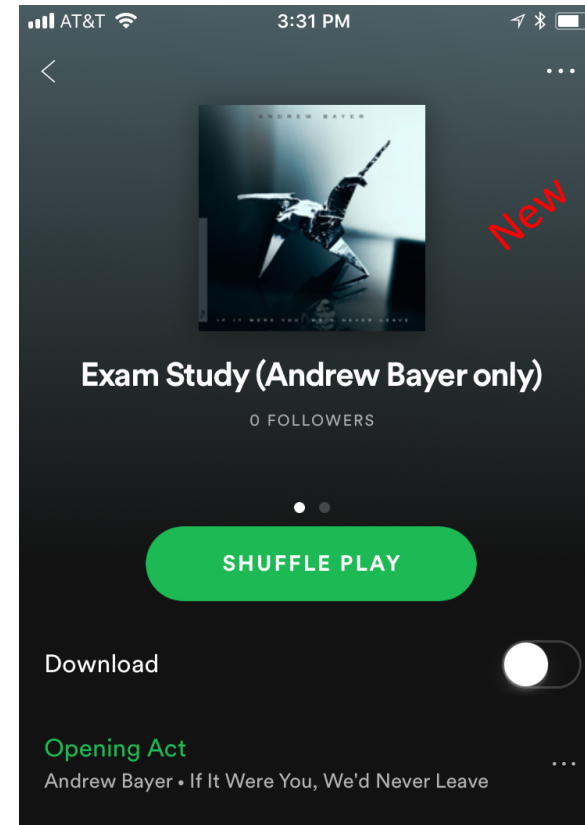
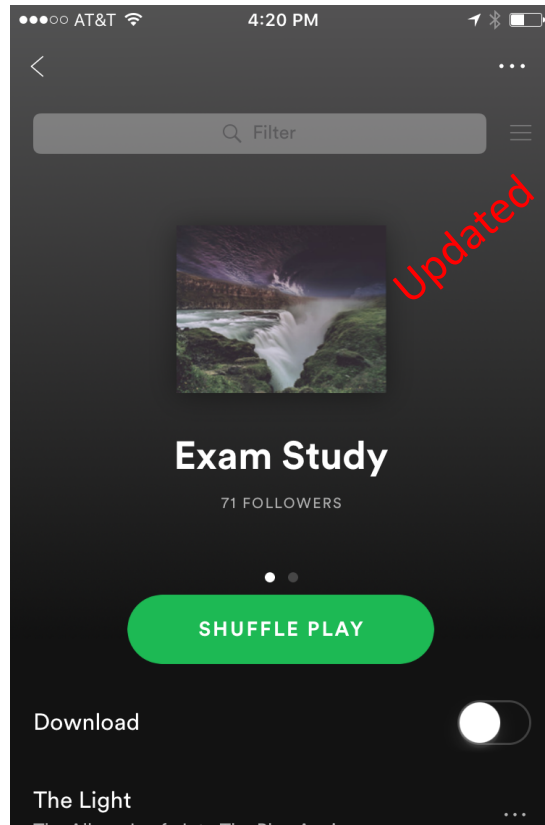


Unit 4 Exam Review

BONDING PART II, IMF'S, LIQUID AND SOLID PROPERTIES

Most Important Exam Announcement:



(Jimmy Wadman, spotify)

Learning Objectives – Unit 4

Bonding, Part II

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

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

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

Differentiate between localized and delocalized electrons within a structure.

Diagram orbital hybridization using orbital notation.

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

Differentiate between constructive interference and destructive interference of

atomic orbitals.

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.

IMF's, Liquids, and Solids

Define the three major intermolecular forces (IMFs) that can exist in condensed phases: dipole-dipole, hydrogen bonding, and dispersion.

Predict the types of IMFs that a compound can exhibit based on its structure.

Using bonding theories and IMFs, predict the chemical and physical properties of organic materials.

Explain how size, shape and polarizability

affect the magnitude of dispersion forces.

Relate the IMFs of a compound to liquid properties such as boiling point, vapor pressure, viscosity, and surface tension.

Explain how liquid properties vary with temperature.

Fully describe (atomic arrangement/microscopic view) and visually depict the four types of solids (covalent, ionic, metallic, molecular).

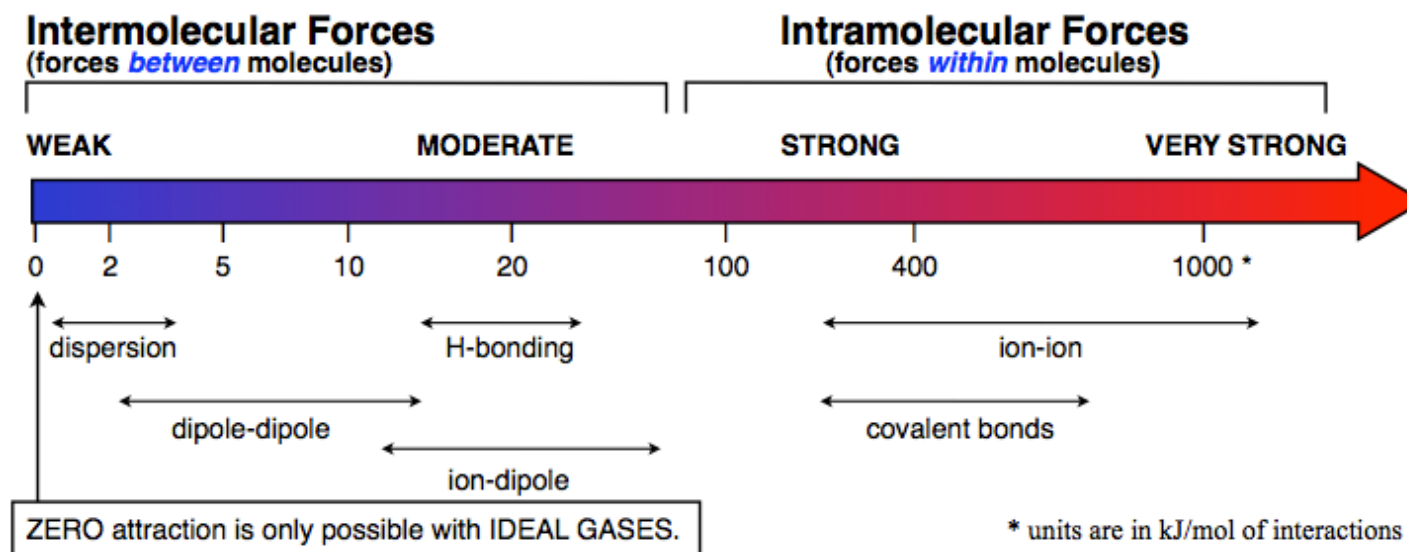
Summarize how the macroscopic properties of solids (e.g. melting point, hardness, conductivity) can be explained by the microscopic model of solids.

Use physical data to deduce the type of bonding within solids.

Go from Chemical Formula > Structure > ID the IMFs

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. Radius between interactions



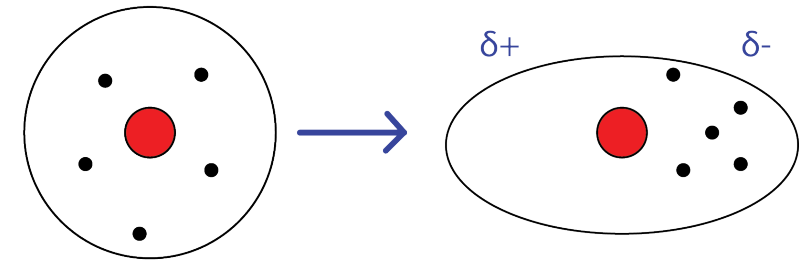
Dispersion Forces

All molecules have dispersion forces

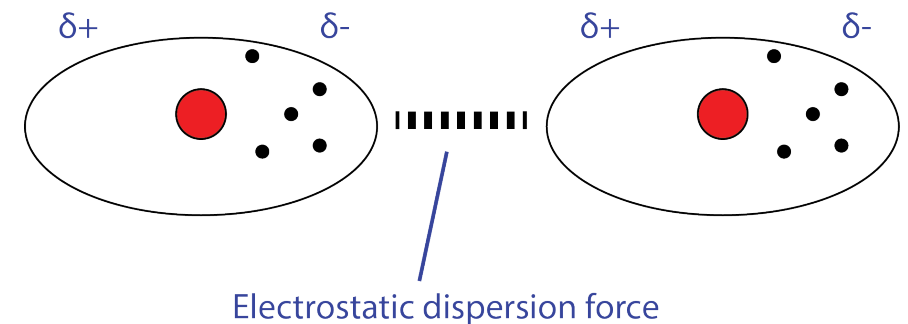
Dispersion forces depend on a molecule's ability to spontaneously induce a dipole. Its ability to do this is called its **polarizability** and is directly influenced by the **molecular weight** of the molecule.

