

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.



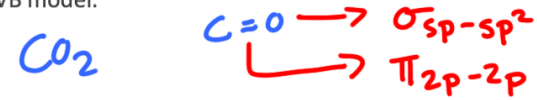
2. Assess if a molecule is polar based on polar bonds and its molecular geometry.



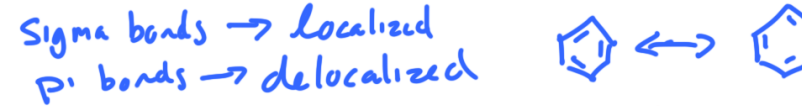
3. Identify the orbital hybridization for any atom in a given molecule using the VB model.



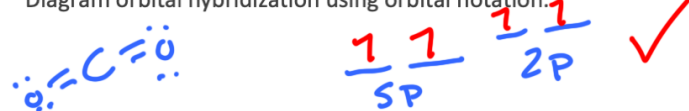
4. Describe the type of bond (e.g. sigma, pi) and the atomic orbitals that are associated with the bond using the VB model.



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



6. Diagram orbital hybridization using orbital notation.



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

\rightarrow whole molecule geometry
* Computer *

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

Constructive interference: Bonding, stable, Low Energy
 Destructive interference: Antibonding, unstable, High energy

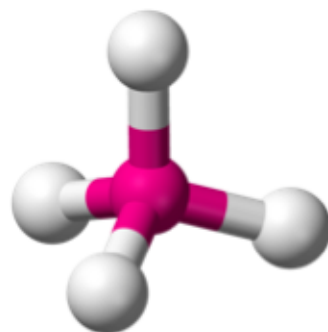
9. Construct and fully interpret a MO diagram, including identifying the bond order, the lowest energy electronic excitation energy (HOMO-LUMO gap), and the magnetism (paramagnetic or diamagnetic) for a compound.

For $\text{H}_2, \text{He}_2, \text{Li}_2 \rightarrow \text{F}_2$ 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)



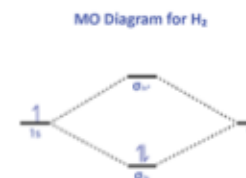
- **Valence Bond Theory**


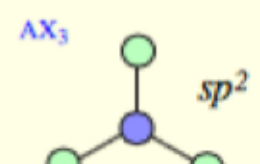



- **Hybrid Orbitals: sp , sp^2 , sp^3 , sp^3d , sp^3d^2**
- Sigma and pi bonds
- Identifies the overlapping orbitals to "name" the bonds
- Focuses on the electron "clouds"
- Depends on the number of electron-dense regions
- Easy navigation of central atoms



- **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)

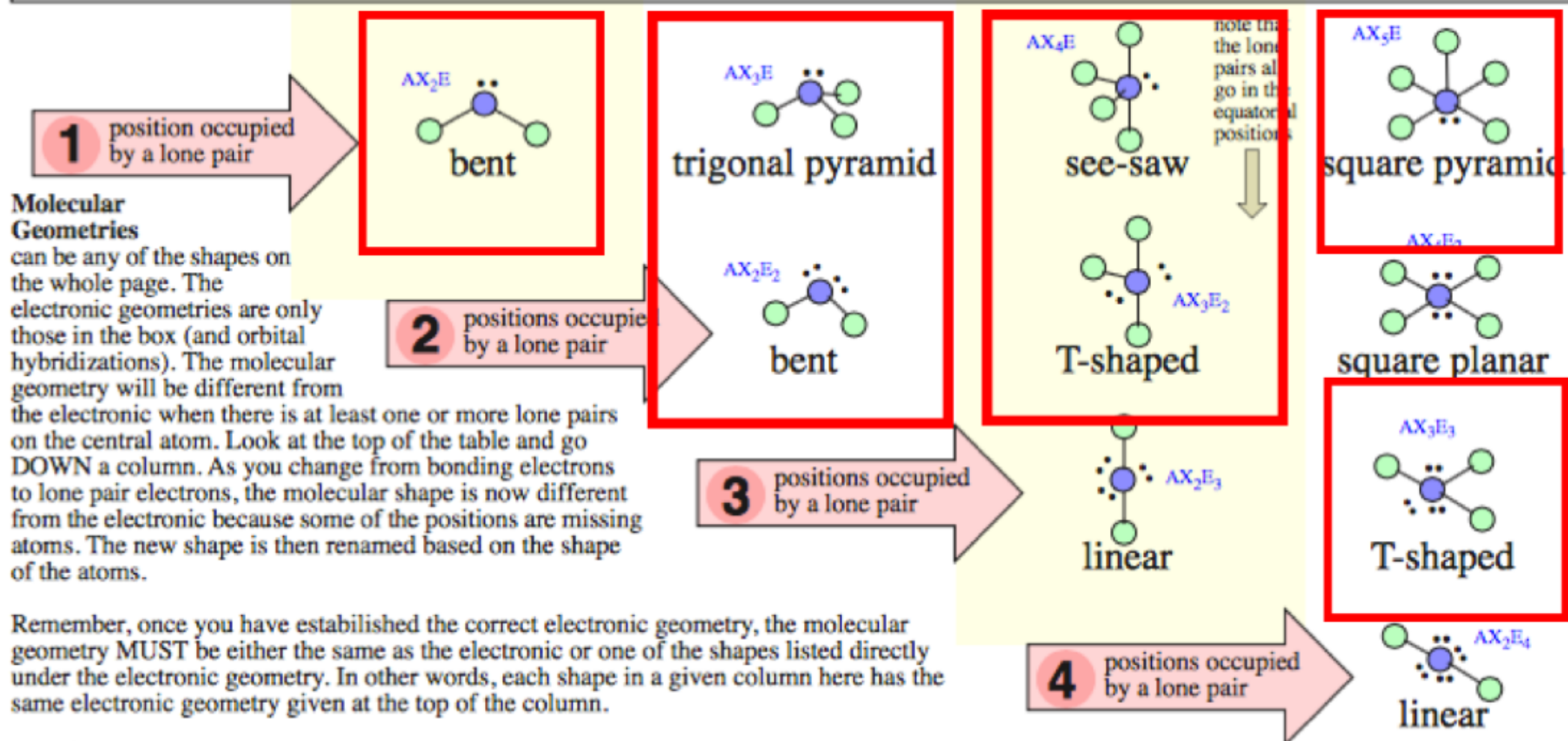


2 electron regions	3 electron regions	4 electron regions	5 electron regions	6 electron regions
AX_2  <i>sp</i>	AX_3  <i>sp²</i>	AX_4  <i>sp³</i>	AX_5  <i>sp³d</i>	AX_6  <i>sp³d²</i>
linear	trigonal planar	tetrahedral	trigonal bipyramid	octahedral

