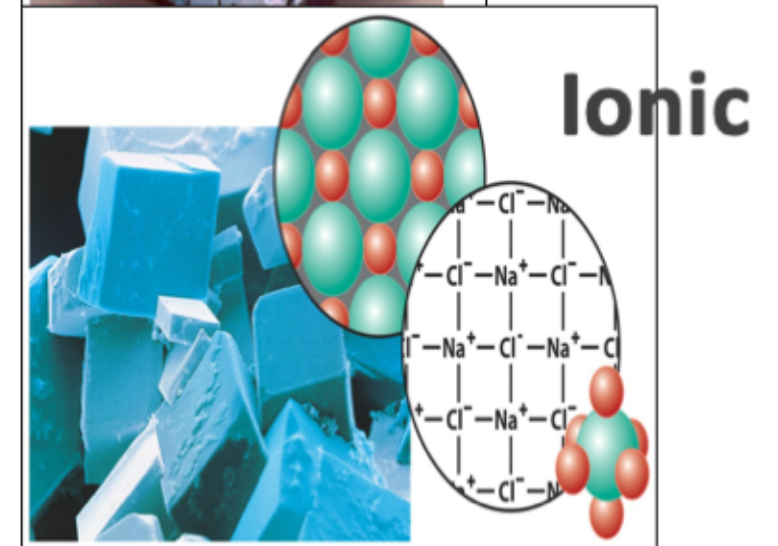
# Molecular vs. Covalent Network Solids

- Molecular and Covalent Network solids are often confused because they can appear very similar on paper ( $\text{CO}_2$  is molecular, while  $\text{SiO}_2$  is a covalent network)
- Covalent network solids are atoms held together by **intramolecular forces** (covalent bonds in this case), resulting in extremely high (over 1000K) melting points.
- Molecular solids are molecules held together by **intermolecular forces**, resulting in low melting points (usually maxed out around 500-600K).
- **Covalent solids have small molecular weights** (think of diamond, MW = 12.01g/mol). **Molecular solids can be small or very large** (sucrose = 342 g/mol; oxytocin = 1009 g/mol)
- **Both are negligible conductors of electricity**



# Ionic vs. Metallic Solids

- Ionic and metallic solids have similar melting points (about 1000 K) and both have interactions with electricity.
- **The delocalized electrons of metallic bonds allow metallic solids to conduct electricity**
- **Ionic solids only conduct electricity when liquid or dissolved in water**
- We say that ionic solids are hard and brittle, while metallic solids are malleable and ductile.
- This is one reason why metallic solids are used for wires and ionic solids are more like grains (think table salt)





$C_6H_6$ ,  $KCl$ ,  $NaCl$ ,  $H_2O$ , diamond

## Properties of Solids: Melting Points

When comparing melting points of solids, think about the type of force you are overcoming:

- **Lowest melting points: molecular solids**
  - For molecular solids, you are overcoming IMFs
  - Stronger IMFs = higher MP
  - Dispersion < Dipole-Dipole < H-bonding
- **High melting points: ionic solids**
  - For ionic solids, you are beginning to overcome ion-ion forces
  - Higher charge density (think Coulomb's Law) = higher melting point
- **Highest melting points: covalent network solids**
  - For covalent solids, you are overcoming the network of hybridized covalent bonds



diamond

$\frac{q_1 q_2}{r^2}$

# Bonding Theories

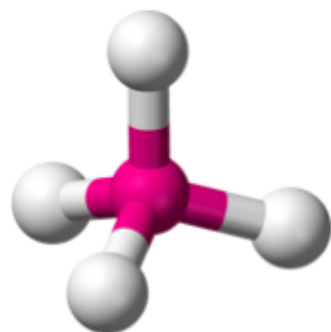
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VSEPR, VB, AND MO

# Bonding Theories Compared

## VSEPR Theory:

- **Shapes: molecular and electronic geometries**
- Explains pure and imperfect bond angles
- Quickly depicts molecular symmetry, which can be used to predict symmetry
- Focuses on the electron "regions"
- Depends on the number of electron-dense regions (bonding and lone-pair regions)



## Valence Bond Theory



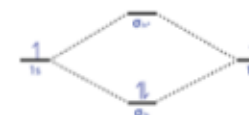
- **Hybrid Orbitals:  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$**
- Sigma and pi bonds
- Identifies the overlapping orbitals to "name" the bonds
- Focuses on the electron "clouds"
- Depends on the number of electron-dense regions
- Easy navigation of central atoms
- **Practical for big molecules, but falls short when it comes to certain physical properties (like magnetism) and delocalized electrons**

