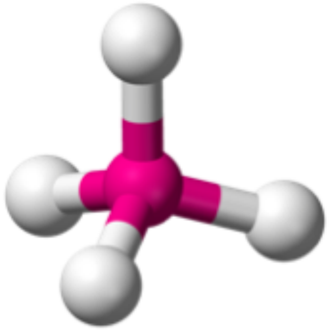
Unit 3 Review 1

BONDING THEORIES: VSEPR AND VB

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)



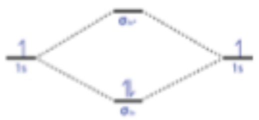
- ## Valence Bond Theory
  - **Hybrid Orbitals: sp, sp^2, sp^3, sp^3d, sp^3d^2**
  - Sigma and pi bonds
  - Identifies the overlapping orbitals to “name” the bonds
  - Focuses on the electron “clouds”
  - Depends on the number of electron-dense regions

sp^3

These theories might seem like a lot of information, but if you tie them together and simplify their conclusions, they actually make a lot of sense and don’t require too much memorization.

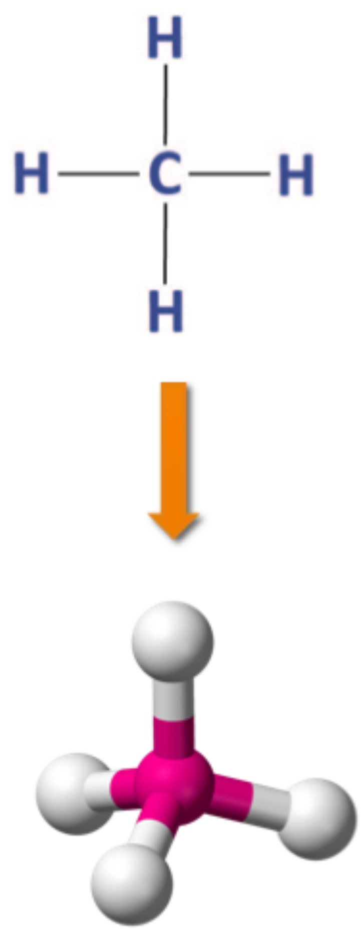
- ## Molecular Orbital Theory
  - **Diagrams**
  - Answers three fundamental questions regarding your molecule: bond order, magnetism, HOMO-LUMO gap
  - Sigma and pi bonds and anti-bonds
  - Focuses on the electrons as “waves”
  - Depends on the number of electrons

MO Diagram for H_2



VSEPR Theory Definitions

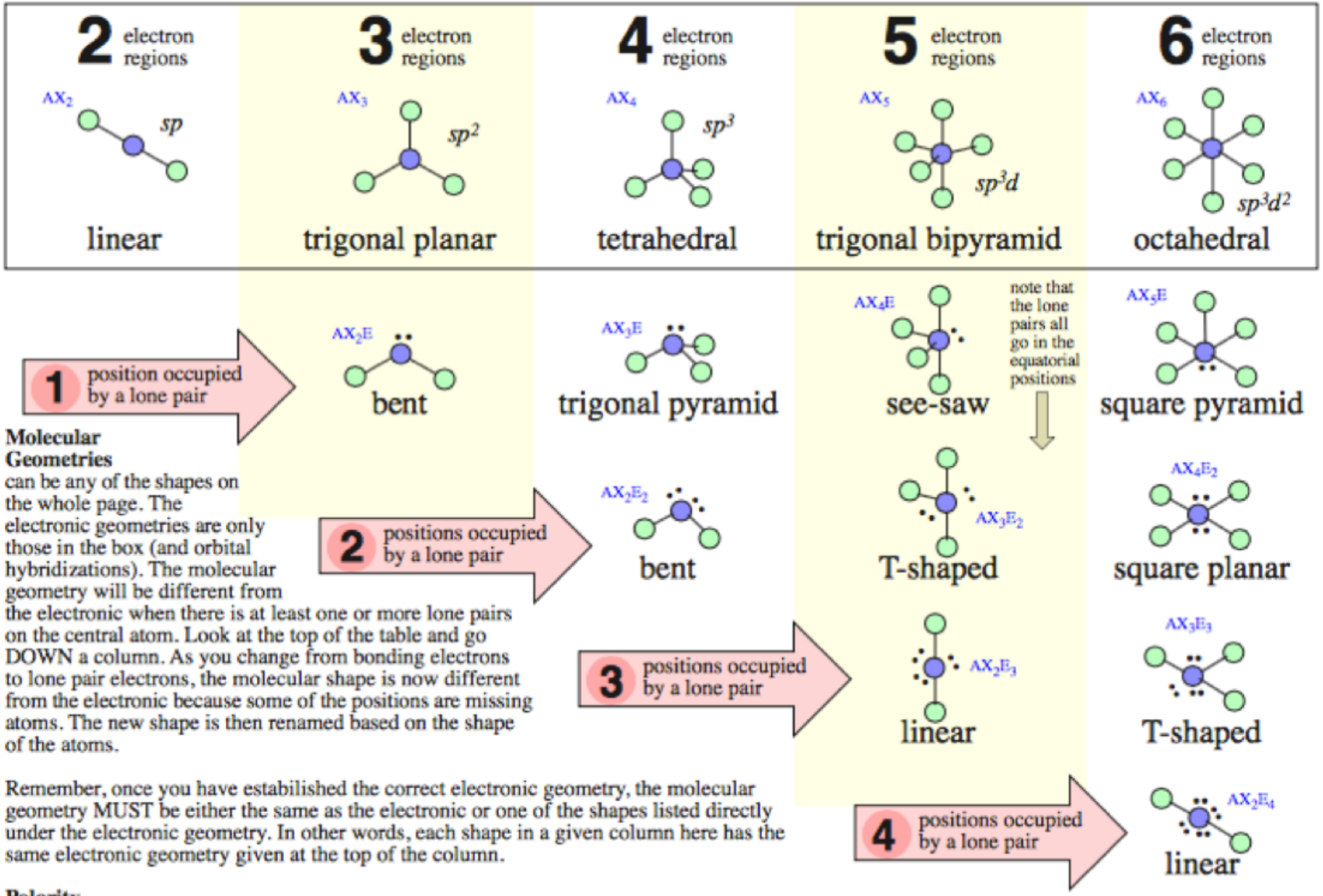
- VSEPR theory is an empirical method of understanding molecular shapes in three dimensional space.
- The theory gets its name from the fact that electron regions have **the lowest energy** when repulsions are minimized.
  - In other words, **electron-dense regions want to be as far away from each other as possible** in 3D space.
- VSEPR gives us two different 3D geometries: **electronic geometry and molecular geometry**.
  - **Electronic geometry**: the shape of all electron-rich regions around a central atom (lone pair regions and bonding regions)
  - **Molecular geometry**: the shape of only the bonding regions around a central atom
- Knowing the geometry around a central atom can clue you in on the approximate bond angles that exist around the central atom and whether the molecule is polar or nonpolar.



2D to 3D image of methane

e^- geometries

Starting point



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Remember, once you have estabilished 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.

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Exam Question

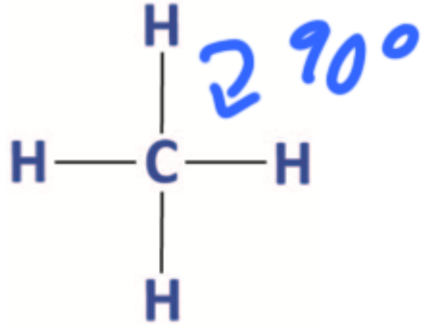
What are the approximate bond angles around the central atom of methane (CH_4) in 3D space?

a. 90 degrees

[✓ b. 109.5 degrees]

c. 120 degrees

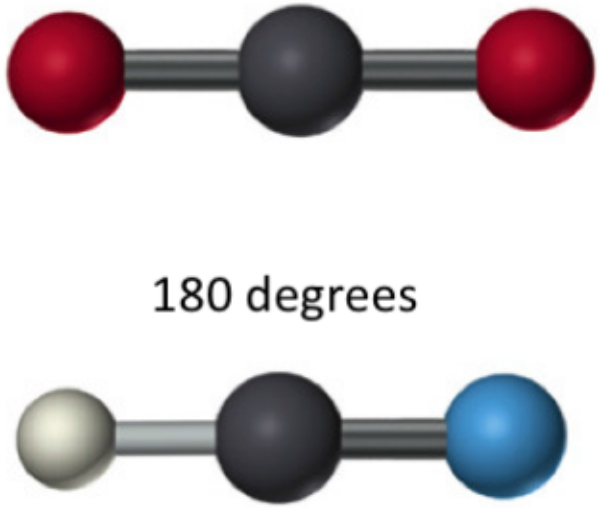
d. 180 degrees



Remember: VSEPR gives the lowest energy positions of peripheral atoms in three dimensional space.