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



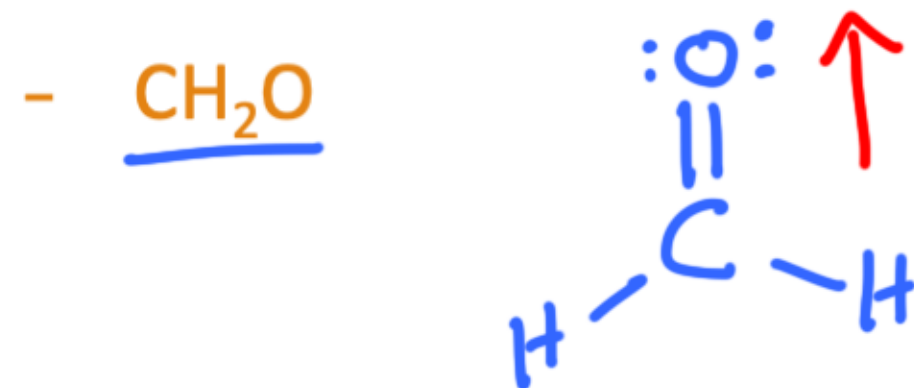
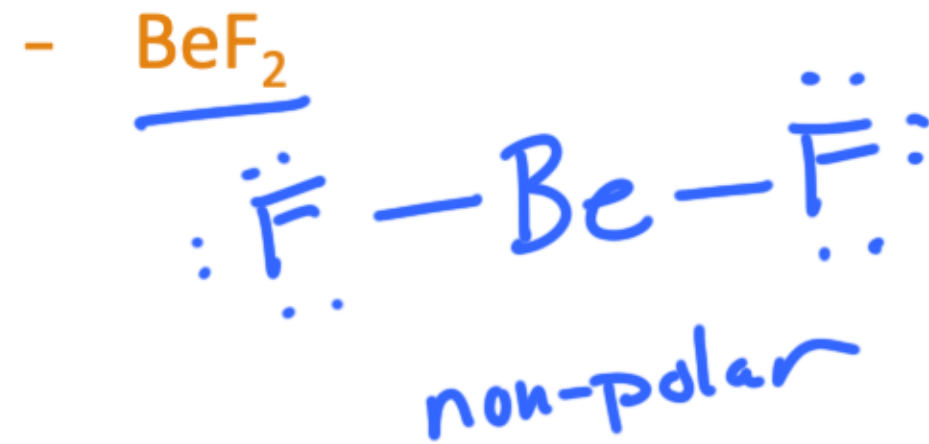
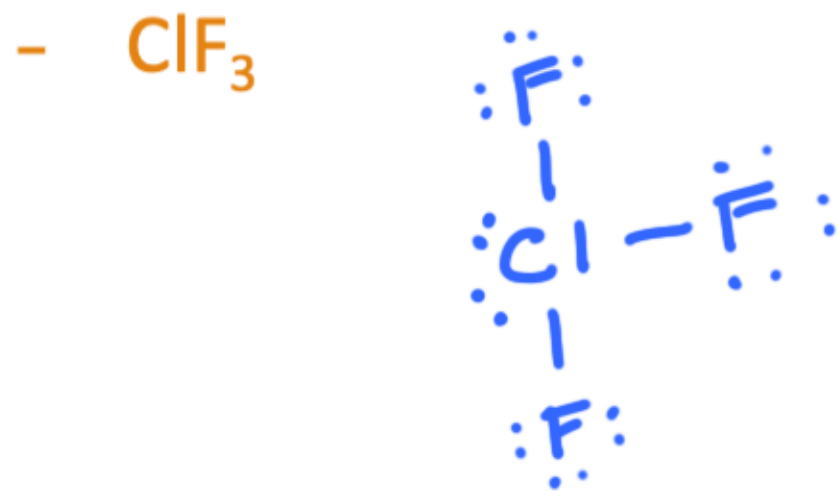
Remember, once you have established the correct electronic geometry, the molecular geometry MUST be either the same as the electronic or one of the shapes listed directly under the electronic geometry. In other words, each shape in a given column here has the same electronic geometry given at the top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

Formula
↓
e⁻ geometry
↓
molecular

Shape and Molecular Polarity



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

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

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

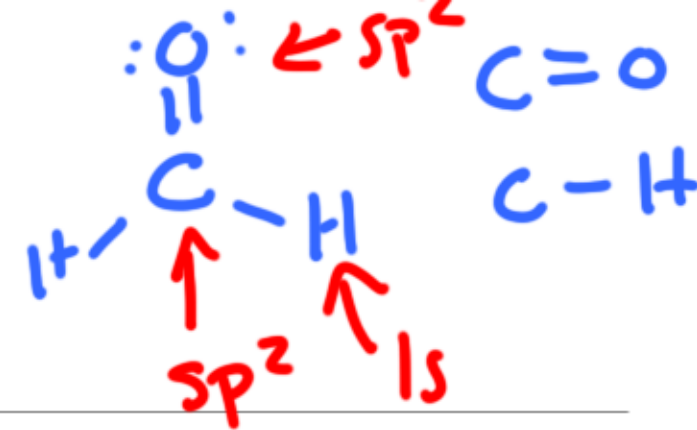
Single Bonds: 1 sigma bond

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)

✓ σ hybrid-hybrid



✓ σ hybrid-1s

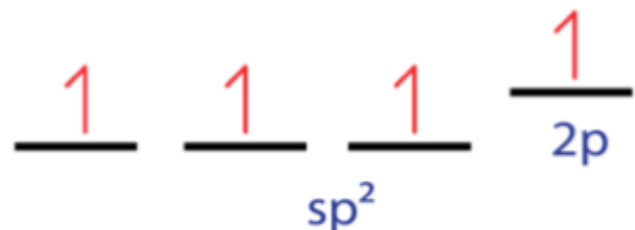


✓ π valence p-valence p



VB Challenge Questions (Last Week)