$sp^3$

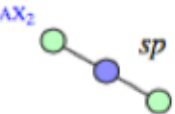
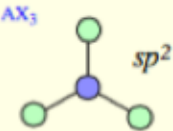
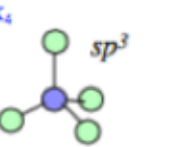

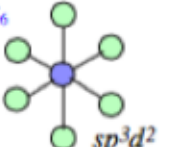
## Molecular Orbital Theory

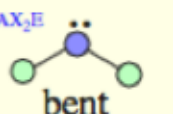

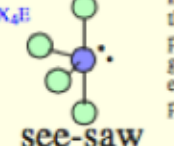



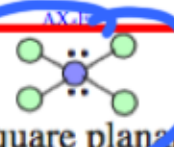
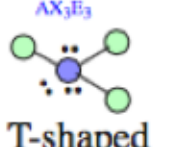
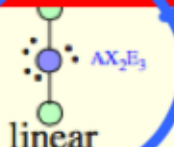
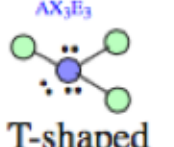
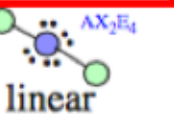
- **Diagrams**
- Answers fundamental questions regarding your molecule related to bond order, magnetism, HOMO-LUMO gap
- Sigma and pi bonds and **anti-bonds**
- Focuses on the electron orbitals as "waves"
- Depends on the number of electrons
- Whole molecule geometry with computers (Hard, good information but a disadvantageous process)
- **Accurate, but very complex for polyatomic molecules; important for physical properties and delocalization of electrons, but not ideal for quickly navigating big organic molecules**

MO Diagram for  $H_2$



# VSEPR and Molecular Polarity

2 electron regions	3 electron regions	4 electron regions	5 electron regions	6 electron regions
$AX_2$  <i>sp</i> linear	$AX_3$  <i>sp^2</i> trigonal planar	$AX_4$  <i>sp^3</i> tetrahedral	$AX_5$  <i>sp^3d</i> trigonal bipyramid	$AX_6$  <i>sp^3d^2</i> octahedral

<p><b>1</b> position occupied by a lone pair</p> <p><b>Molecular Geometries</b> 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.</p>	<p><math>AX_2E</math></p>  <p>bent</p>	<p><math>AX_3E</math></p>  <p>trigonal pyramid</p>	<p><math>AX_4E</math></p>  <p>see-saw</p> <p><small>note: the lone pairs all go in the equatorial positions</small></p>	<p><math>AX_5E</math></p>  <p>square pyramid</p>	
	<p><b>2</b> positions occupied by a lone pair</p>	<p><math>AX_2E_2</math></p>  <p>bent</p>	<p><math>AX_3E_2</math></p>  <p>T-shaped</p>	<p><math>AX_4E_2</math></p>  <p>square planar</p>	<p><math>AX_5E_3</math></p>  <p>T-shaped</p>
	<p><b>3</b> positions occupied by a lone pair</p>	<p><math>AX_2E_3</math></p>  <p>linear</p>	<p><math>AX_3E_3</math></p>  <p>T-shaped</p>	<p><math>AX_4E_4</math></p>  <p>linear</p>	
	<p><b>4</b> positions occupied by a lone pair</p>				

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.

Lewis structure  
 ↓  
 bond angles  
 ↑  
 $e^-$  geometry  
 ↓  
 actual bond angles  
 ↑  
 molecular

→ non-polar

All red shapes are polar

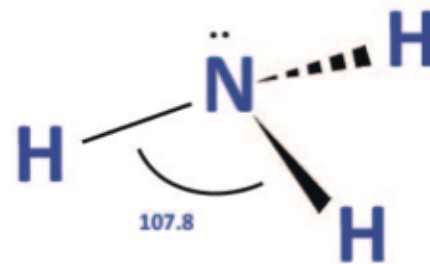
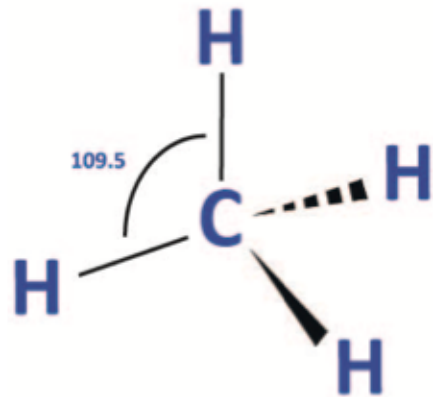
Basic rules for molecular polarity:

1. Look for asymmetry in connectivity. (example:  $CH_3Cl$ )
2. Look for lone pair asymmetry. EVERYTHING with lone pairs is polar, except for the linear and square planar geometries

# The Effect of Lone Pairs on Bond Angles

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- Lone pairs occupy more space on the central atom than a bonding pair of electrons, **meaning they end up being more repulsive than bonding regions**
- The electron density of lone pairs is **ALL on the one central atom** – not shared out over two – as in a conventional bond
- This affects the bond angles at the central atom, making them smaller than expected for a perfect geometry





# Shape and Molecular Polarity

A theoretical central atom has three bonding regions and two lone pair(s). What is the hybridization of this atom?

1.  $sp^3d$   $e^-$ : trig. bipyramidal  
mol: T-shaped  
Polar
2.  $sp^3d^2$
3.  $sp$
4.  $sp^2$
5.  $sp^3$

A theoretical central atom has five bonding regions and no lone pair(s). What is the hybridization of this atom?

1.  $sp^3$   $e^-$ : molecular
2.  $sp$
3.  $sp^3d^2$  trig. bipyramidal
4.  $sp^3d$  non-polar
5.  $sp^2$

A theoretical central atom has three bonding regions and three lone pair(s). What is the hybridization of this atom?

1.  $sp$   $e^-$ : octahedral
2.  $sp^3d$  mol: T-shaped
3.  $sp^2$
4.  $sp^3$  Polar
5.  $sp^3d^2$

# Valence Bond Summary

Hybrids

# of Electron-Dense Regions	Hybridization
2	sp
3	sp <sup>2</sup>
4	sp <sup>3</sup>
5	sp <sup>3</sup> d
6	sp <sup>3</sup> d <sup>2</sup>

1 single  
1 double  
1 triple  
1 L.P.

} = 1 RHEID

Types of Bonds

**Single Bonds:** 1 sigma bond

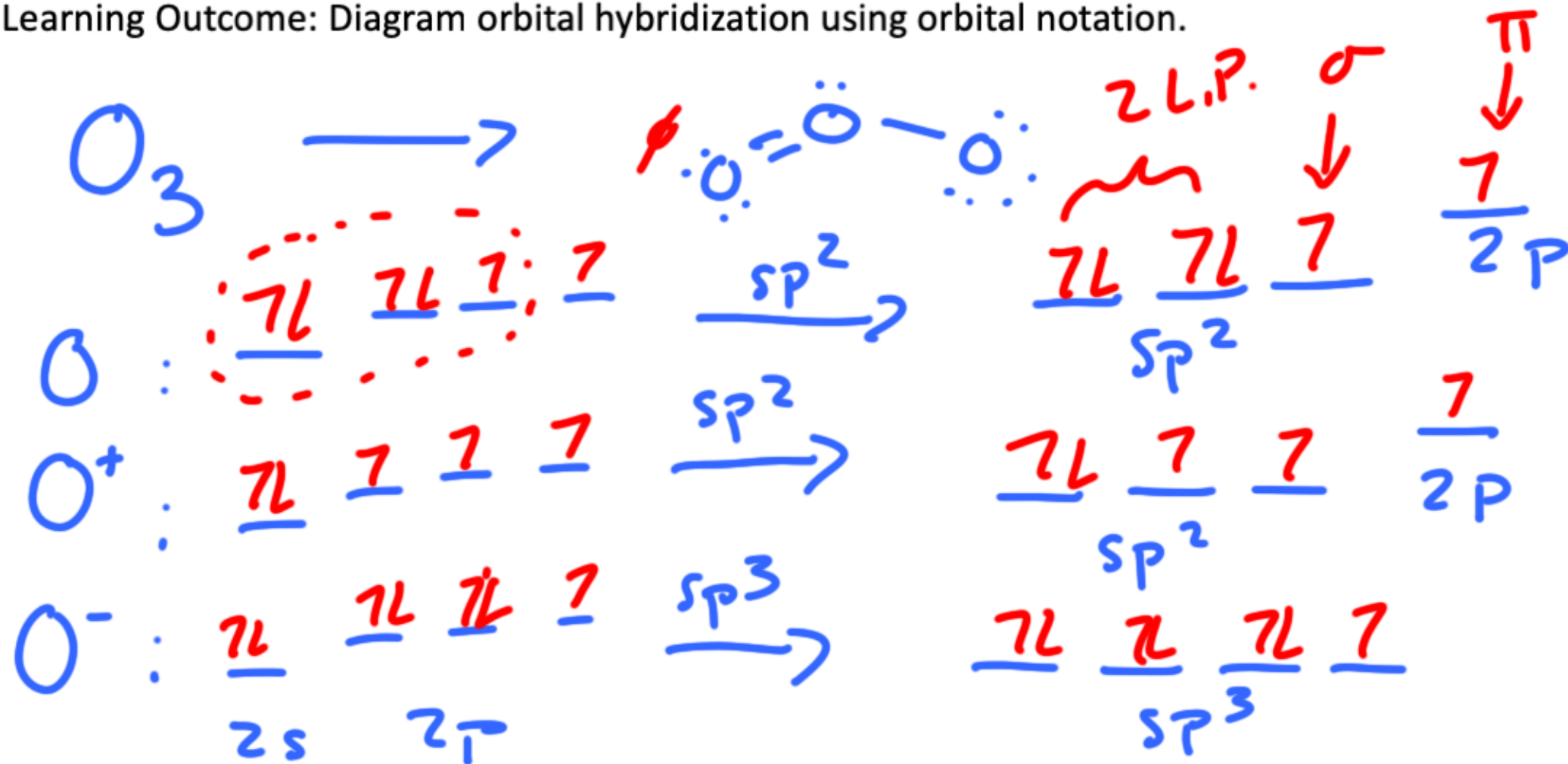
**Double Bonds:** 1 pi bond and 1 sigma bond