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

1. Formation of a spontaneous dipole



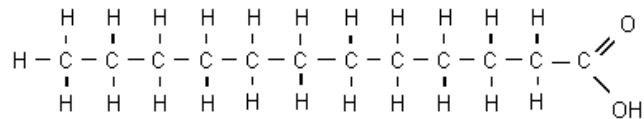
2. Induction of a second molecule



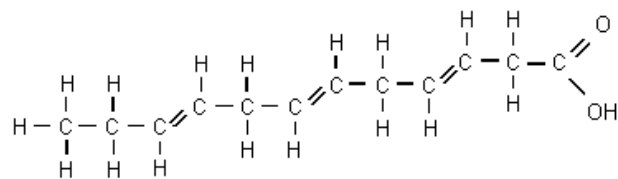
Dispersion Forces - Polarizability

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

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



Saturated Fatty Acid



Unsaturated Fatty Acid

Gas:



Lowest Polarizability,
Lowest IMF's

Liquid:



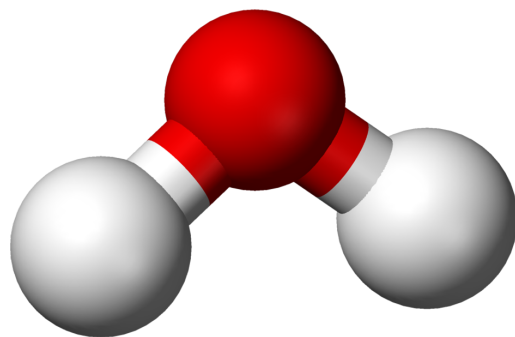
Solid:



Highest Polarizability,
Highest IMF's

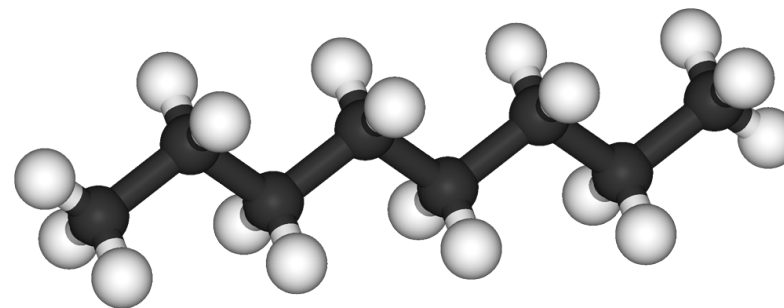
Size - Comparing IMF's

- 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!**



BP: 100°C

Dominant IMF: Hydrogen Bonding

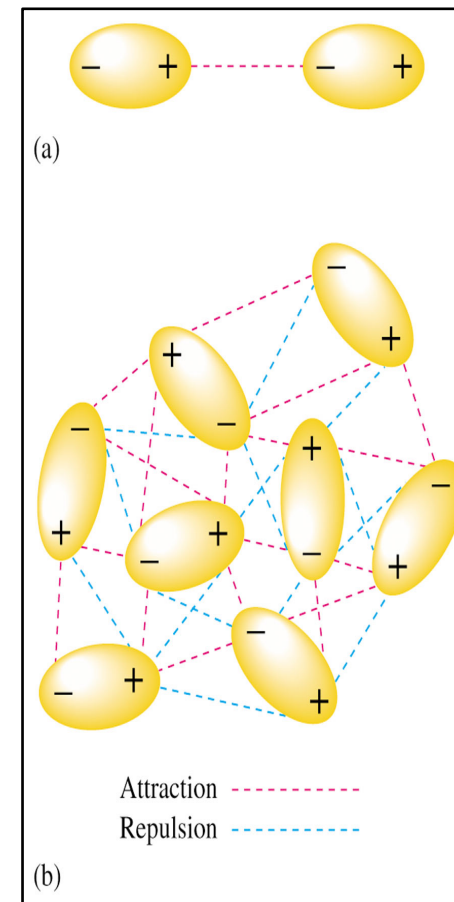
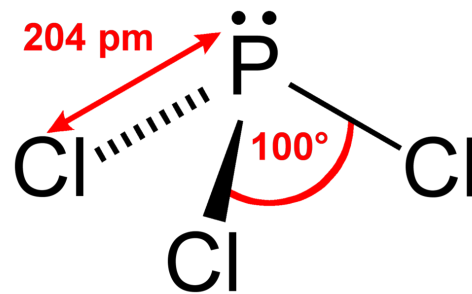
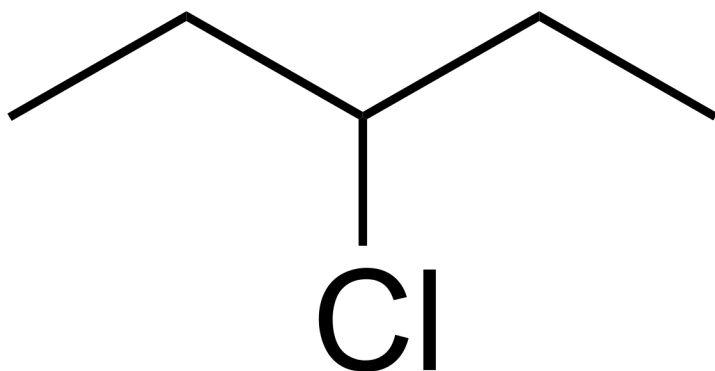


BP: 125°C

Dominant IMF: Dispersion

Dipole-Dipole Forces

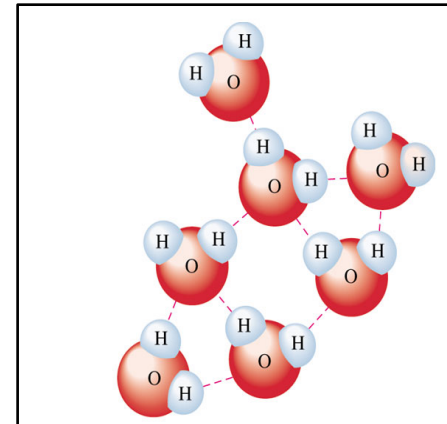
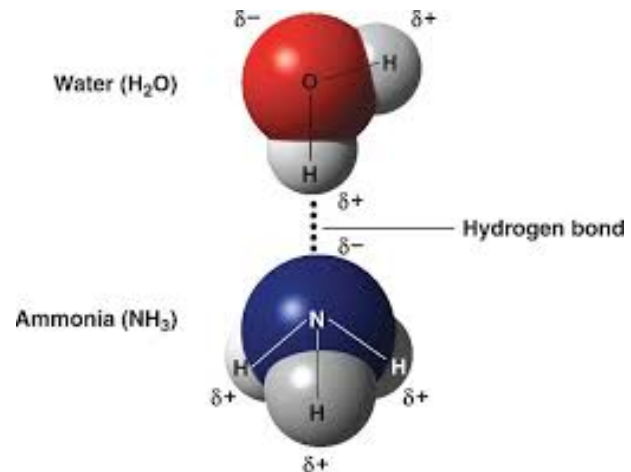
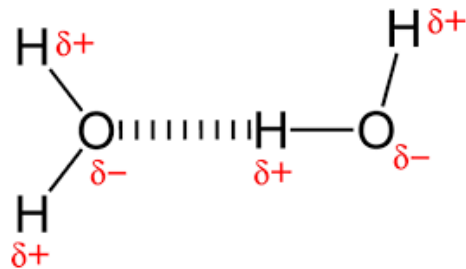
- Dipole-dipole forces require a permanently fixed dipole on a molecule.
- **Because the dipole moment is permanent, dipole-dipole forces are stronger than dispersion forces.**
- **Dipole-Dipole forces can be easily identified if you can spot out a polar molecule**