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

NO_3^-

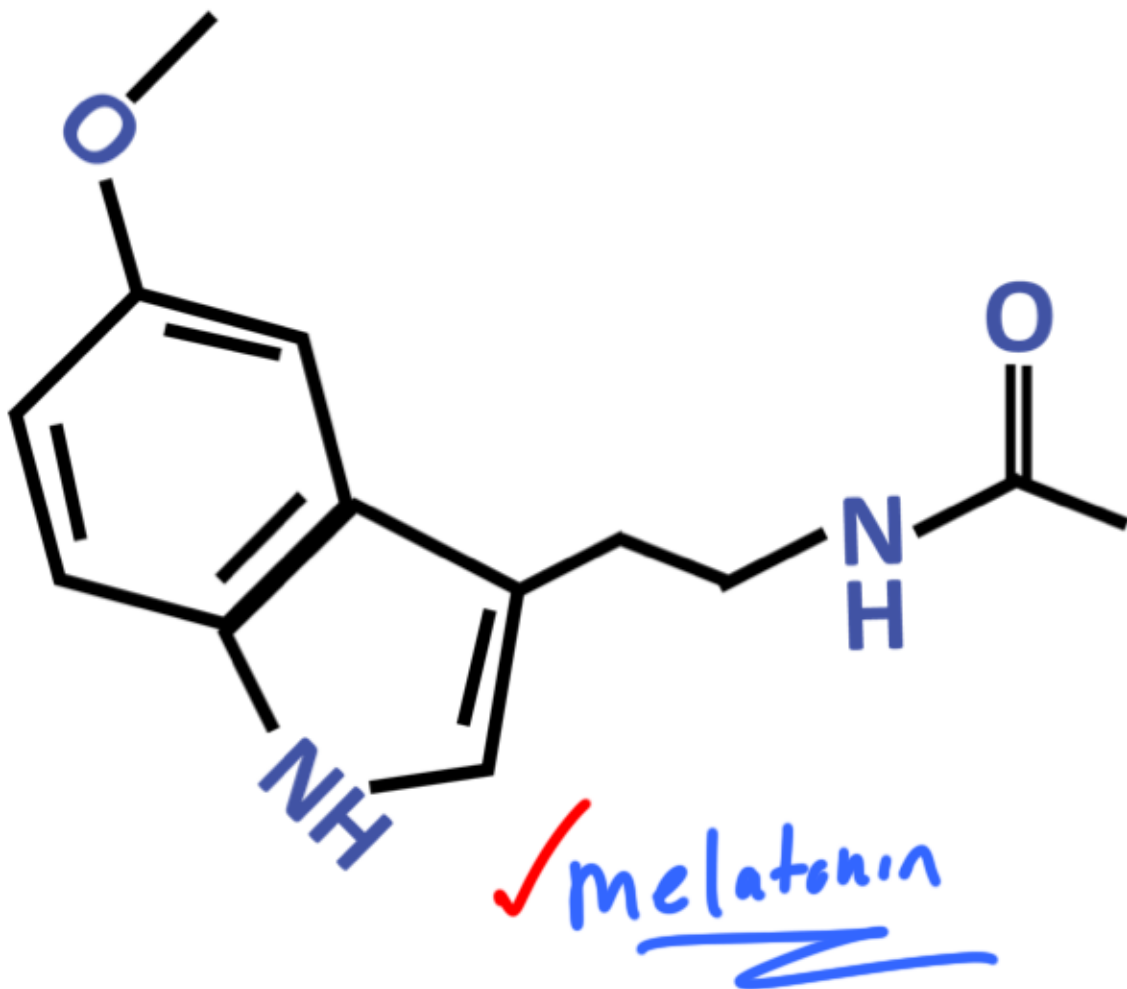
CO_3^{2-}

CO_2

Consider the compound ethene, C_2H_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. π ; sp^2
2. π ; $1p$
3. π ; $2p$
4. σ ; sp^2
5. σ ; 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**