**Triple Bonds:** 2 pi bonds and 1 sigma bond



# Valence Bond Orbitals

Learning Outcome: Diagram orbital hybridization using orbital notation.



# Bonding Names Overview

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✓ Name bonds by identifying the “overlapping” orbitals:

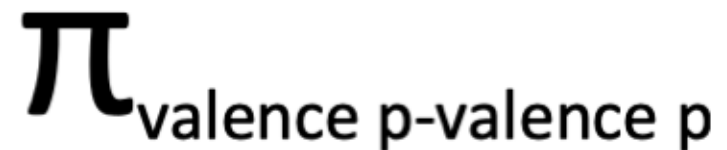
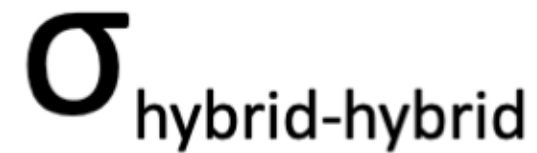
1. Identify the bond(s) present
2. Identify the hybridization of each bonding atom
3. Name the bond based on the type of bond and overlapping orbitals

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 (one region of overlap)

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)



# Organic Molecules

1. How many pi bonds are in this molecule?

4

2. How many sigma bonds are in this molecule?

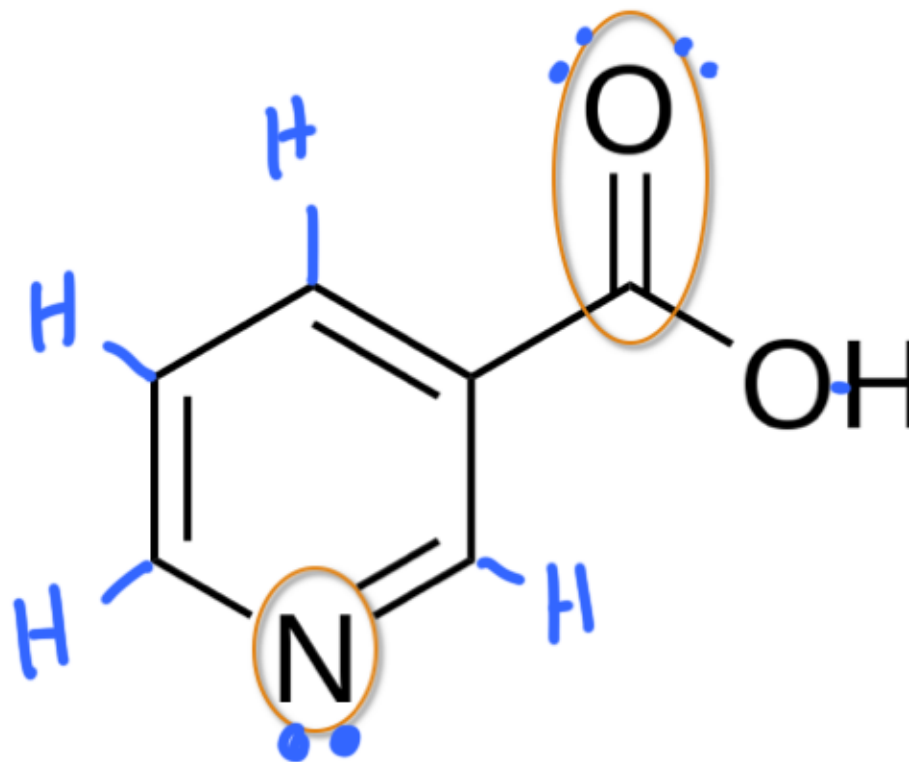
... 14

3. What are the names of the bonds circled between C=O?

$\sigma_{sp^2-sp^2}$   
 $\pi_{2p-2p}$

4. What are the bond angles around the circled nitrogen?