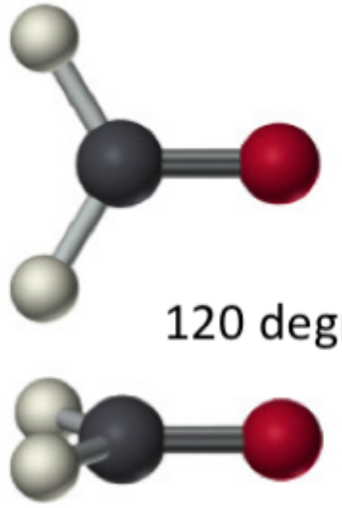
VSEPR Theory: Simple Geometries

- VSEPR Theory electronic geometries are named after the shape you observe if you enclose your electron-dense regions in a 3D structure.



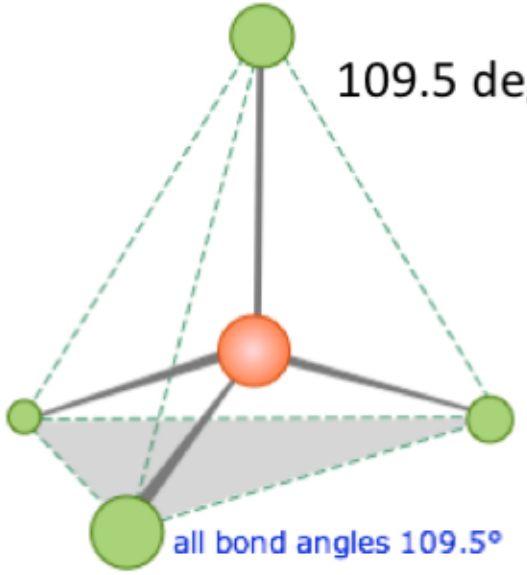
180 degrees

Linear



120 degrees

Trigonal Planar



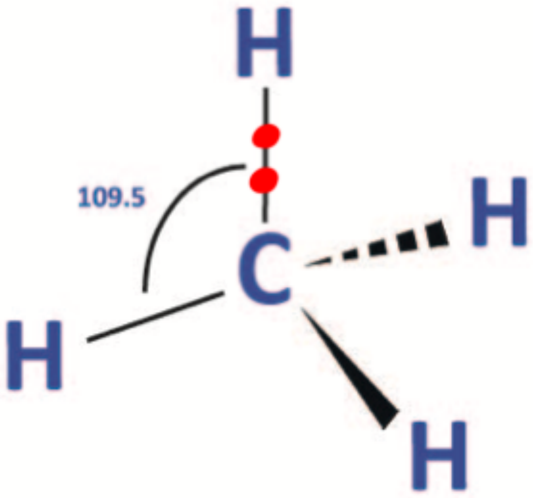
109.5 degrees

Tetrahedral

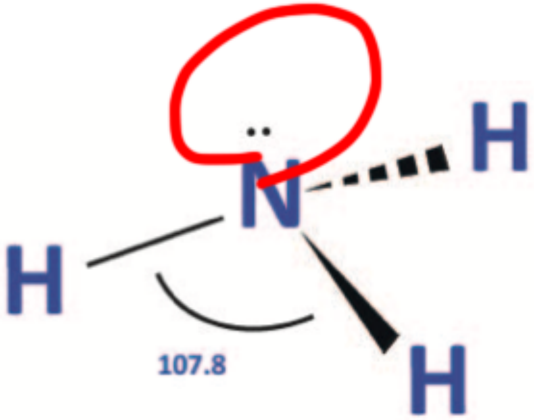
Note: these examples have the same electronic and molecular geometries because there are no lone pairs (the number of electron-dense regions is equal to the number of bonding regions).

VSEPR Geometries: 4 e^- Regions

- What happens when we have fewer bonding regions than total electron-dense regions?
- In other words, what happens when we replace a bond with a lone-pair region?
  - Your molecular geometry is determined by looking first at the number of electron-dense regions and then at the number of bonding regions.