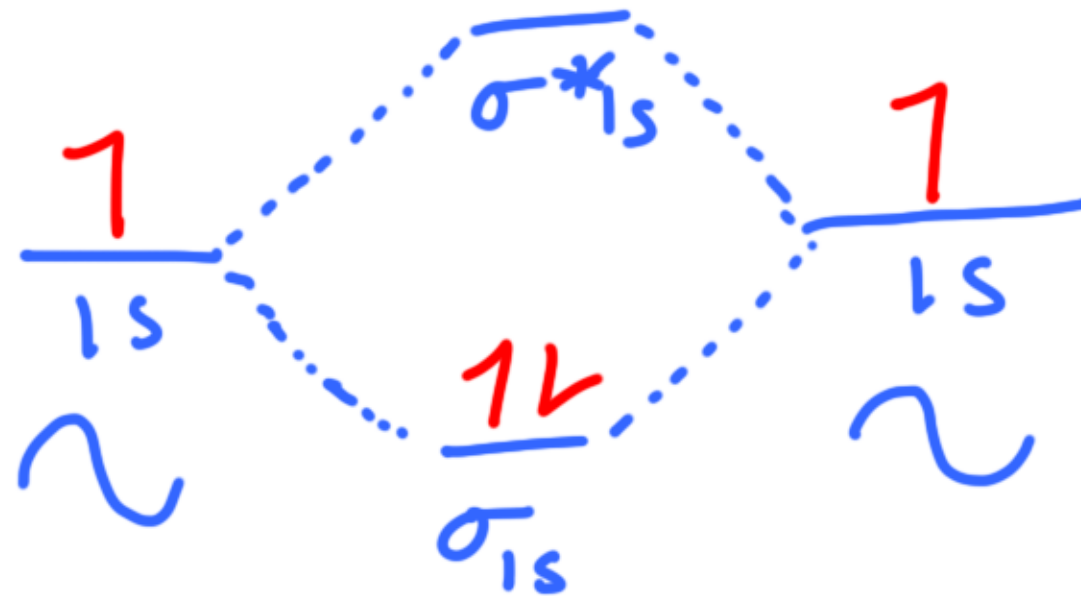
• Molecular Orbital Theory

- 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**

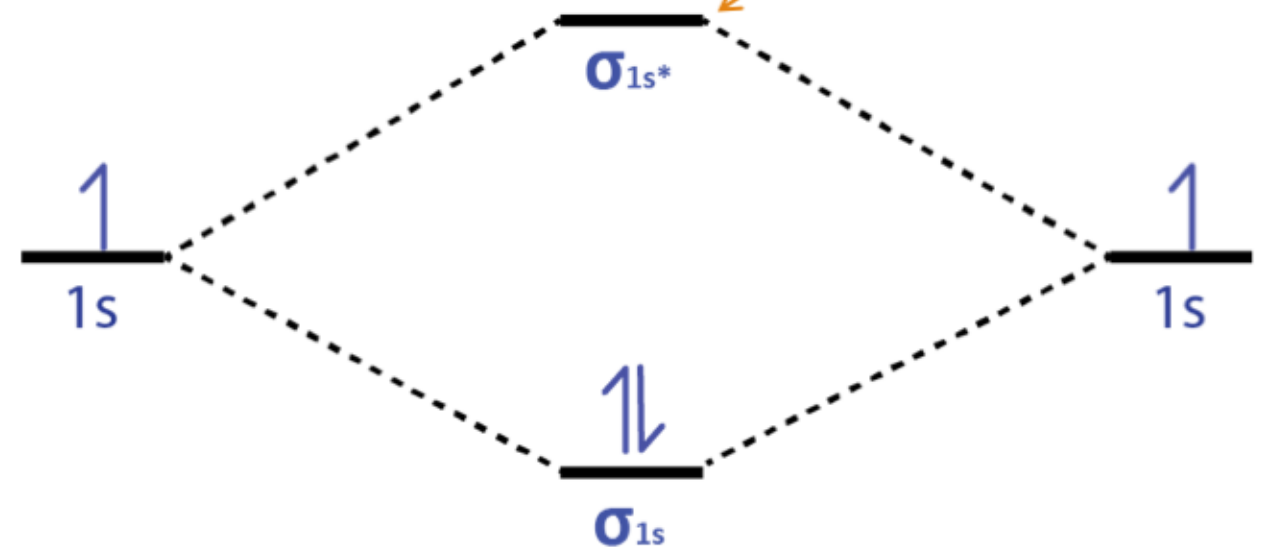


Molecular Orbital Theory

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

- 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**

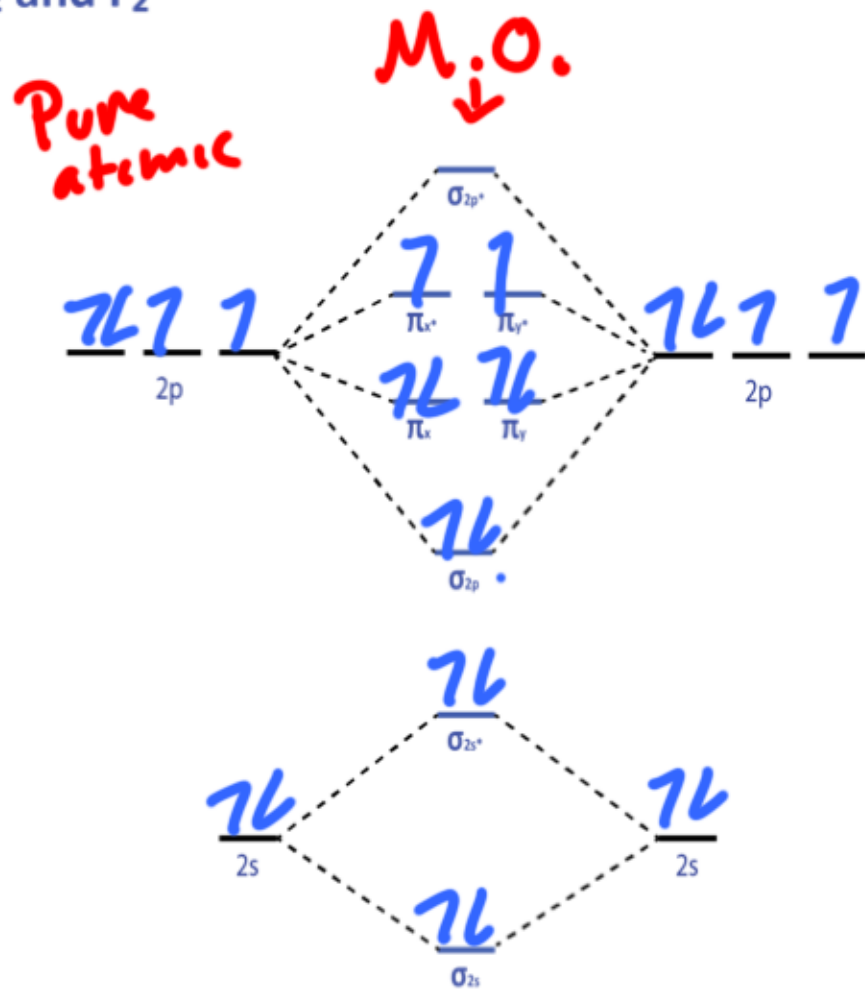
MO Diagram for H₂



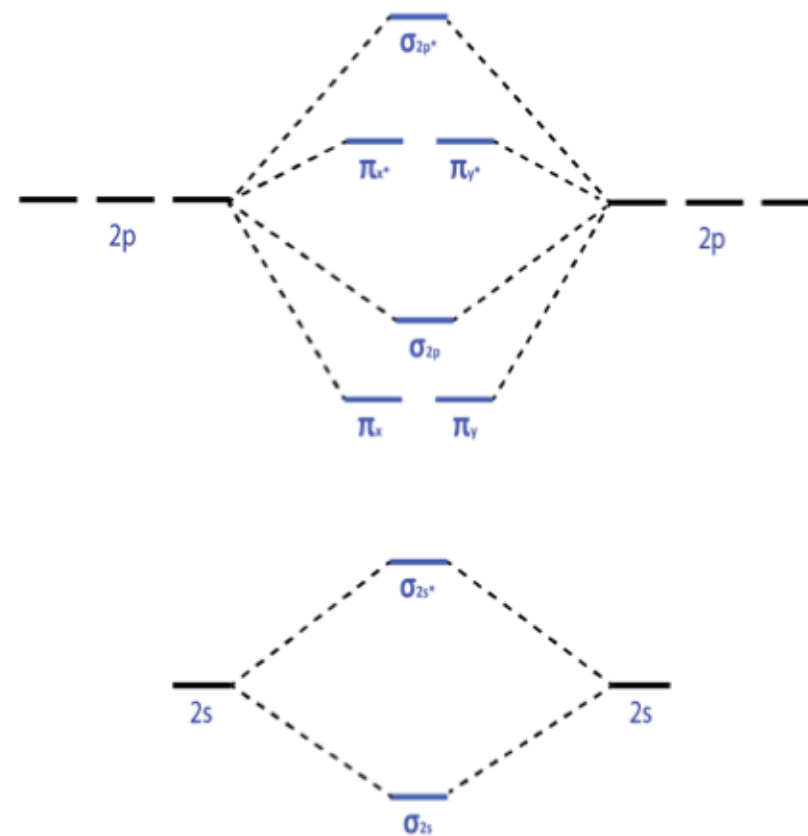
Note: our focus in this class will be on Hydrogen, Helium, row 2 diatomics, and their ions