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

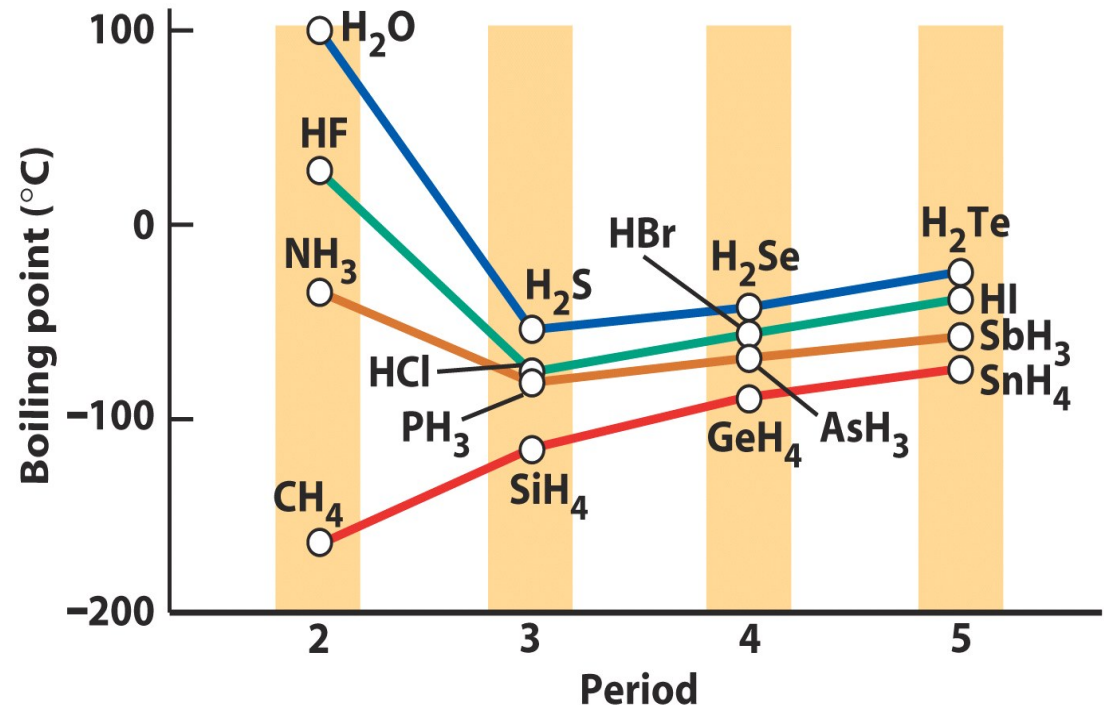
Hydrogen Bonds

- 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.**



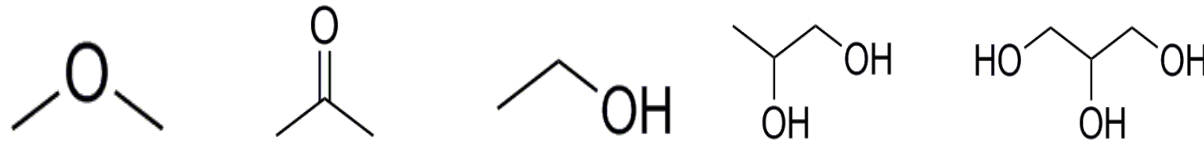
IMF Comparisons

- 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)**



Hydrogen Bonds

- The number of hydrogen bonds is important. **The more hydrogen bonds, the stronger the overall IMF's.**
- Here you can see the relationship trend in boiling point from slightly polar (dimethyl ether) to 3 H-bonds (glycerol; Propane-1,2,3 triol)

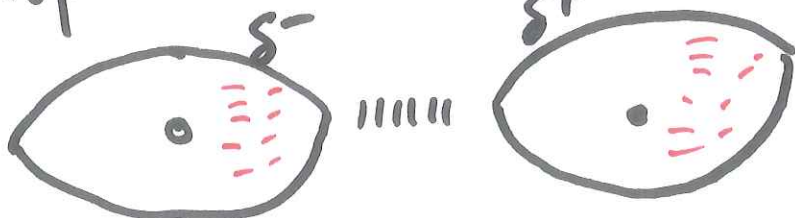


Boiling Point -24 °C 56 °C 79 °C 188 °C 554 °C

of H Bonds 0 0 1 2 3

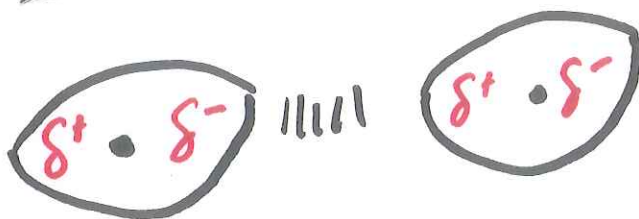
IMFs (increasing strength per interaction)

• Dispersion Forces



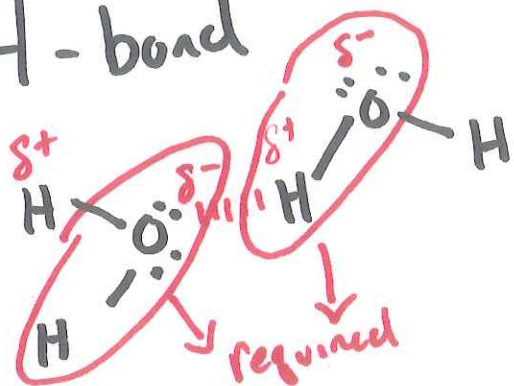
induced, temporary
 CH_4 , CCl_4 , Br_2

• Dipole - Dipole



fixed, permanent
 CH_3Cl , PCl_3

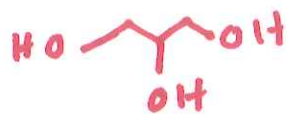
• H-bond



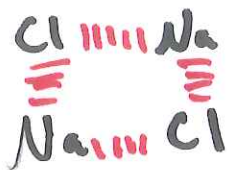
Required:

- Hydrogen directly bonded to N, O, or F

H-F , H_2O , CH_3OH ,



• Ion-Ion



- 1) Identify the IMFs present
- 2) Determine the strongest IMF out of a range of molecules

IMF Comparisons


Why does X have a higher/lower BP than Y?