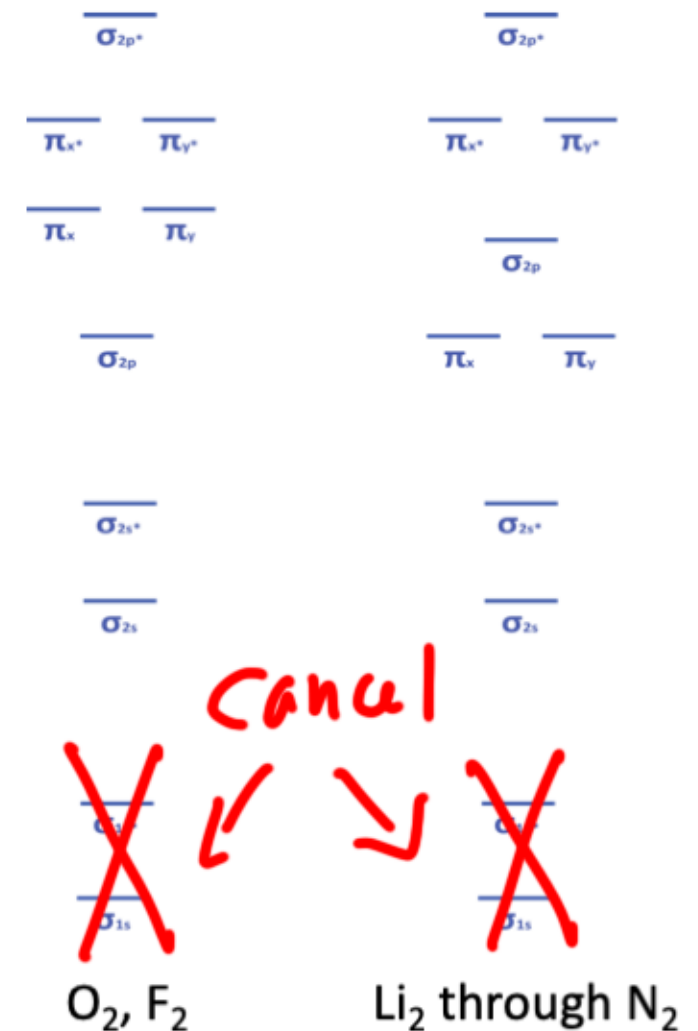
$\angle 120$   
117 ... slightly less than 120



\*Keep doing this for as many regions of the molecule until you see the consistencies in your answers

# MO Theory: The one with the “Diagrams”

- **MO Theory is a quantum mechanical model for bonding that merges pure atomic orbitals into molecular orbitals**
- This theory is important because it gives us the following conclusions that VB and VSEPR cannot:
  - Stability can be described by bond order
  - **(BO = (bonding electrons – antibonding electrons)/2)**
    - Bonding electrons aid in stability
    - Antibonding electrons lead to instability
  - Magnetism can be identified by the presence of paired or unpaired electrons in the highest occupied orbital
    - Diamagnetic: all electrons are paired, repelled from magnetic field
    - Paramagnetic: there electrons that are unpaired, attracted to magnetic field
  - And of course, HOMO-LUMO...