Tetrahedral



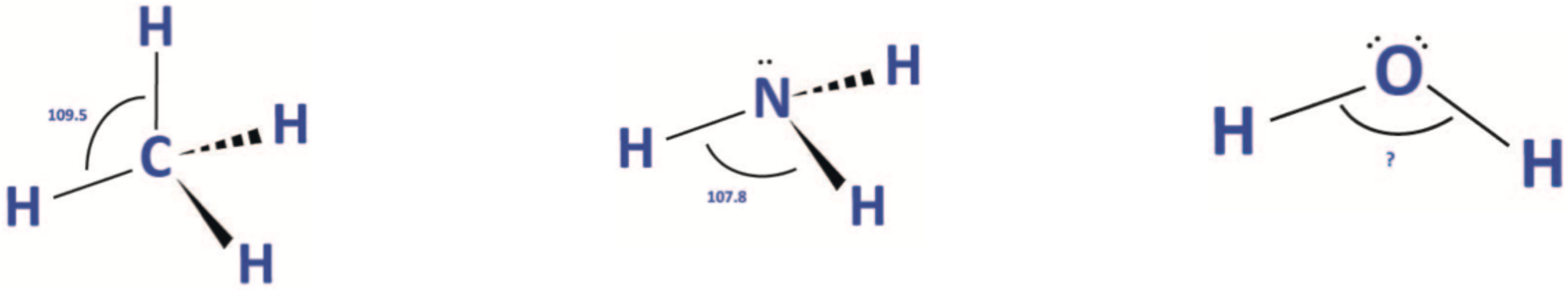
Trigonal Pyramid

Bent

All of the above have tetrahedral electronic geometry

The Effect of Lone Pairs

- 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



VSEPR Geometries: 5 e- Regions

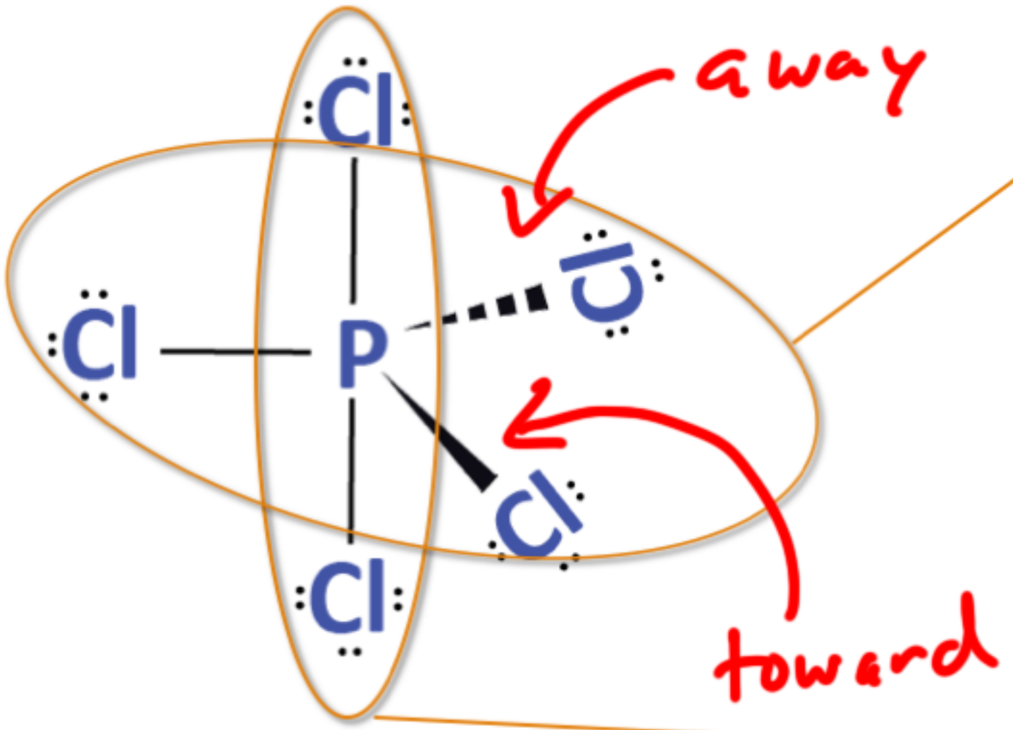
PCl_5

- We now know that we can have more than 4 electron regions around a central atom. Five electron regions gives a trigonal bipyramidal electronic geometry

Electronic: Trigonal Bipyramid

Molecular: Trigonal Bipyramid

Pure bond angles: 180 on axial plane, 120 on equatorial plane, 90 degrees from axial to equatorial atoms



The Equatorial Position bonds look like a trigonal planar structure

The Axial position bonds are linear

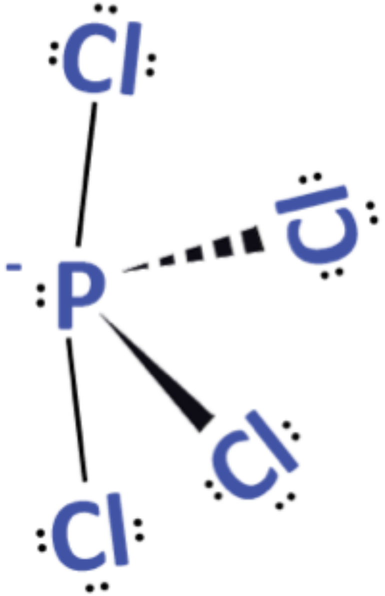
VSEPR Geometries: 5 e- Regions

- The equatorial and axial positions have differing stability.
- If you want to replace a bond with a lone pair in the trigonal bipyramidal electronic geometry, you must remove an equatorial bond.
- **It is more stable to add lone pairs to the equatorial position**
- Notice the effect of the lone pair on ”tweaking” the pure bond angles

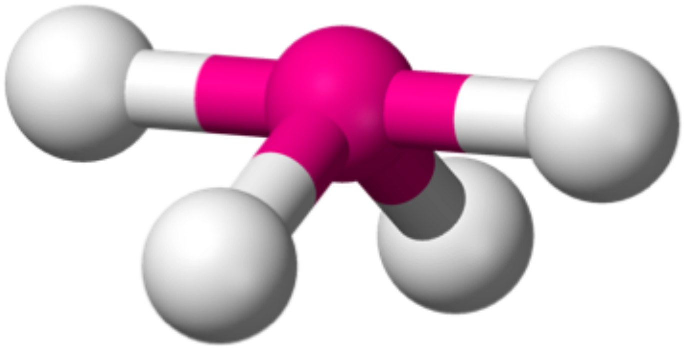
PCl_4^-

Electronic: Trigonal Bipyramid

Molecular: Seesaw



Equatorial Position



Axial Position

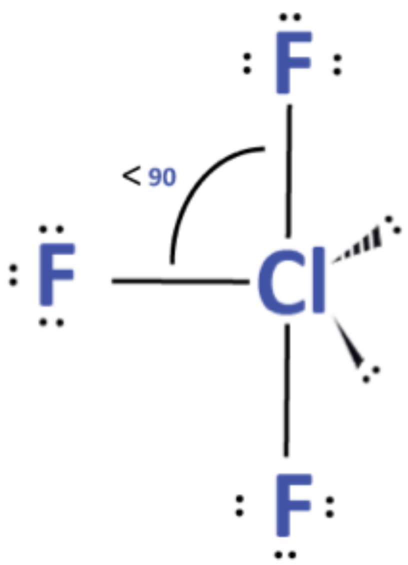
ClF_3

VSEPR Geometries: 5 e- Regions

Electronic: Trigonal Bipyramid

Molecular: T-shaped

- If we continue to replace bonds with lone pairs, we should continue to remove the equatorial positioned bonds



Equatorial Position

Axial Position

T-shape with 2 L.P. in equatorial position

VSEPR Geometries: 5 e- Regions

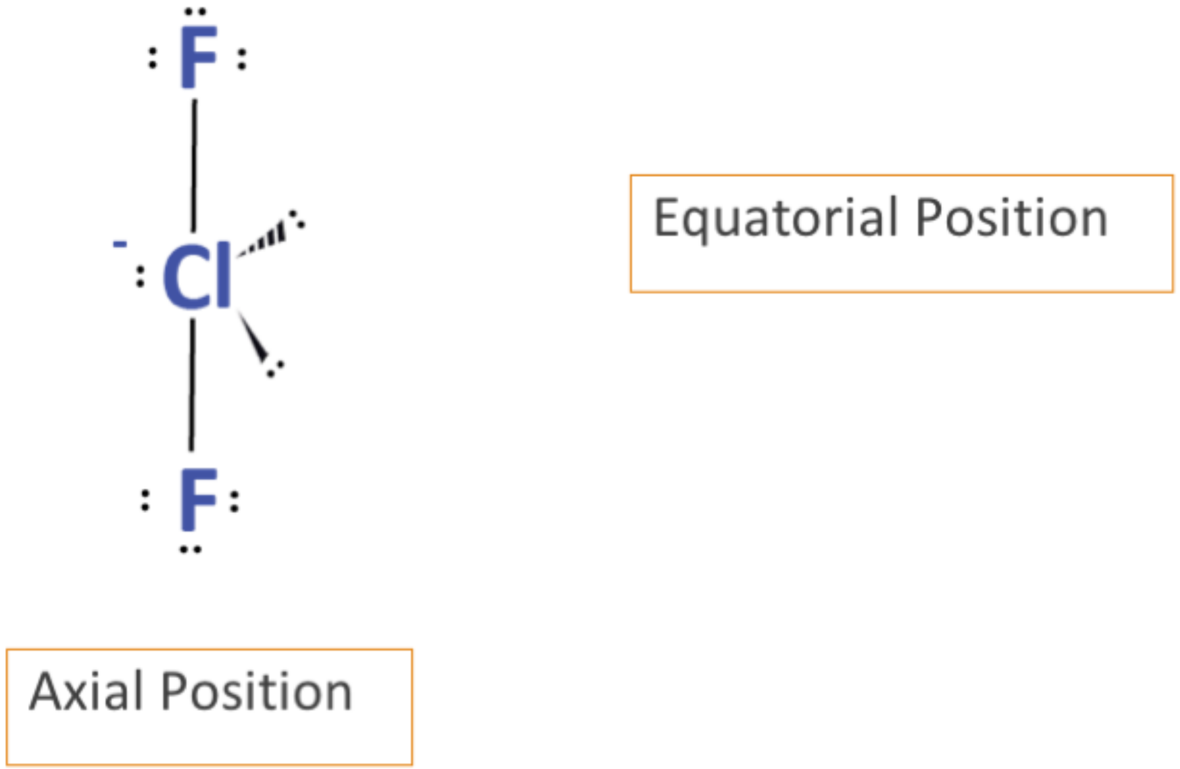
ClF_2^-

- When we remove the last equatorial bond, we end up in a linear geometry with only the most stable axial bonds remaining.