Down a group: Polarizability increases

Across a period: Shape / Polarity / Dipole

if H-bonding occurs: H-bonds

Hydrocarbons:

- More surface area & Higher Polarizability
 - Higher MW 
-

Higher IMFs & BP↑, Viscosity↑, Surface Tension↑
FP, MP↑, Lower Energy

Lower IMFs & Vapor Pressure↑, Volatility↑

Liquid Properties Summary

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 - > Lowers IMF Strength, Viscosity, and Surface Tension

High Temperature -> Raises Vapor pressure

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

Viscosity

- 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

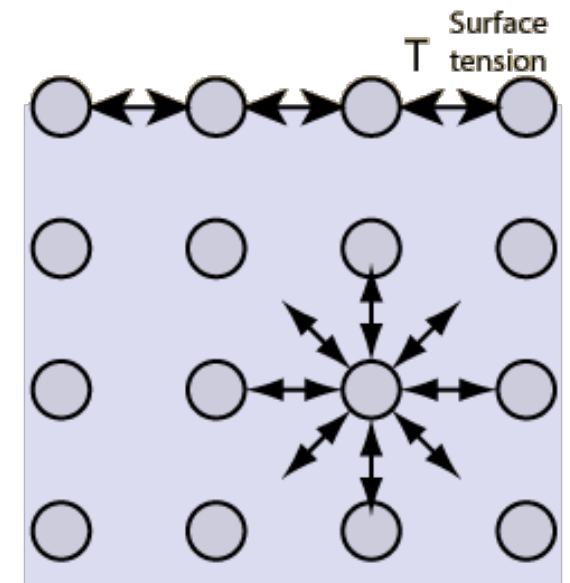
Weak IMF -> Low Viscosity

Surface Tension

- 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**

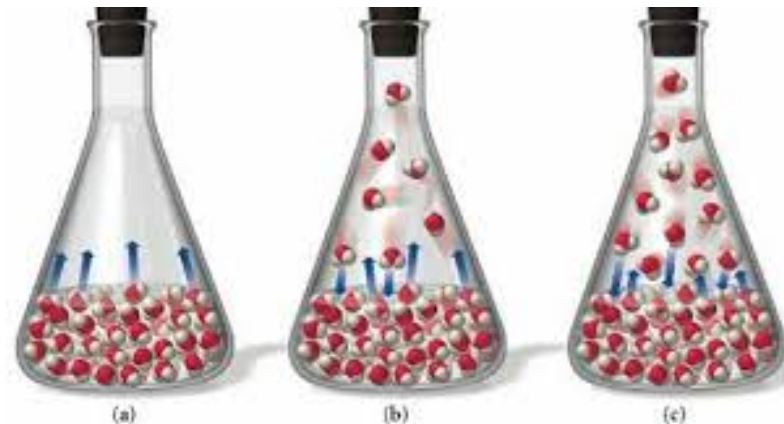
Strong IMF -> High Surface Tension

Weak IMF -> Low Surface Tension



Vapor Pressure

- 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.**
- Vapor pressure is a function of dynamic equilibrium, but more on that in CH302...



- 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

- 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)

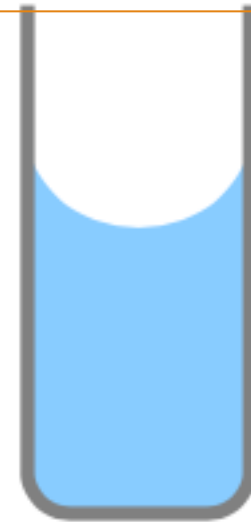
- **Therefore, while IMF's correlate directly with boiling point and viscosity, they correlate inversely with Vapor Pressure.**

Adhesion and Cohesion

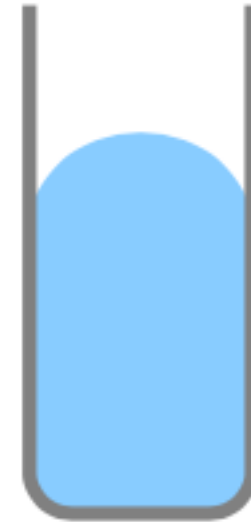
- An important phenomenon that arises as a result of surface tension, liquid stability, and gravity is the formation of a meniscus in a container
 1. Cohesion: the forces between a liquid and itself (think cohesion...cooperate, community, company, etc.)
 2. Adhesion: the forces between two different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

Two scenarios arise from these forces, depending on which one is stronger.

Adhesion Dominates



concave



convex

Cohesion Dominates

Comparing Solids

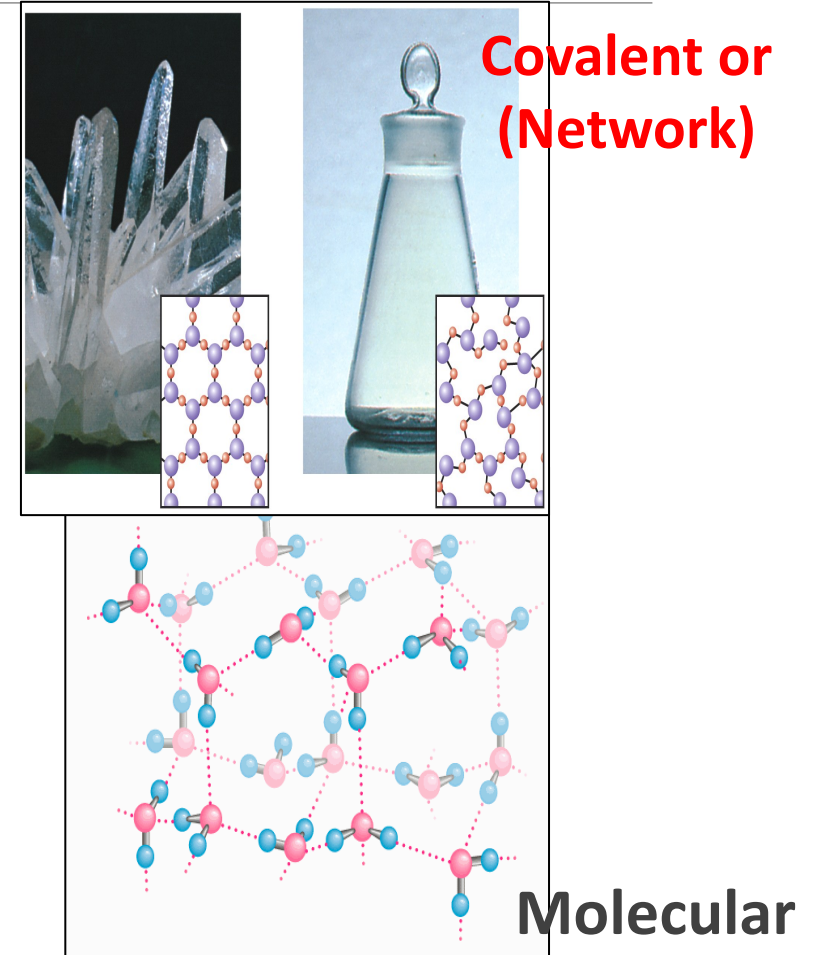
Class	Examples	Characteristics
Ionic	NaCl, KNO ₃ , CuSO ₄ •H ₂ O	Hard, rigid, brittle; high melting/boiling points; those soluble in water give conducting solutions
Covalent Network	Carbon (graphite, graphene, diamond) and SiO ₂	Hard, rigid, brittle; very high melting points (highest); insoluble in water;
Metallic	<i>s</i> - and <i>d</i> -elements	Malleable, ductile, lustrous; electrically and thermally conducting
Molecular	BeCl ₂ , S ₈ , P ₄ , I ₂ , ice, glucose	Relatively low melting/boiling points; brittle if pure

Comparing Solids

Class	Electrons	Conductivity
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

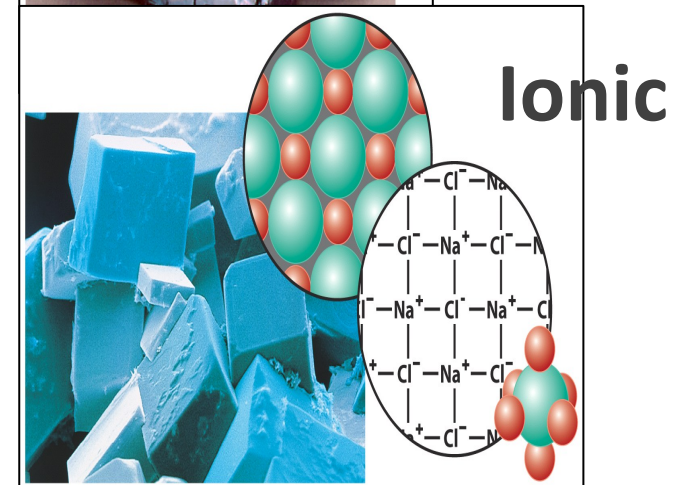
Molecular vs. Covalent Network Solids

- Molecular and Covalent Network solids are often confused because they can appear very similar on paper (CO_2 is molecular, while SiO_2 is 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