ONLY the Valence Molecular Orbital Theory

O₂ and F₂



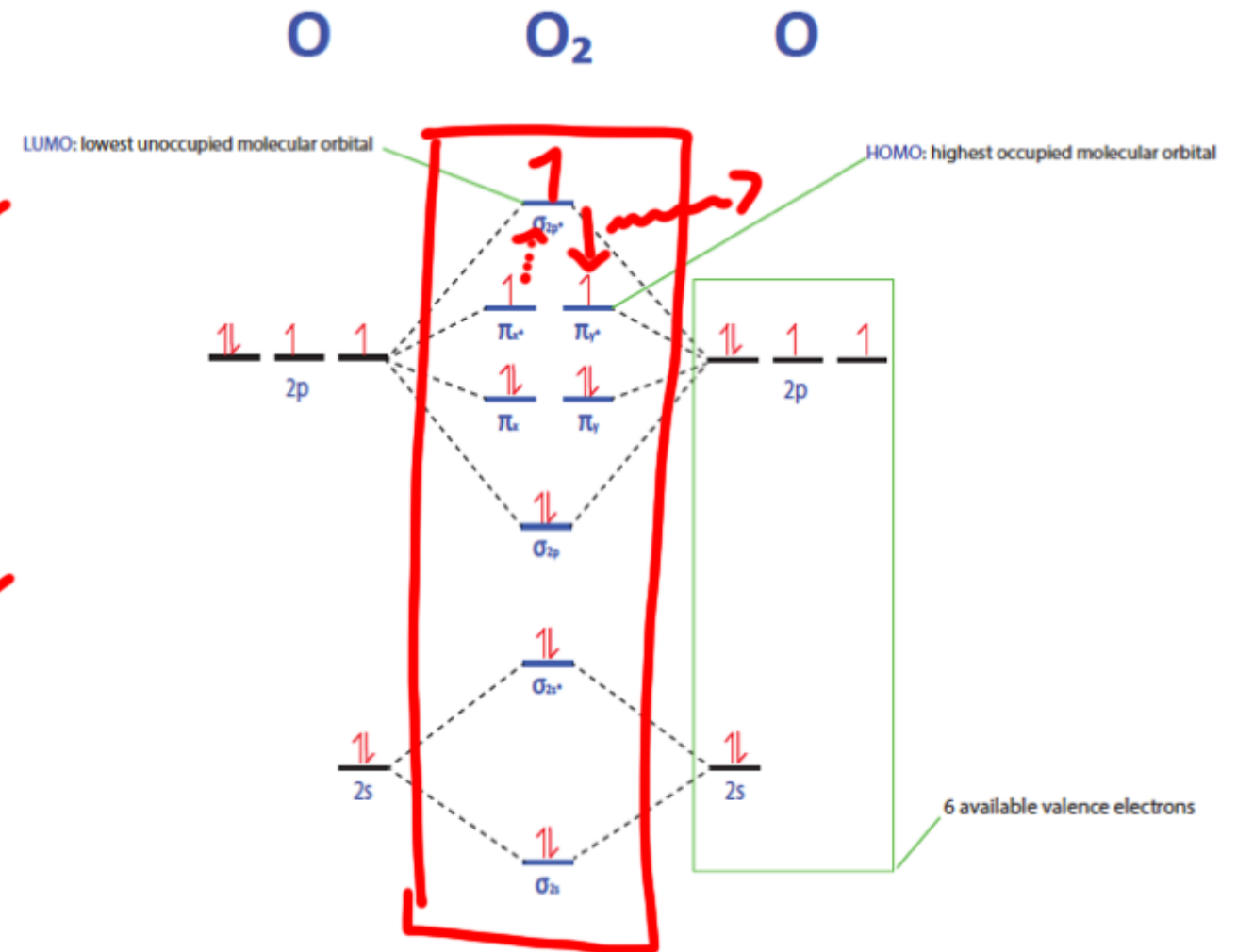
B₂, N₂, and C₂



$$\frac{\text{Bonding } e^- - \text{Antibonding } e^-}{2} = \text{B.O.}$$

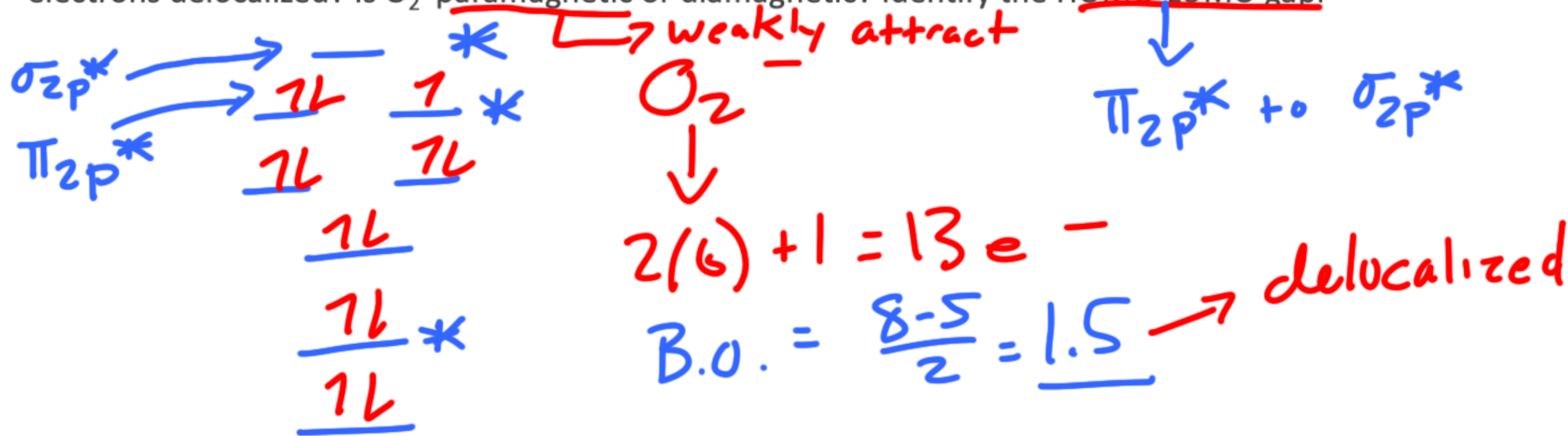
Molecular Orbital Theory: Conclusions

- 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

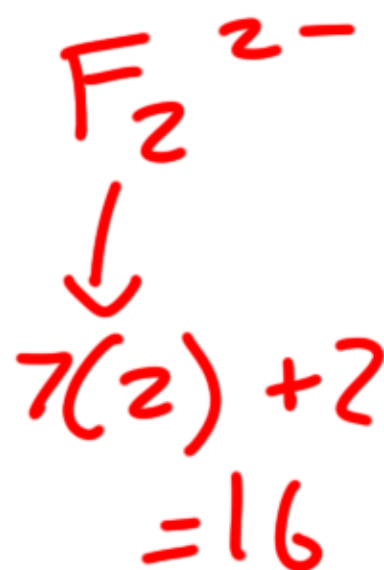
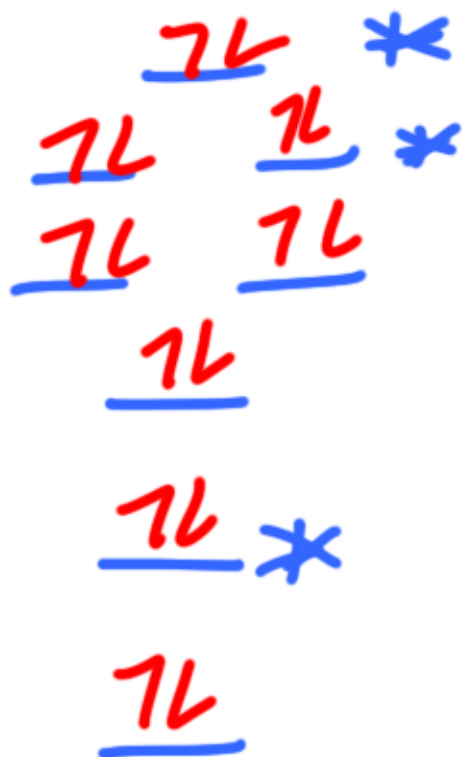
What is the molecular orbital electron configuration for O_2^- ? What is the bond order? Are the electrons delocalized? Is O_2^- paramagnetic or diamagnetic? Identify the HOMO-LUMO gap.