Remember: when we remove a bond and replace with a lone pair in the trigonal bipyramid geometry, we ALWAYS remove from the equatorial position

Electronic: Trigonal Bipyramid

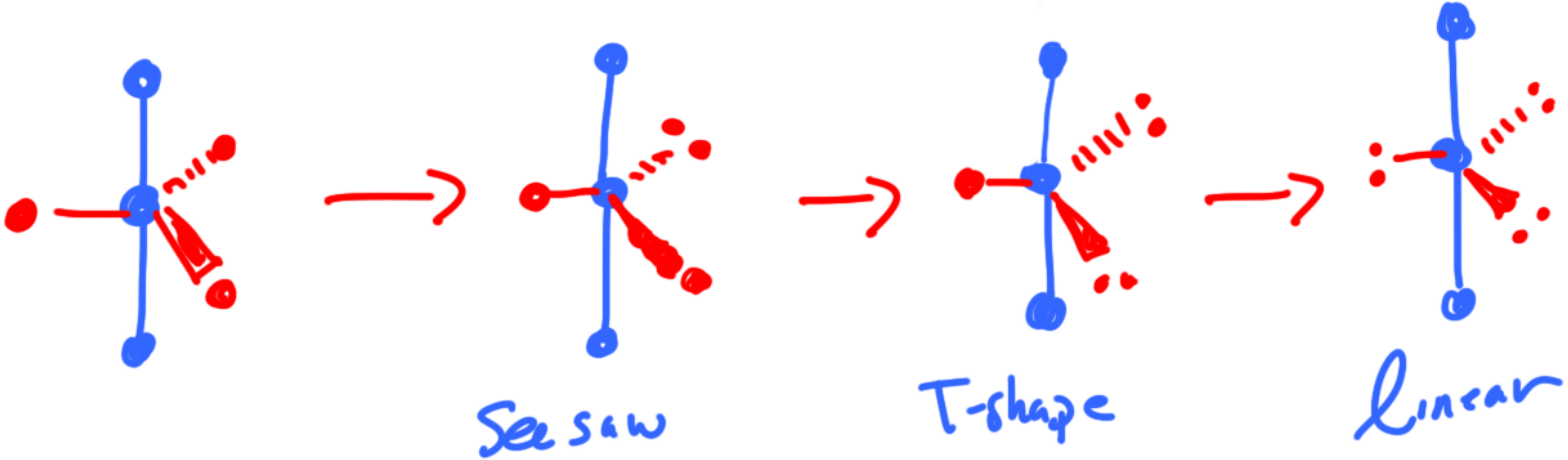
Molecular: Linear



5 Regions Overview

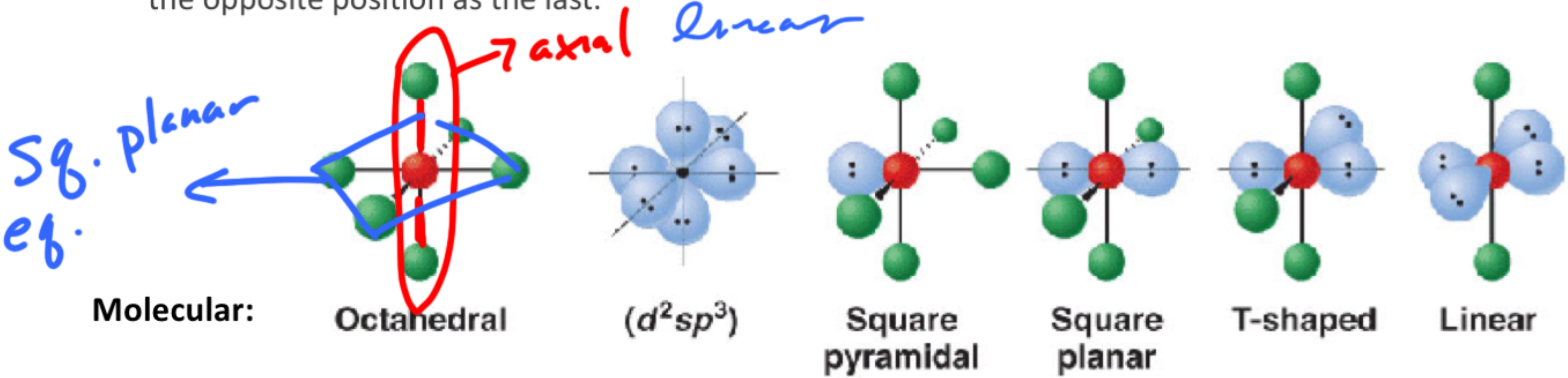
Electronic: Trigonal Bipyramid

* Preserve linear axial position



VSEPR Geometries: 6 e- Regions

- The octahedral molecular geometry is completely symmetrical, so there is no axial/equatorial preference. However, I like to think of it as linear atoms in the axial position, and a square plane made up by equatorial atoms.
- The one rule when replacing bonds with lone pairs is that you must always remove electrons from the opposite position as the last.



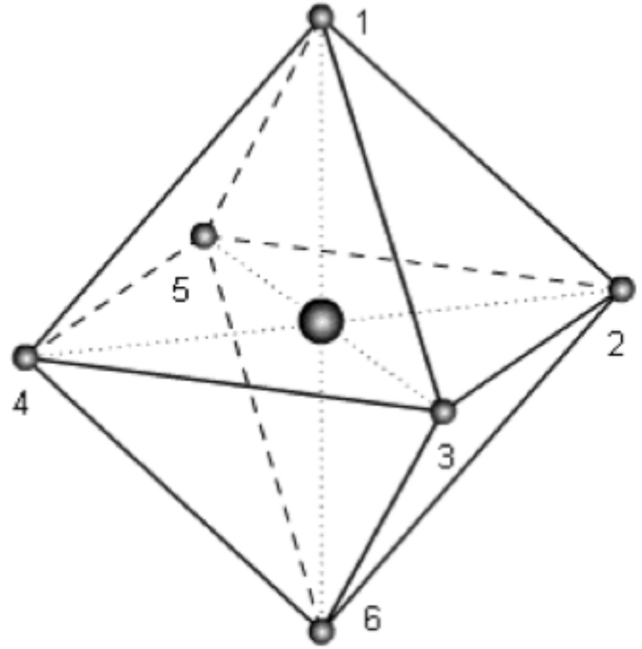
Molecular:

Pure bond angles: 90 and 180

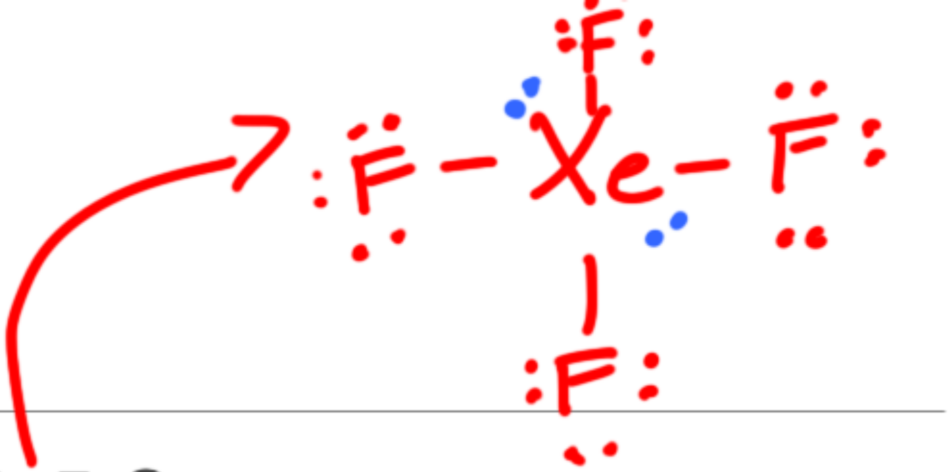
Electronic: Octahedral

VSEPR Geometries: 6 e- Regions

- Why is the geometry called "Octahedral" if it has six peripheral atoms?
- Remember: VSEPR geometries are named after the geometry of the **enclosure**
  - **An octahedral prism has 6 vertices**



Exam Question



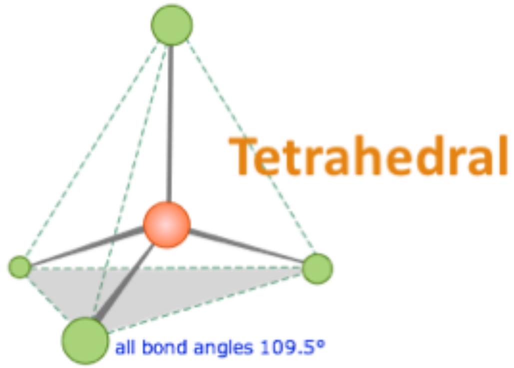
What is the molecular geometry of XeF_4?