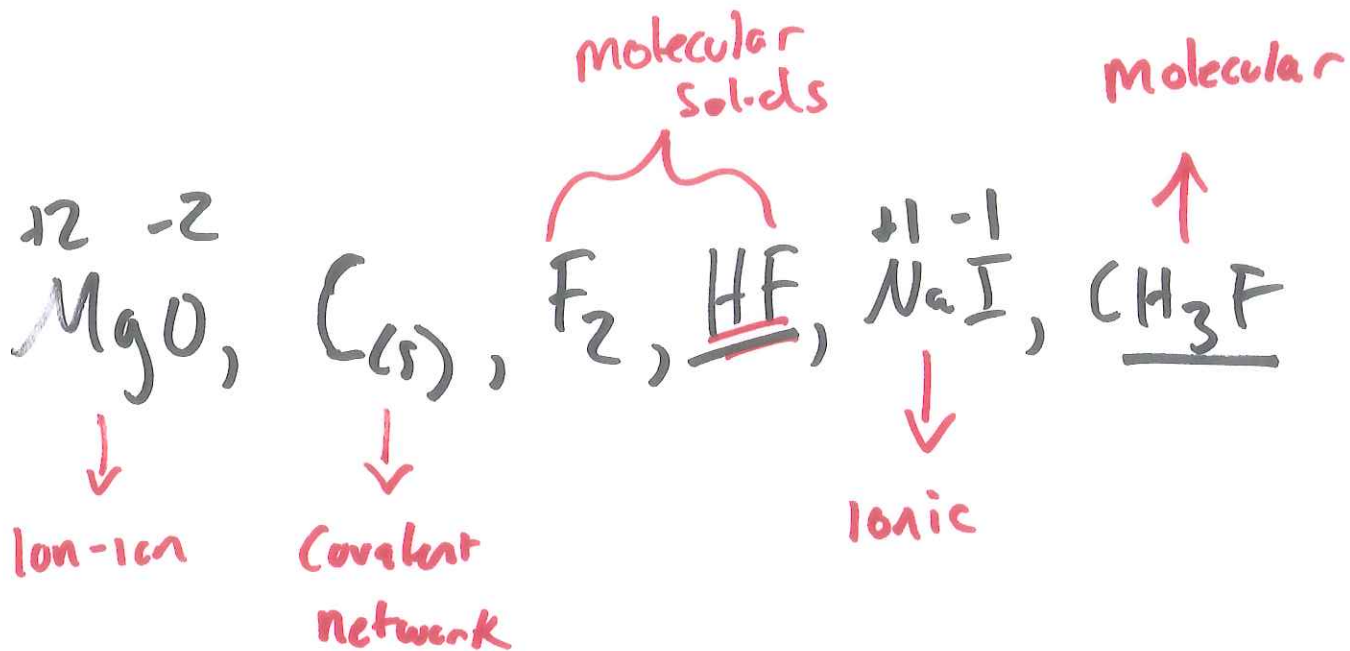
- Ionic and metallic solids have similar melting points (about 1000K) and both have interactions with electricity.
- **The delocalized electrons of metallic bonds allow metallic solids to conduct electricity**
- **Ionic solids only conduct electricity when liquid or dissolved in water**
- We say that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



Ranking All Substances

Rank the following substances according to melting point:

MgO, C(s, graphite), F₂, HF, NaI, CH₃F



Molecular < Ion-Ion < Covalent network

Dispersion < dipole-dipole < charge density
 < H-bonding



Bonding Part II

VALENCE BOND AND MOLECULAR ORBITAL THEORY

Use my last review for the full VB and MO Theory Review

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” around a central atom
- Depends on the number of electron-dense regions
- **Justifies VSEPR by creating hybrid orbitals from pure atomic orbitals** (Unit 2)
- Practical, but not fully accurate especially when it comes to physical properties and delocalized electrons
- **Hybrids**

• 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 quantum mechanical “waves” on the **entire molecule**
- **Accurate, but very complex for polyatomic molecules; important for physical properties and delocalization of electrons**
- **Bonding and Antibonding**

Valence Bond Theory

- **Valence Bond Theory** explains the behavior of the valence orbitals of bonding atoms by suggesting that pure atomic orbitals can form energetically favorable hybrid orbitals
- The conclusions of Valence Bond Theory are:
 1. The hybridization of a bonding atom depends on the number of electron regions (bonding regions plus lone-pair regions)
 2. Bonds can be made between pure and hybrid orbitals
 3. Bonds can be classified as sigma or pi depending on the orientation of the orbitals' overlap (sigma – end-on-end; pi– off axis / side-to-side)

Valence Bond Summary

Hybrids

# of Electron-Dense Regions	Hybridization
2	sp
3	sp ²
4	sp ³
5	sp ³ d
6	sp ³ d ²

Types of Bonds

Single Bonds: 1 sigma bond

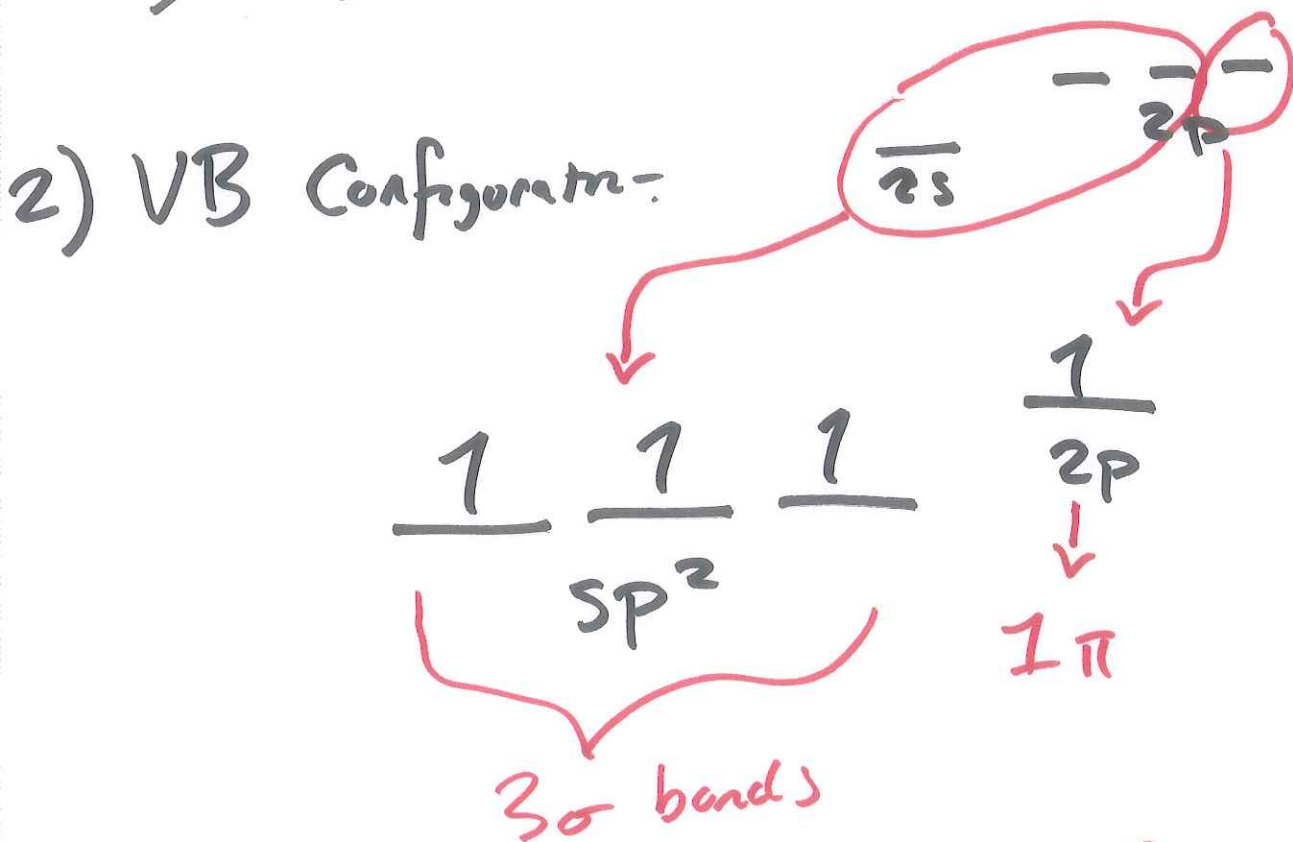
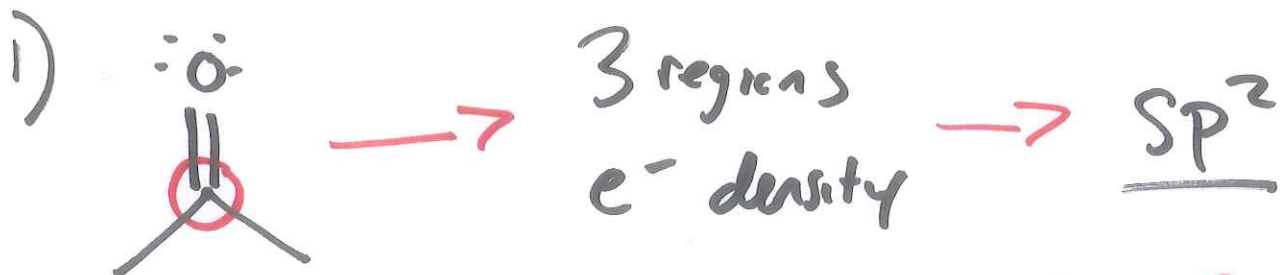
Double Bonds: 1 pi bond and 1 sigma bond