MO Theory Question

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

No



$$\frac{8-8}{2} = \emptyset$$

Molecular Orbital Theory: HOMO-LUMO

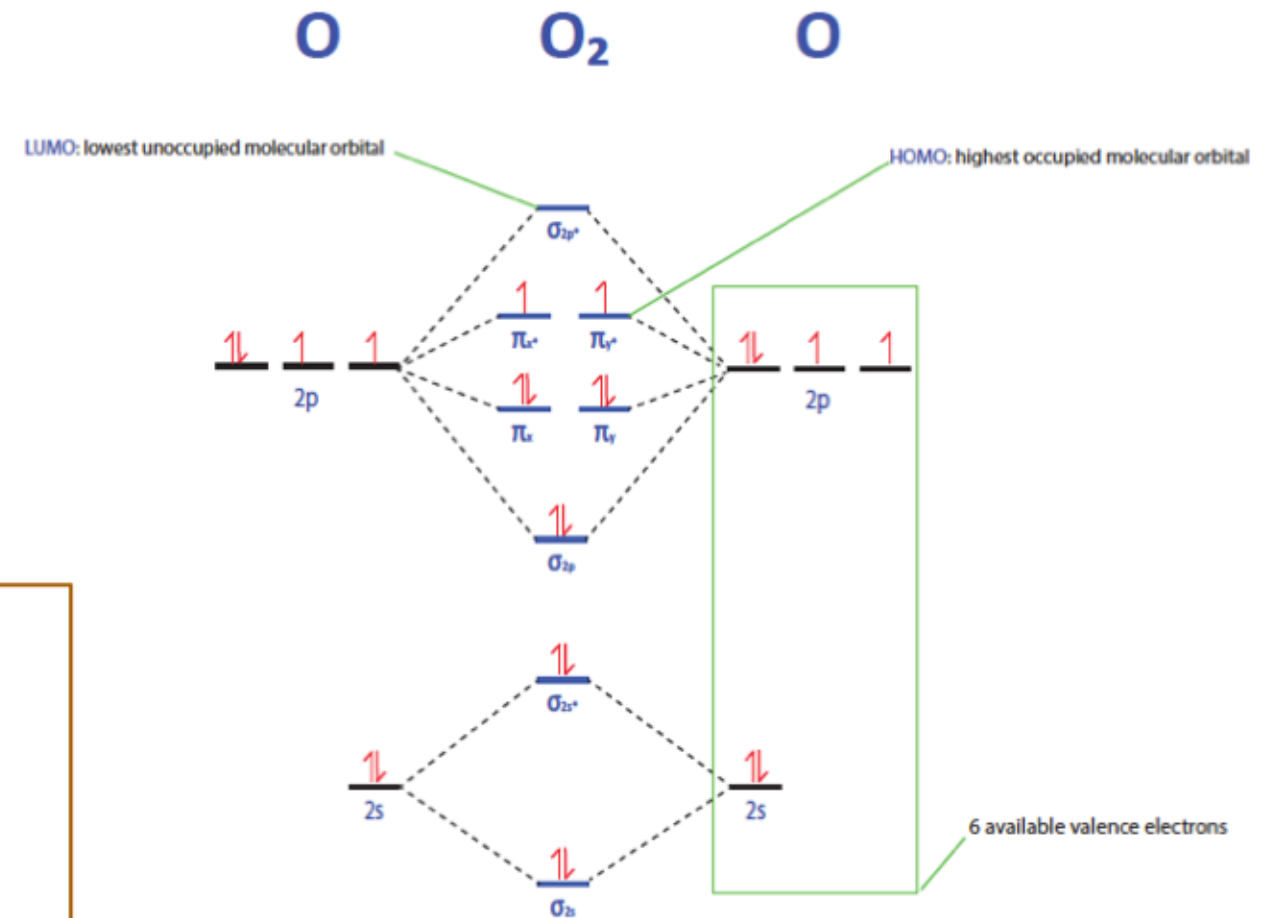
- One of the most important conclusions in molecular orbital theory is the energy difference between the **Highest Occupied Molecular Orbital (HOMO)** and the **Lowest Unoccupied Molecular Orbital (LUMO)**.
- This energy gap is important because it corresponds to energy of the photon emitted when an 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