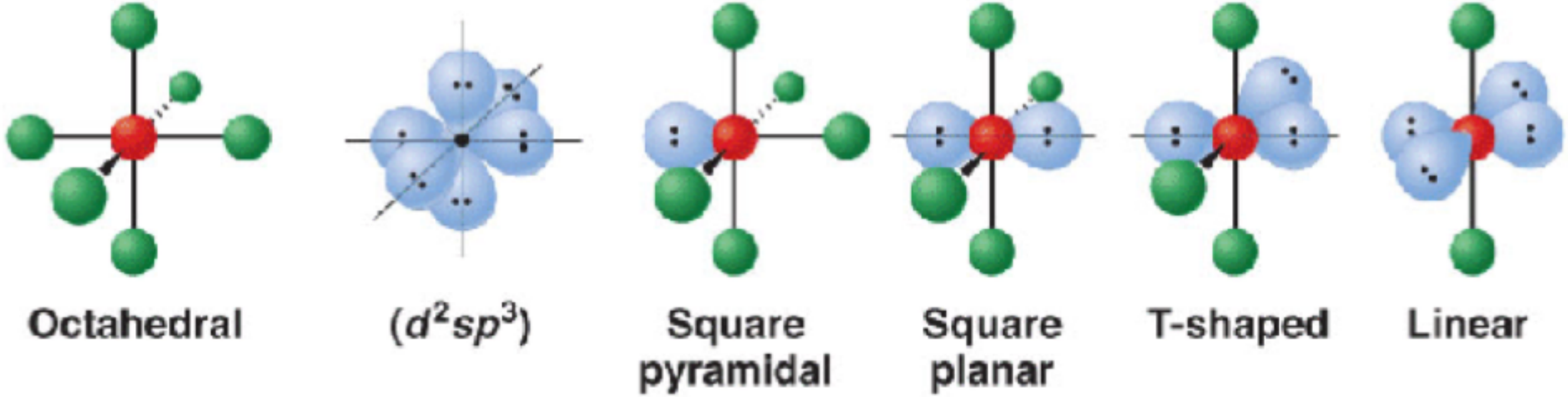
a. Tetrahedral

[✓ b. Square Planar]

c. T-Shaped

d. Square Pyramid



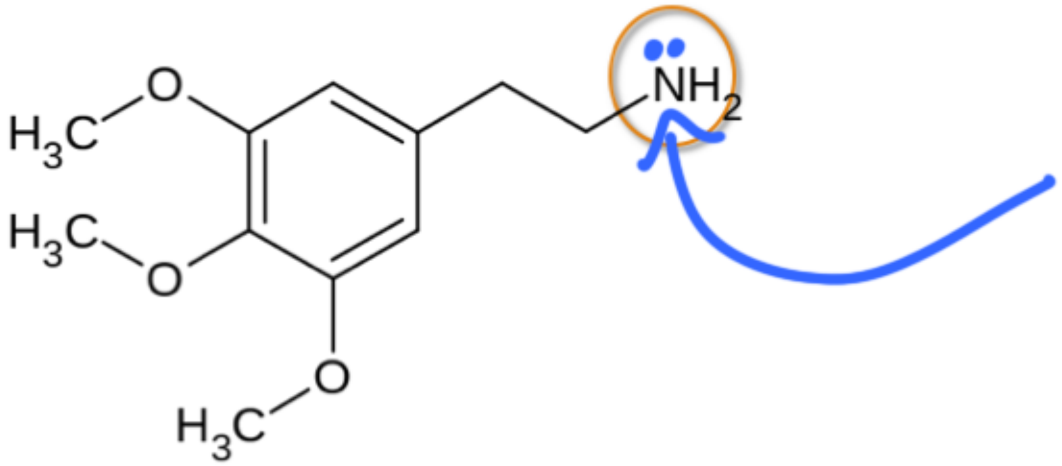


Same as NH_3

Big Molecule Question

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

What are the bond angles around nitrogen?