Triple Bonds: 2 pi bonds and 1 sigma bond

Advanced: the more your practice, you will see that:

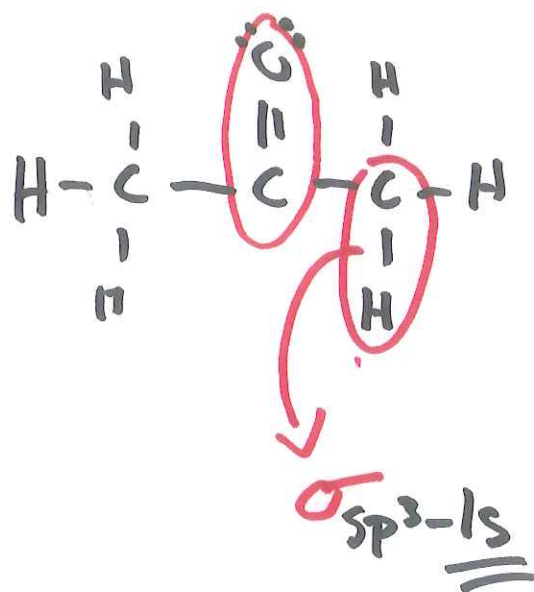
1. Sigma bonds are almost always overlapping hybrid orbitals (with the exception of hydrogen's pure 1s)
2. Pi bonds are always overlapping valence p-orbitals.

VB:



3) # σ & π bonds?

9 σ , 1 π



4) Name & Describe Bonds

π_{2p-2p}

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

Bonding Names Overview

Remember on the exam that naming bonds and identifying the “overlapping” orbitals does not have to be a challenging question. Simplify what you know:

Single Bonds: 1 sigma bond

Double Bonds: 1 pi bond and 1 sigma bond

Triple Bonds: 2 pi bonds and 1 sigma bond

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

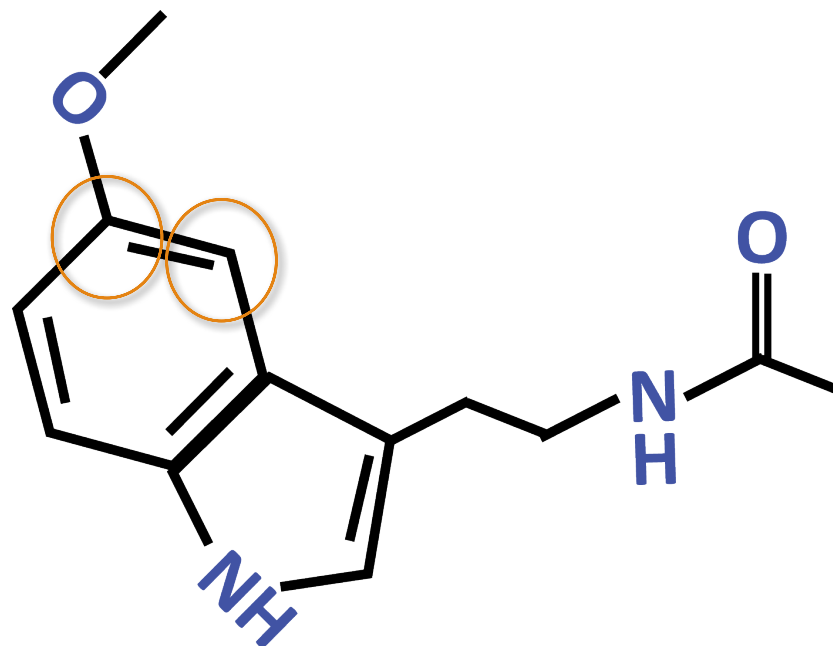
Pi bonds are the **side-by-side (off axis)** overlap between p orbitals

- Pi bonds form above and below the inter-nuclear axis

Organic Molecules

Name the bonds and the overlapping orbitals between the atoms circled below.

- a. σ_{1s-sp^3} ; π_{2p-2p}
- b. $\sigma_{sp^2-sp^2}$; π_{2p-2p}
- c. $\sigma_{sp^3-sp^2}$; π_{2p-2p}
- d. $\sigma_{sp^2-sp^2}$; $\pi_{sp^2-sp^2}$
- e. $\sigma_{sp^3-sp^3}$; $\pi_{sp^3-sp^3}$

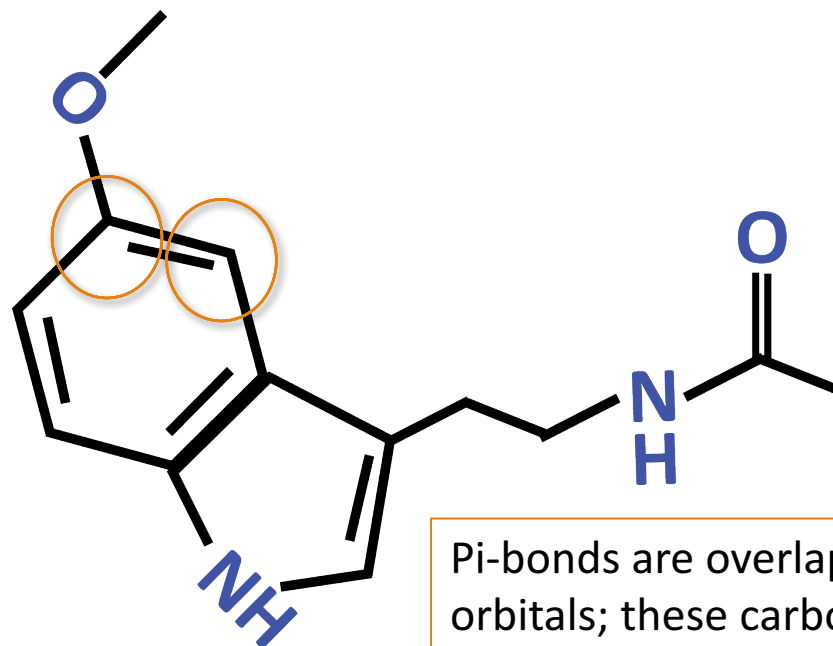


Practice with this, determine the hybridization of all the elements, how many sigma and pi bonds, overlapping orbitals, etc.

Organic Molecules

Name the bonds and the overlapping orbitals between the atoms circled below.