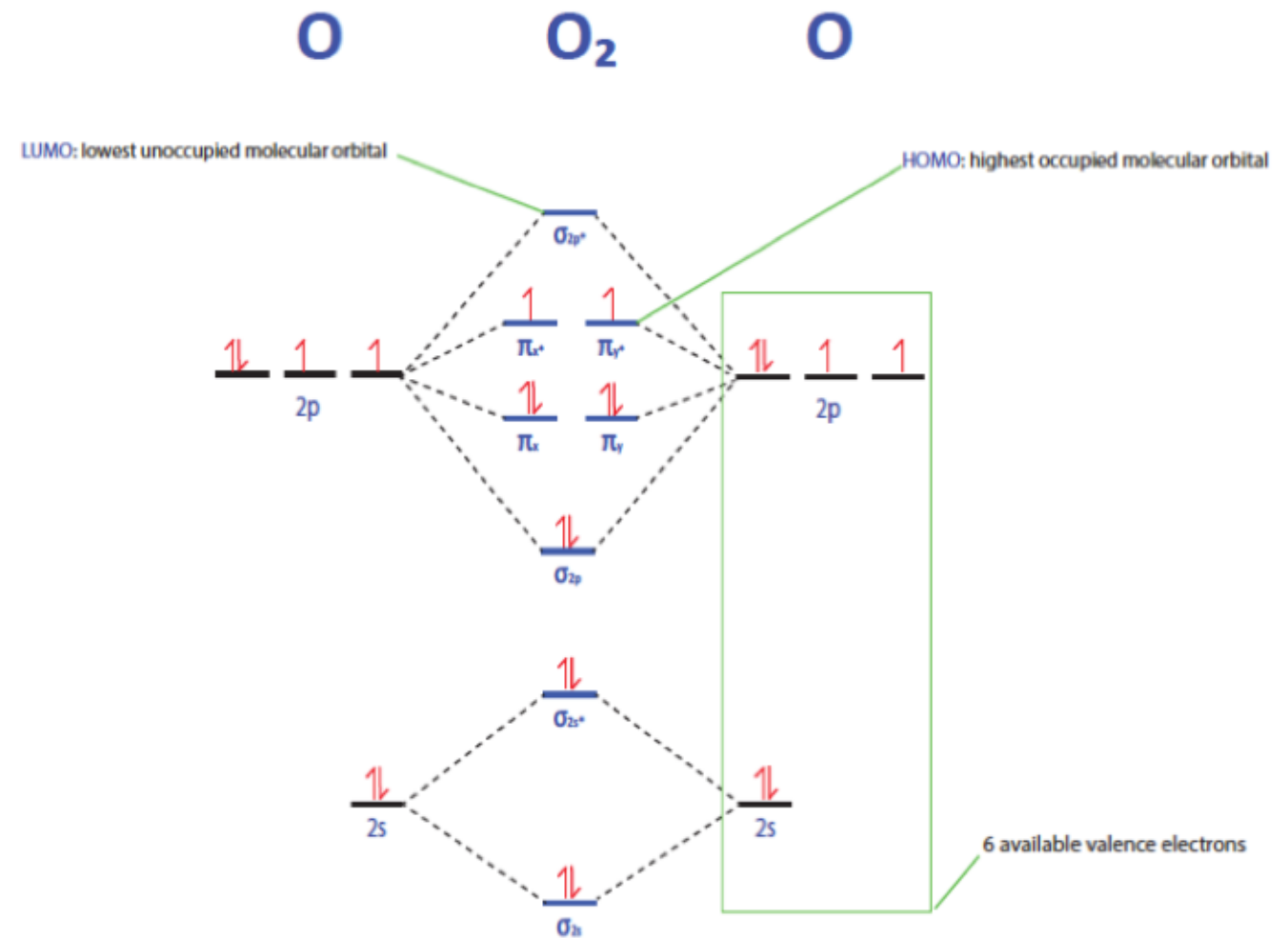
You must memorize the diagrams and orbital labels to the right

# 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**
- $E_{\text{light in}} = E_{\text{HOMO-LUMO}}$
- Because light is important here, remember:

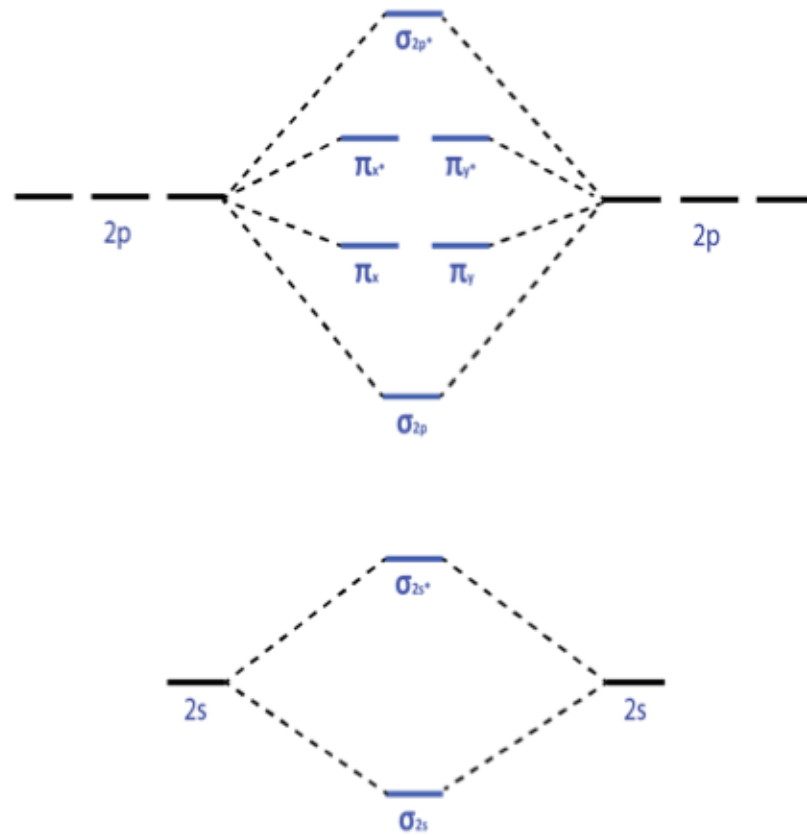
IR....**R.O.Y.G.B.I.V.** ...UV

(---increasing energy, decreasing wavelength-->)

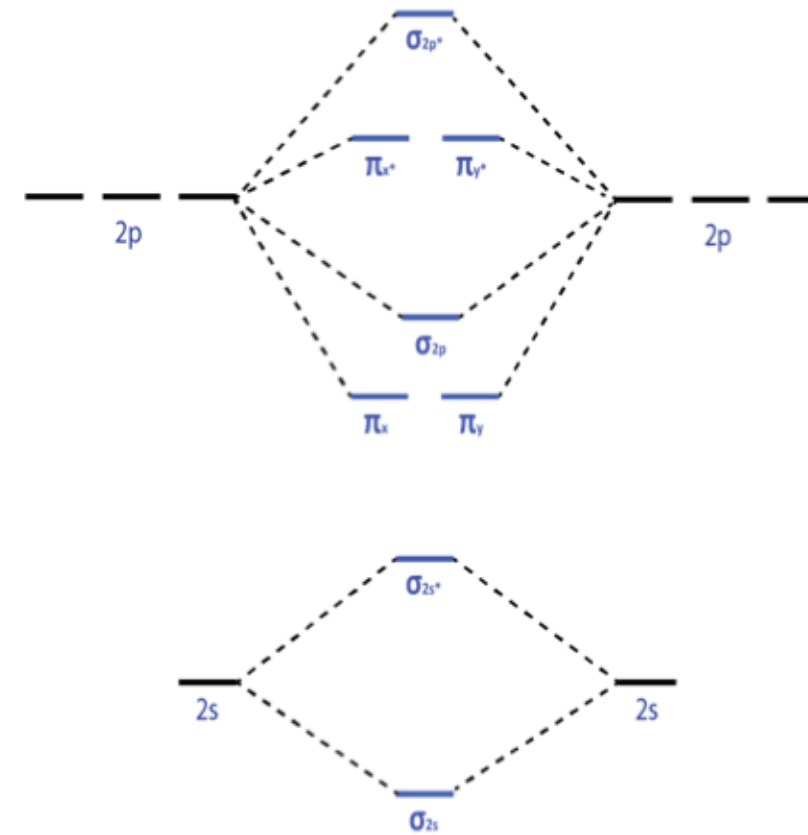


# Molecular Orbital Theory

O<sub>2</sub> and F<sub>2</sub>



B<sub>2</sub>, N<sub>2</sub>, and C<sub>2</sub>





# Extra Stuff

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# Shape and Molecular Polarity

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...then what is the hybridization? Dominant IMF?

# Molecular Polarity

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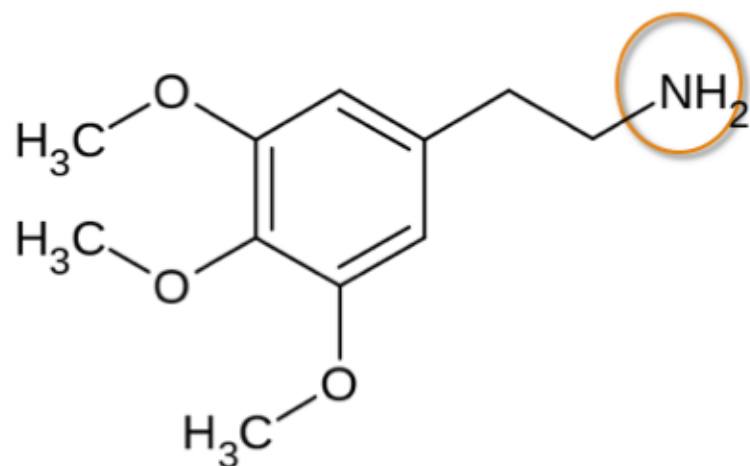
- $O_3$
- $CCl_3F$
- $BF_3$
- $ClF_3$

# Big Molecule Question

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What are the electronic and molecular geometries around the circled nitrogen?