$$E_{\text{light in}} = E_{\text{gap}}$$

UV lower energy



HOMO-LUMO gap
for a complex
molecule

Smaller

- ✓ 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: H₂

Dipole-Dipole

ex: HCl

Hydrogen Bond

ex: HF

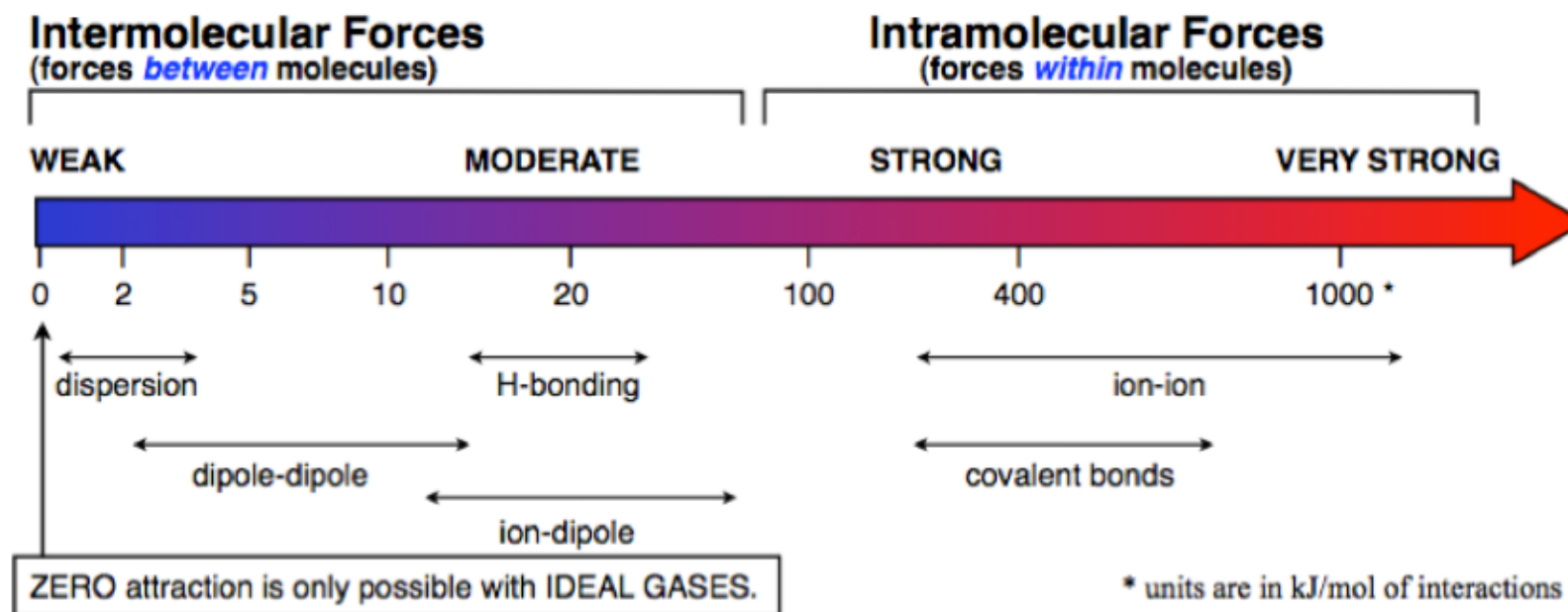
In everything!

Polar molecule

Hydrogen bonded to 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**



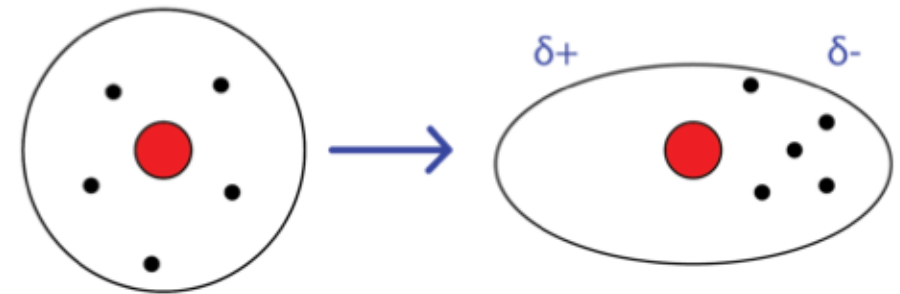
Dispersion Forces

All molecules have dispersion forces

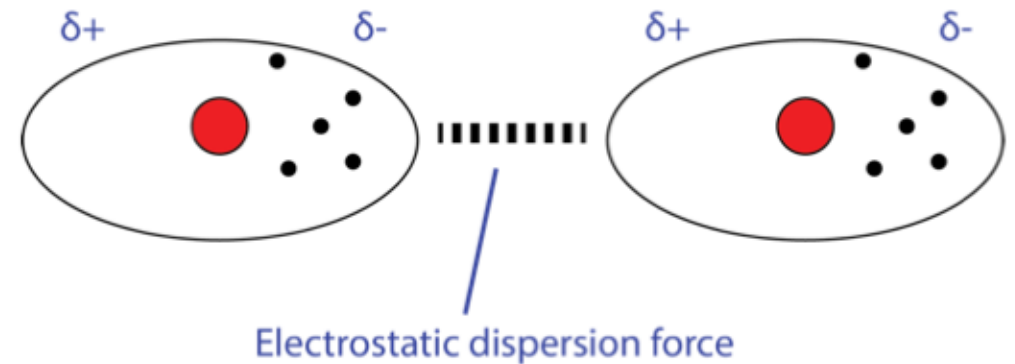
Dispersion forces depend on a molecule's ability to spontaneously induce a dipole. Its ability to do this is called its **polarizability** and is directly influenced by the **molecular weight** of the molecule.

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

1. Formation of a spontaneous dipole



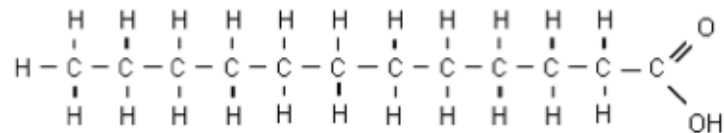
2. Induction of a second molecule



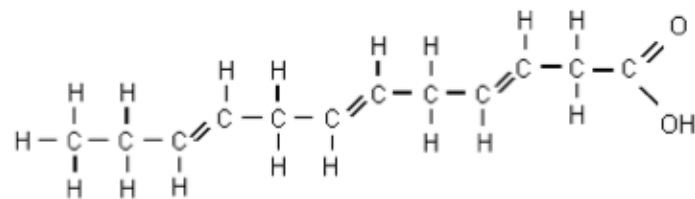
Dispersion Forces - Polarizability

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:



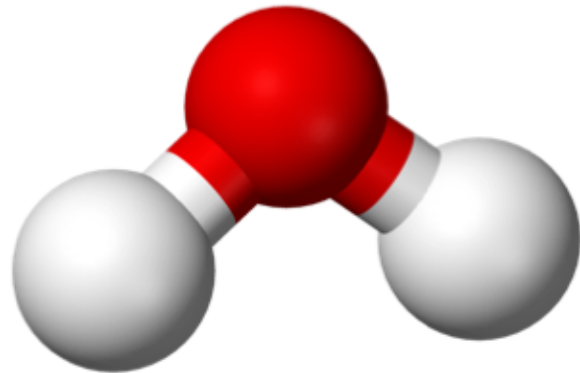
Solid:



Highest Polarizability,
Highest IMF's

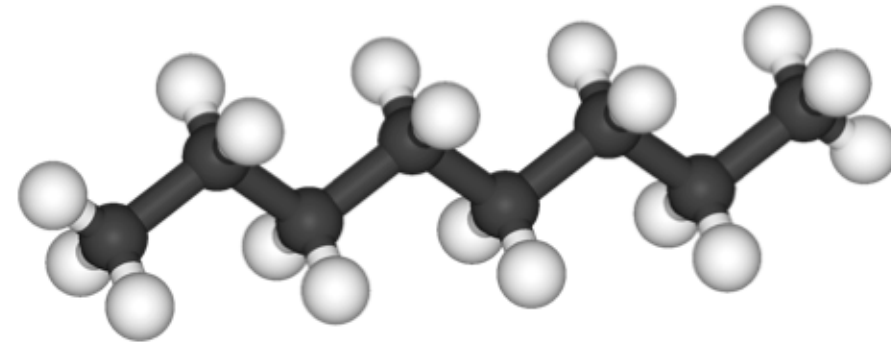
Size - Comparing IMF's

- 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

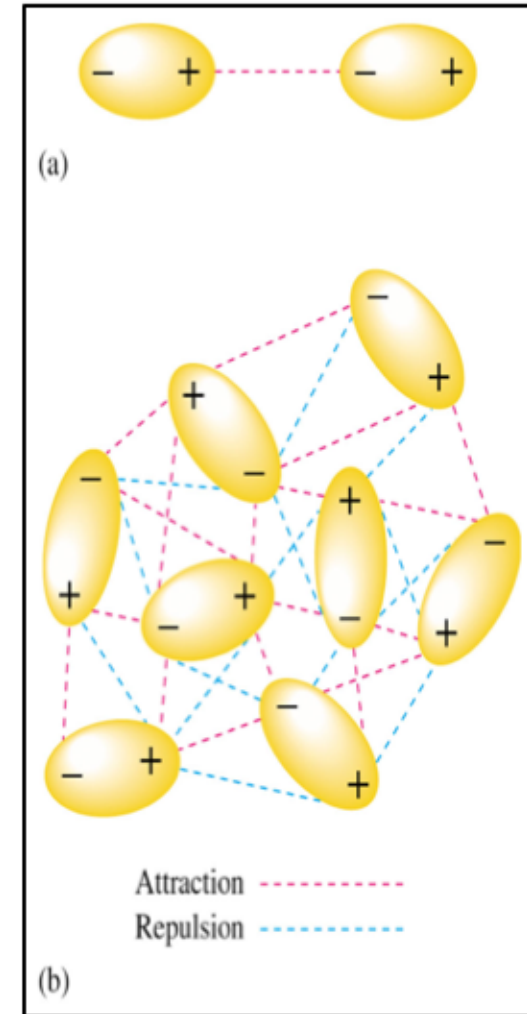
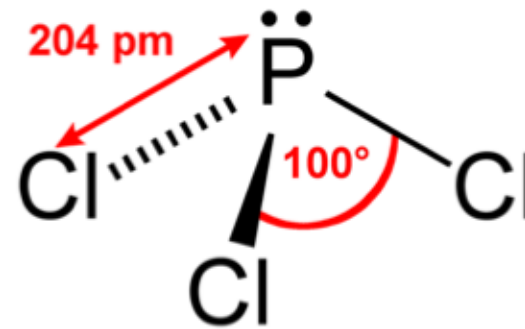
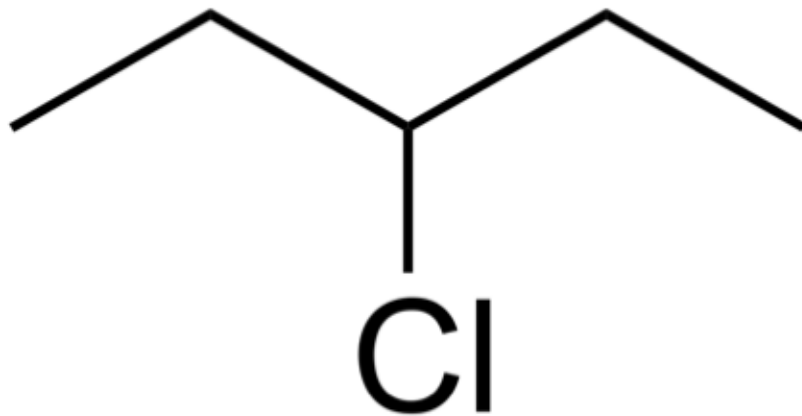


BP: 125°C

Dominant IMF: Dispersion

Dipole-Dipole Forces

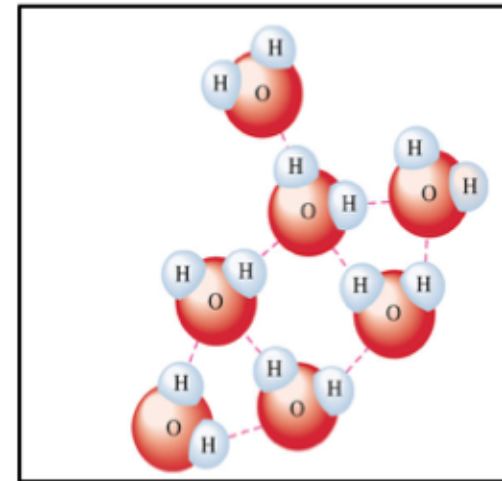
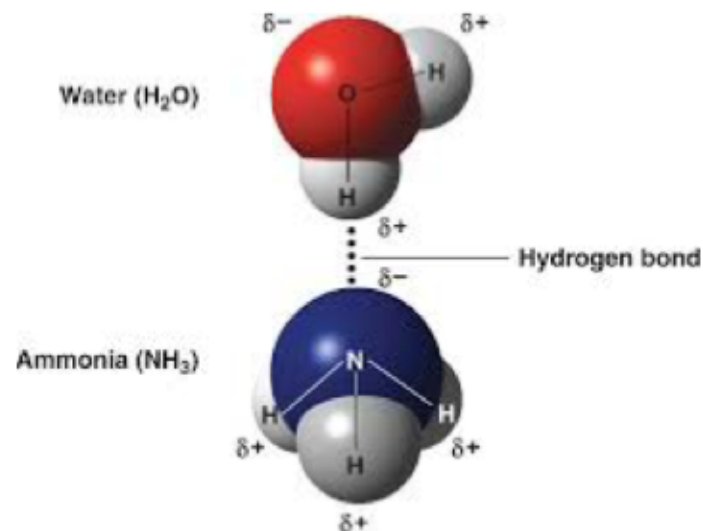
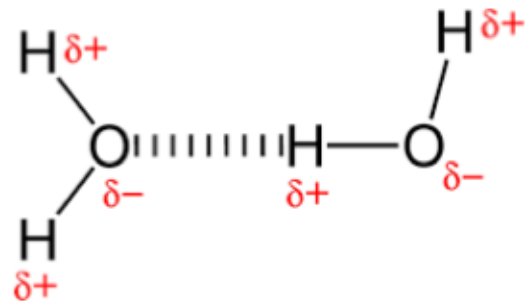
- Dipole-dipole forces require a permanently fixed dipole on a molecule.
- **Because the dipole moment is permanent, dipole-dipole forces are stronger than dispersion forces.**
- **Dipole-Dipole forces can be easily identified if you can spot out a polar molecule**



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)**