- a. σ_{1s-sp^3} ; π_{2p-2p}
- b. $\sigma_{sp^2-sp^2}$; π_{2p-2p}
- c. $\sigma_{sp^3-sp^2}$; π_{2p-2p}
- d. $\sigma_{sp^2-sp^2}$; $\pi_{sp^2-sp^2}$
- e. $\sigma_{sp^3-sp^3}$; $\pi_{sp^3-sp^3}$



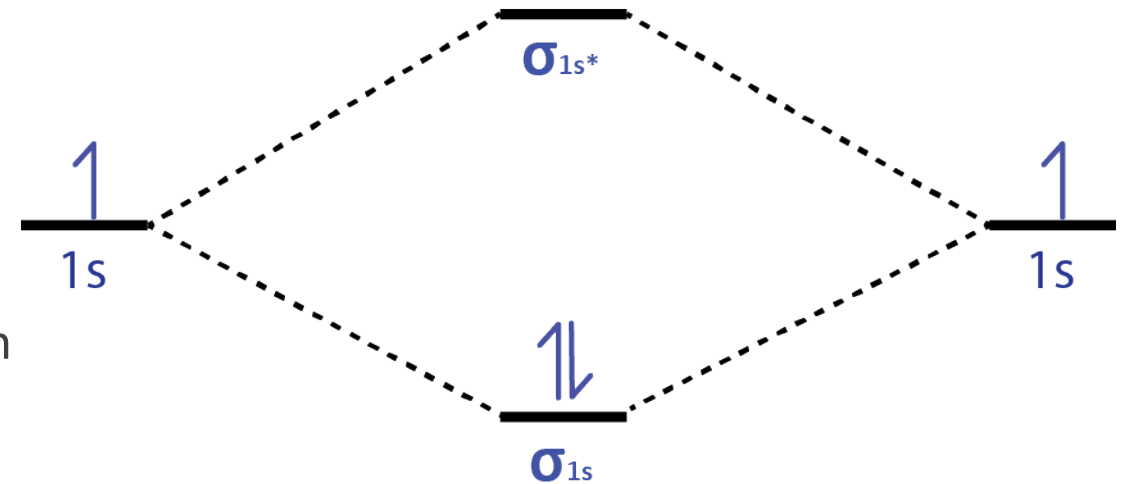
Pi-bonds are overlapping p-orbitals; these carbons are sp^2 hybridized, so the sigma bond is sp^2-sp^2

Molecular Orbital Theory

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

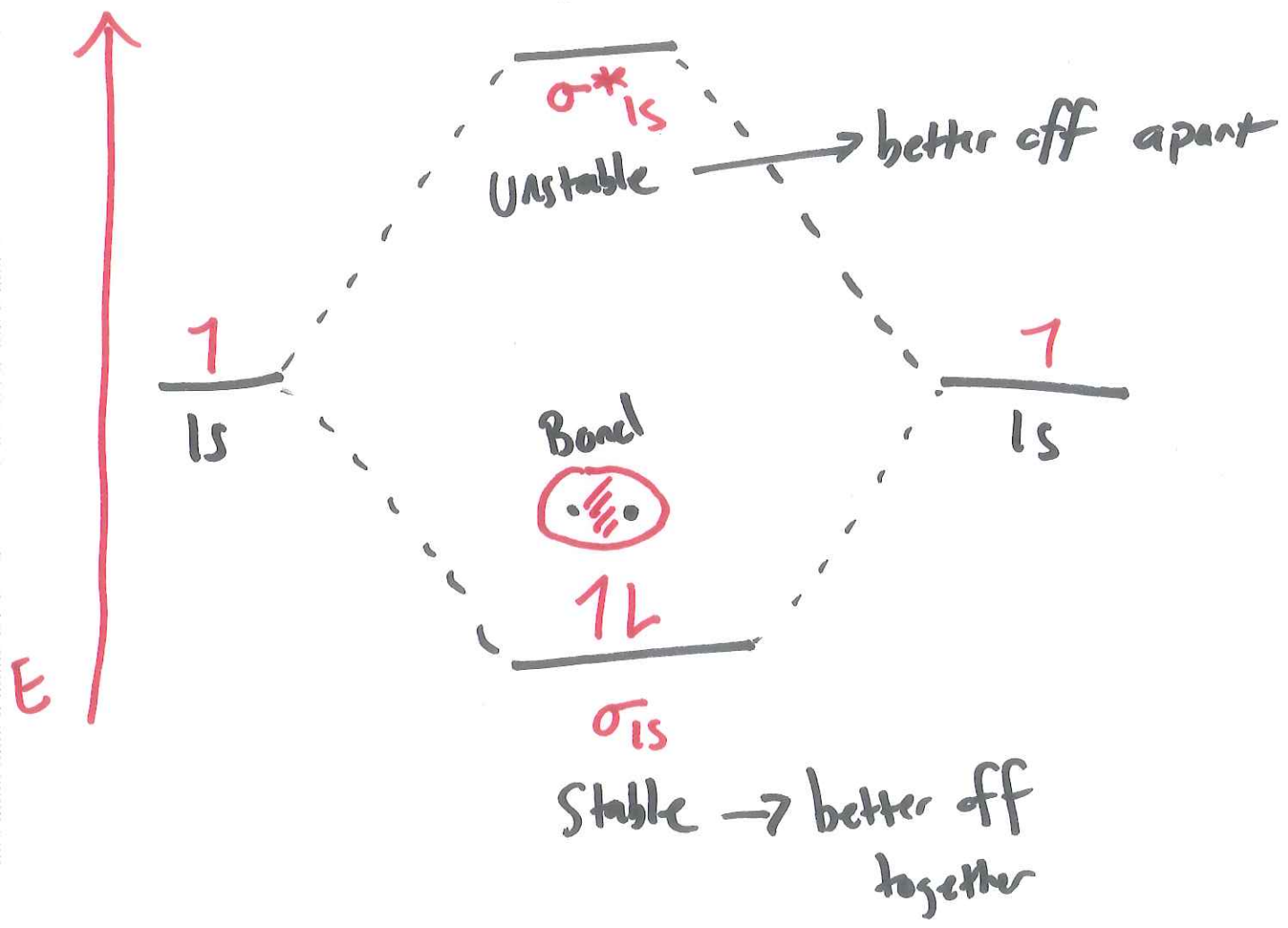
- Molecular Orbital Theory is a quantum mechanical approach to bonding
- This theory looks at bonds as regions with a high probability of electron density according to the Schrödinger Equation
- **Constructive interference** results in a high electron density (bond)
 - **Low Energy**
 - **More stable than atomic orbital**
- **Destructive interference** results in repulsion (zero electron density; anti-bond)
 - **High Energy**
 - **Less stable than atomic orbital**

MO Diagram for H₂



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

- 1) Conservation of orbitals
- 2) Conservation of energy

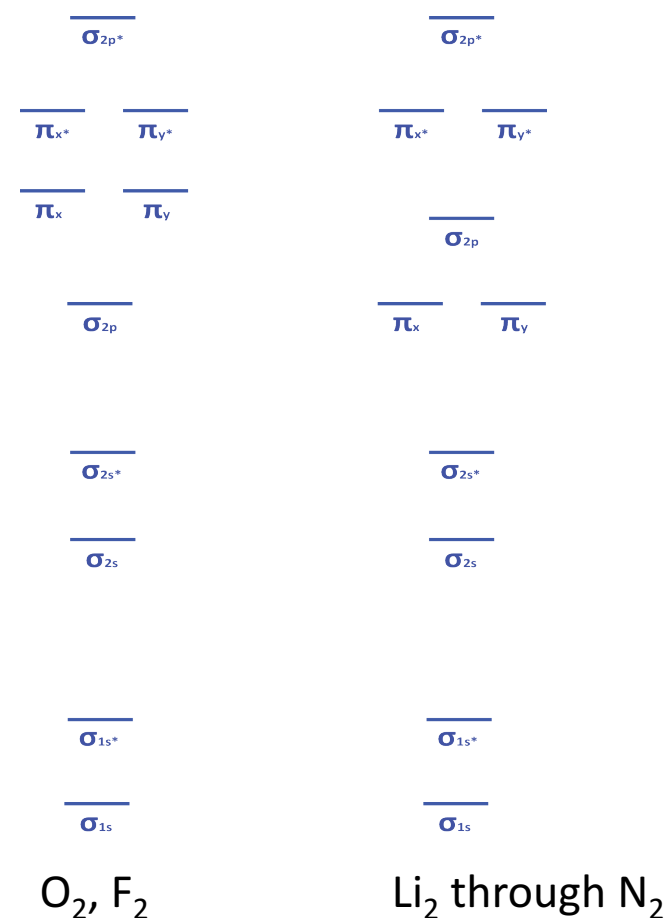


✓ f $BO > O$, molecule can exist

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**)
 - 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: paired electrons, repelled from magnetic field
 - Paramagnetic: unpaired electrons, attracted to magnetic field
 - And of course, HOMO-LUMO...