What are the bond angles around nitrogen?



- a. 120 degrees
- b. 109.5 degrees

- c. Just less than 109.5 degrees
- d. Just more than 109.5 degrees

# VB Challenge Questions (Last Week)

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Consider the VB electron configuration for the valence of a central atom:



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

HCN

$\text{NO}_3^-$

$\text{CO}_3^{2-}$

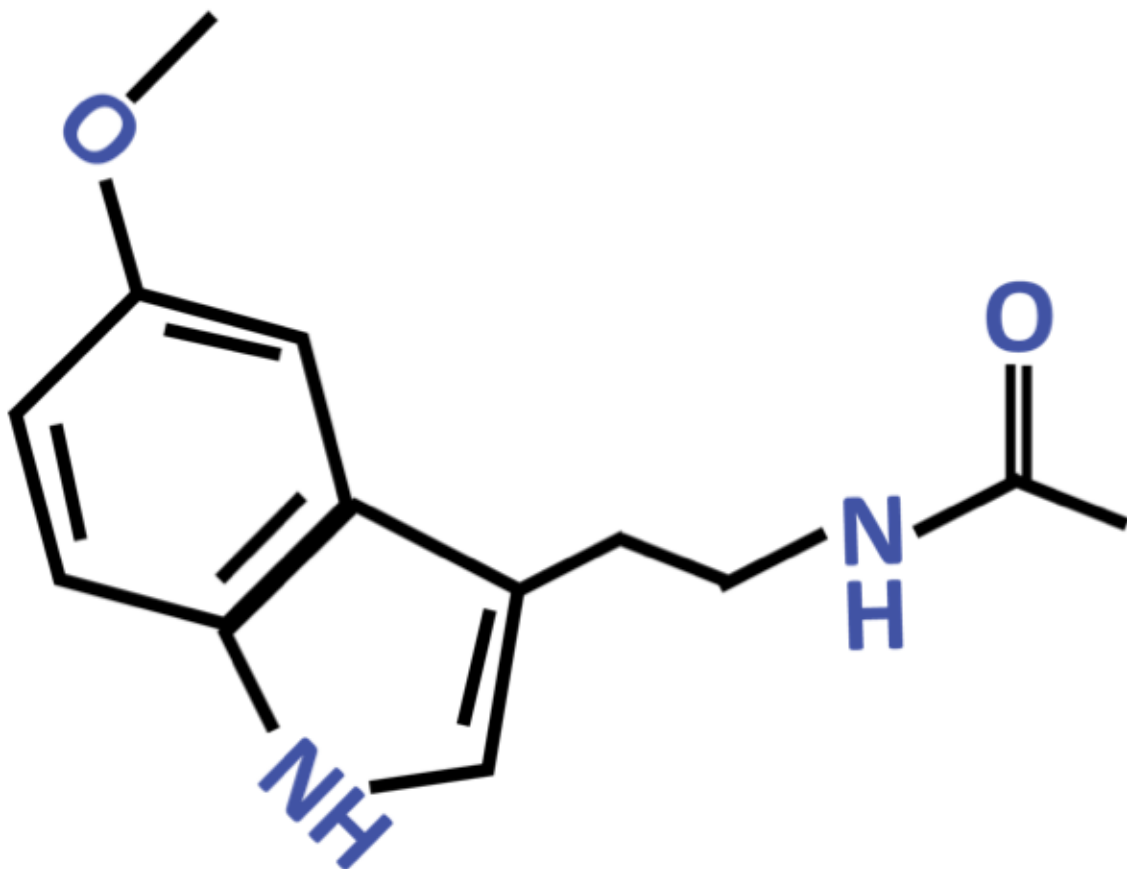
$\text{CO}_2$

Consider the compound ethene,  $\text{C}_2\text{H}_4$ . 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.  $\pi$ ;  $sp^2$
2.  $\pi$ ;  $1p$
3.  $\pi$ ;  $2p$
4.  $\sigma$ ;  $sp^2$
5.  $\sigma$ ;  $sp^3$

# Organic Molecules

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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



# MO Theory Question

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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.

# MO Theory Question

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Does  $F_2^{2-}$  exist? How does molecular orbital theory prove this?