You must memorize the diagrams to the right, their labels, and the pure atomic orbitals that go into making them.



Molecular Orbital Theory: HOMO-LUMO

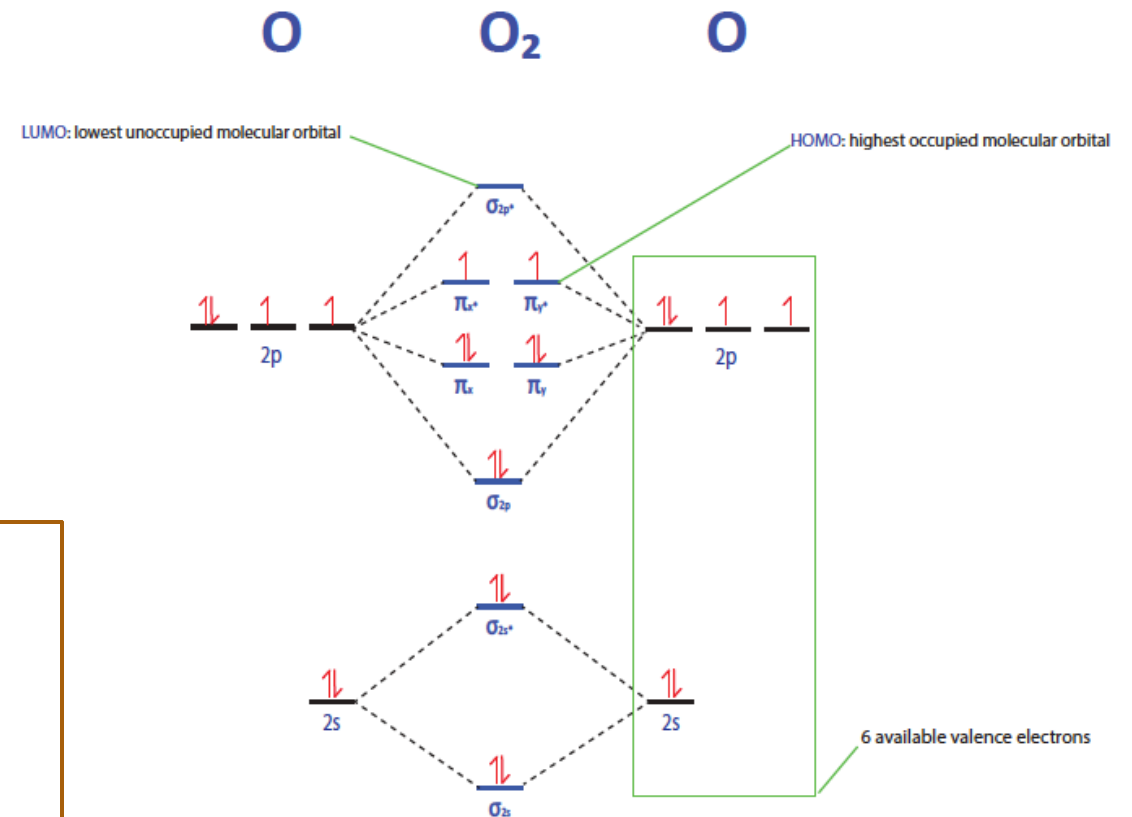
- One of the most important conclusions in molecular orbital theory is the energy difference between the **Highest Occupied Molecular Orbital (HOMO)** and the **Lowest Unoccupied Molecular Orbital (LUMO)**.
- This energy gap is important because it corresponds to energy of the photon emitted when an excited electron falls back down to ground state. **This can be applied to far more complicated molecules/materials**

- Because light is important here:

Remember:

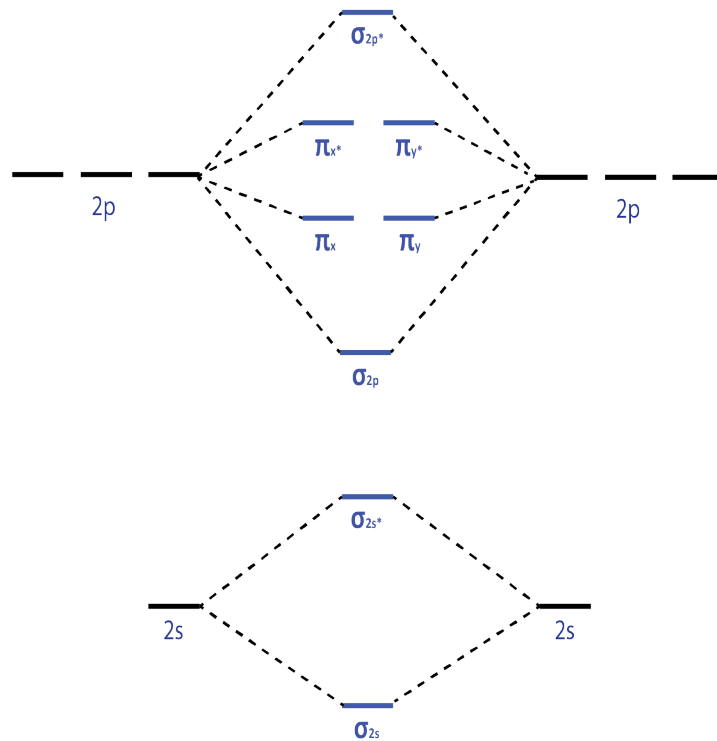
IR....**R**.**O**.**Y**.**G**.**B**.**I**.**V**. ...UV

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

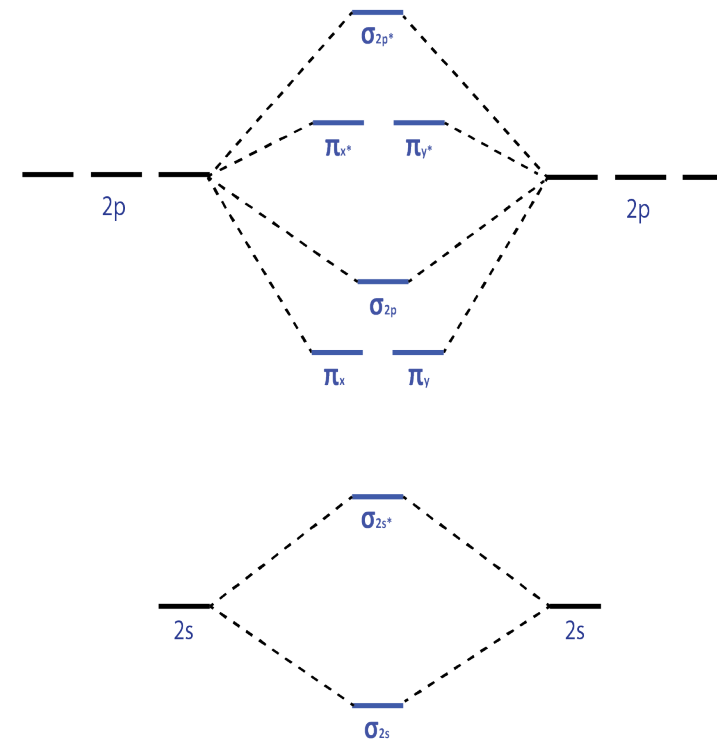


Molecular Orbital Theory

O_2 and F_2



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)