tetrahedral

↓

109.5

a. 120 degrees

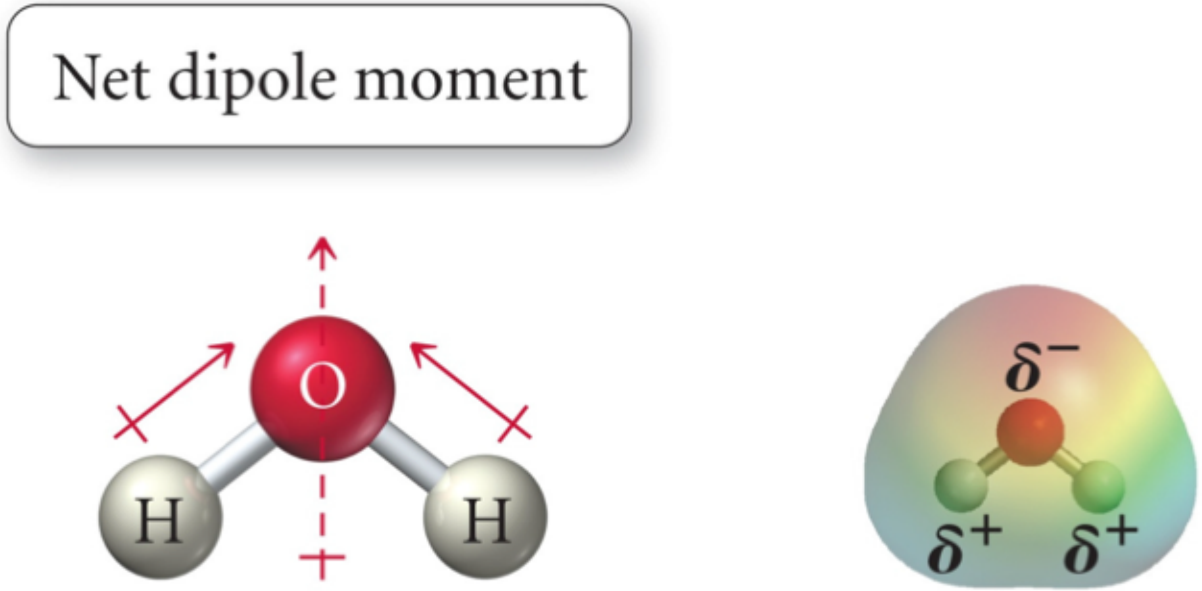
b. 109.5 degrees

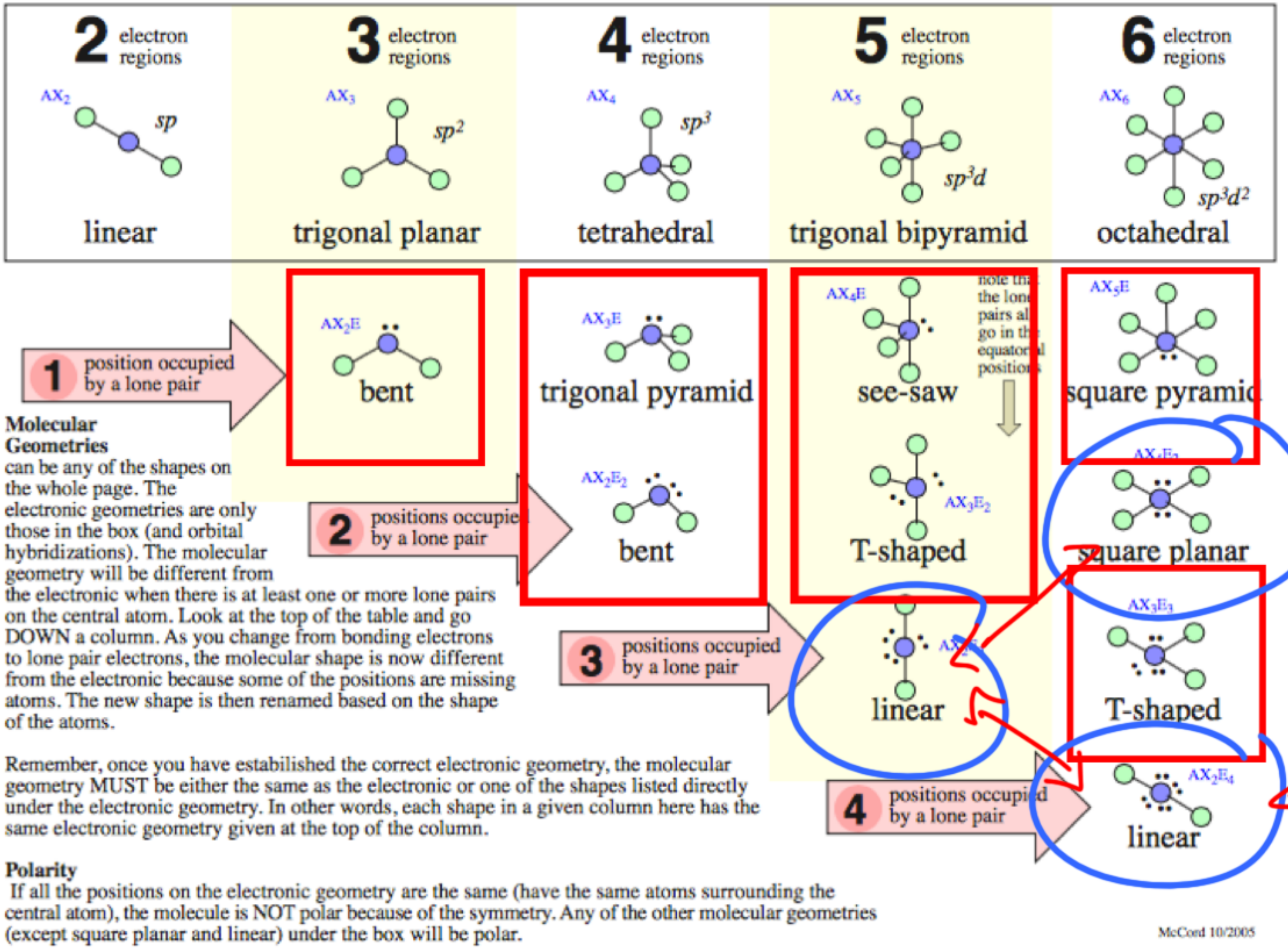
[✓ c.] Just less than 109.5 degrees

d. Just more than 109.5 degrees

VSEPR Theory: Molecular Polarity

- VSEPR is important because the shape of the molecule plays an important role in the chemical and physical properties of the molecule.
- An important conclusion that can be made based on VSEPR shapes is **molecular polarity**.
- Polarity in a bond occurs when one species disproportionately pulls the electrons closer, causing a dipole moment.
- Polarity in a molecule occurs when there are polar bonds and there is a net dipole moment on the molecule.
  - A perfectly symmetrical molecule will always be nonpolar.
  - A central atom bound to different peripheral atoms will be polar, as long as there is a single polar bond. (EXCEPTION: if the axial positions are the same and the equatorial positions are the same, the dipoles will cancel. Still a perfectly symmetrical molecule)
  - Lone pairs are generally an indication that the molecule is polar, except in the square planar and linear molecular geometries





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theoritical

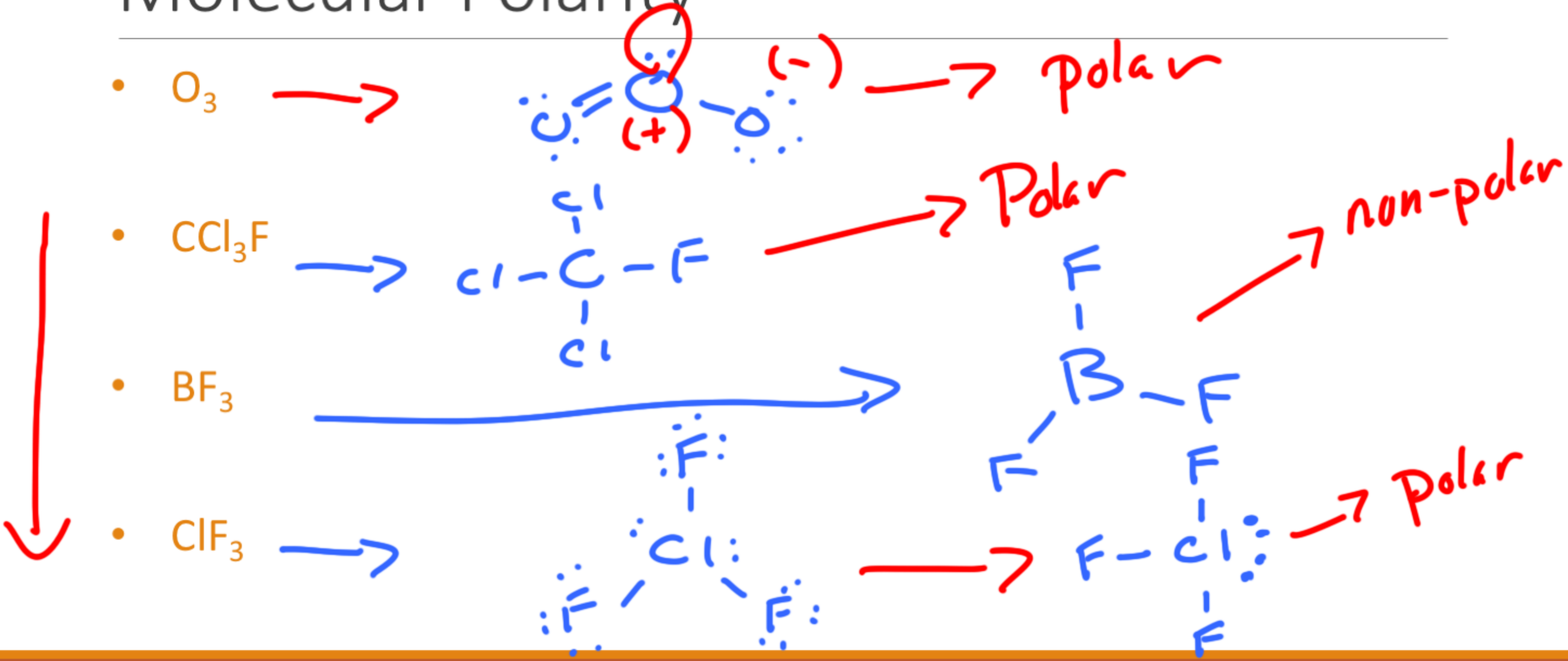
All red shapes are polar

Basic rules for molecular polarity:

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

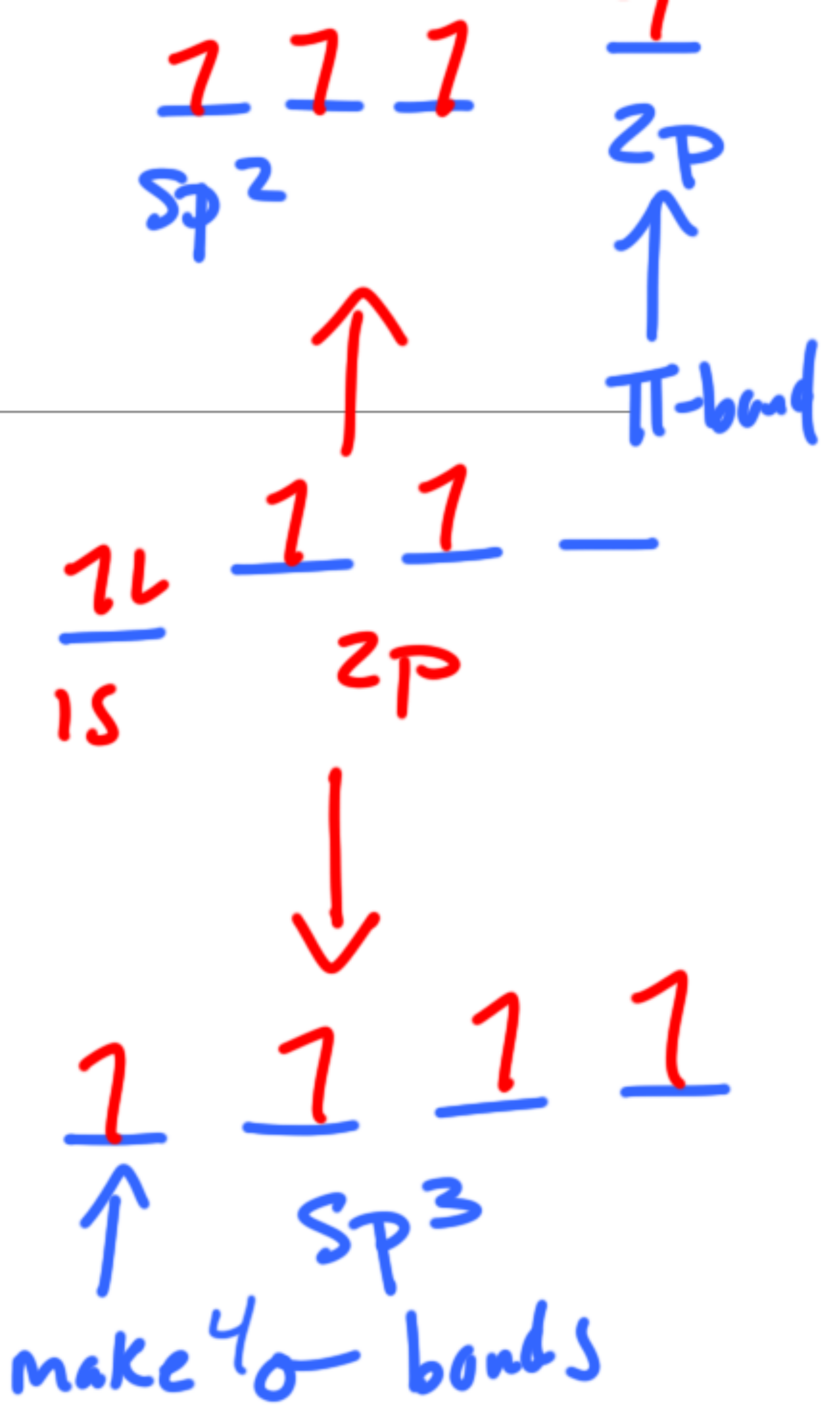
Molecular Polarity

- O_3
- CCl_3F
- BF_3
- ClF_3



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

1 e^- region = lone pair, single bond, double bond, OR triple bond

Hybrids

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

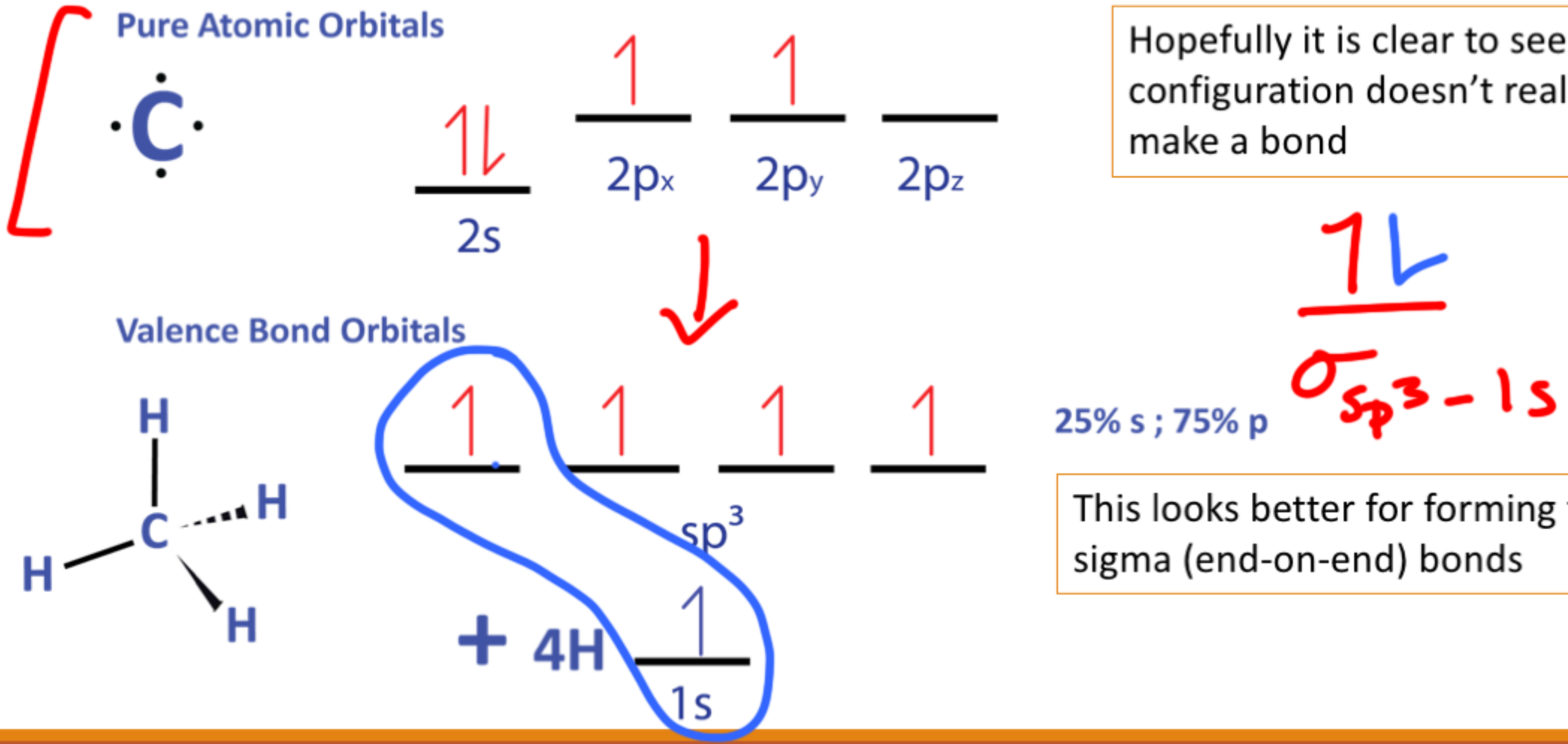
Single Bonds: 1 sigma bond

Double Bonds: 1 pi bond and 1 sigma bond

Triple Bonds: 2 pi bonds and 1 sigma bond

Valence Bond: sp^3

- The sp^3 hybridization is observed when a central atom has 4 electron-dense regions



Hopefully it is clear to see that this configuration doesn't really help us make a bond

This looks better for forming four sigma (end-on-end) bonds

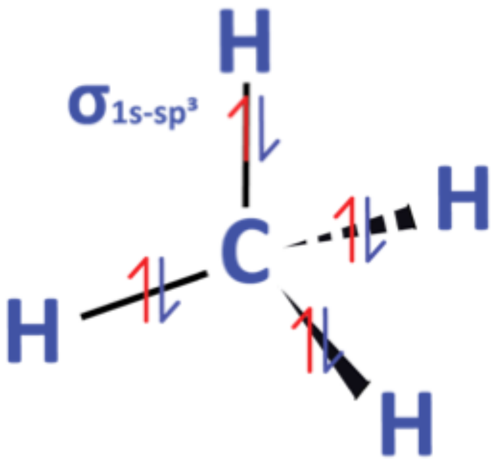
Valence Bond: sp^3

- Methane forms 4 sigma bonds to fill Carbon’s octet

What you form:

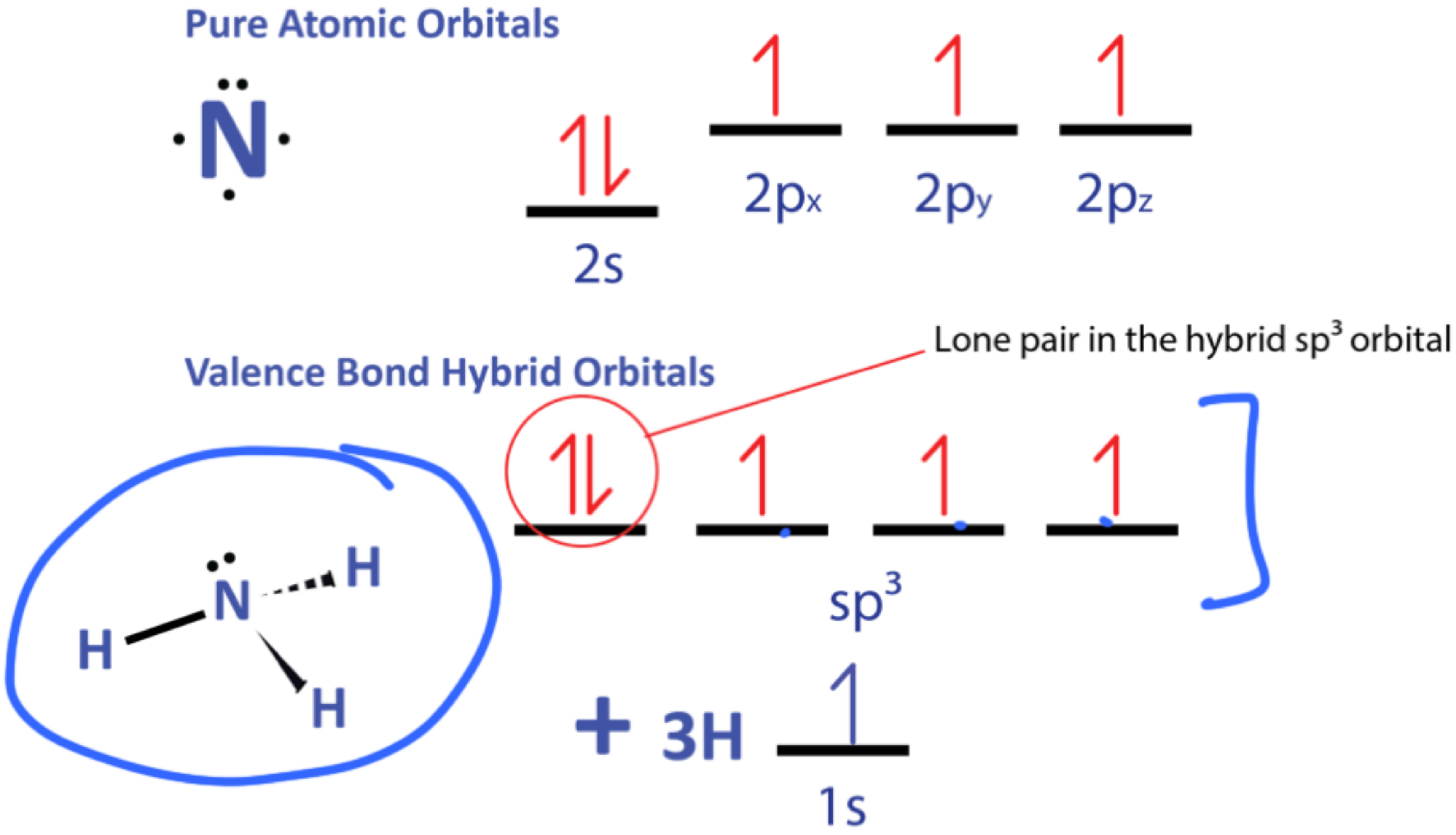
4 End-on-End overlaps (sigma bonds) between the pure 1s of H and the hybrid sp^3 of C

$\sigma_{1s\text{-}sp^3}$ ↿⇂



Valence Bond: sp^3 with 3 bonding regions

- Ammonia has sp^3 hybridization with only 3 bonding regions
- This is because ammonia still has a tetrahedral electronic geometry, resulting in paired electrons in one of the sp^3 orbitals

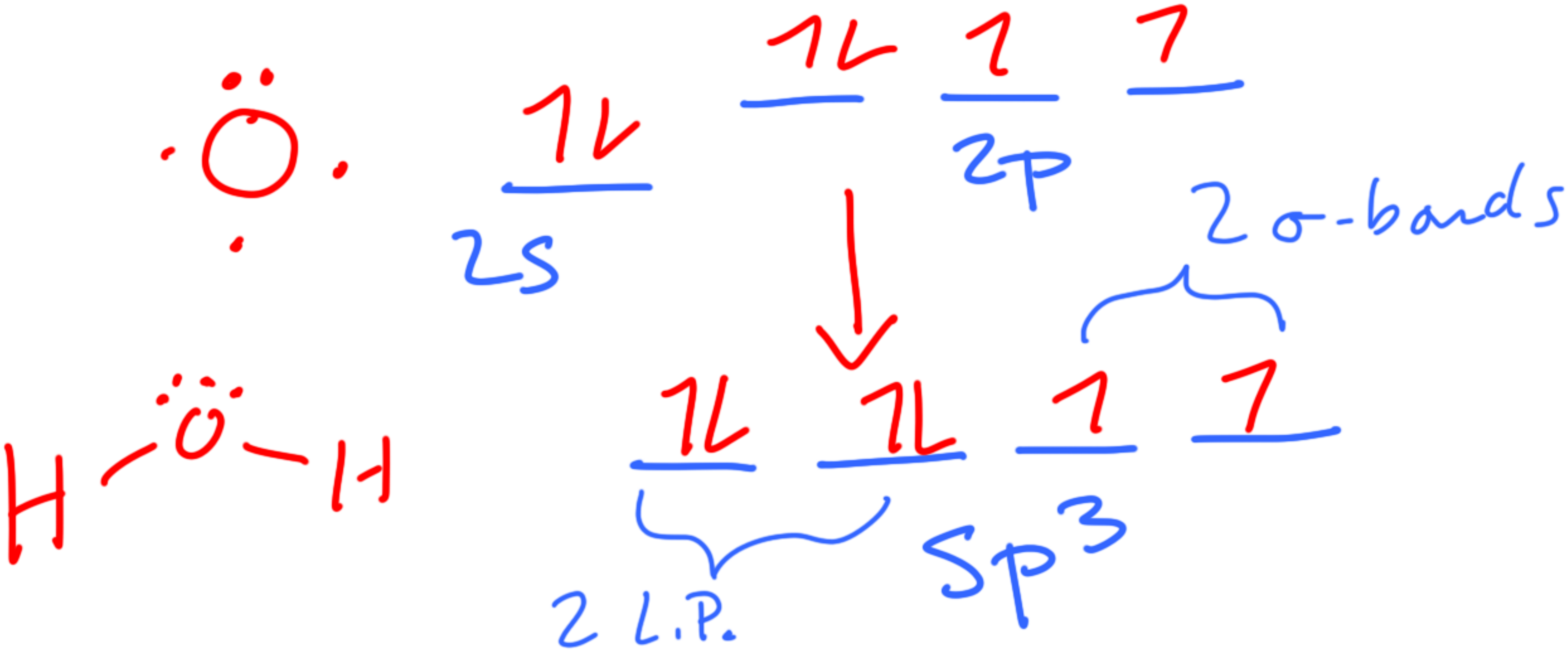


Pure Atomic Orbitals

Valence Bond Hybrid Orbitals

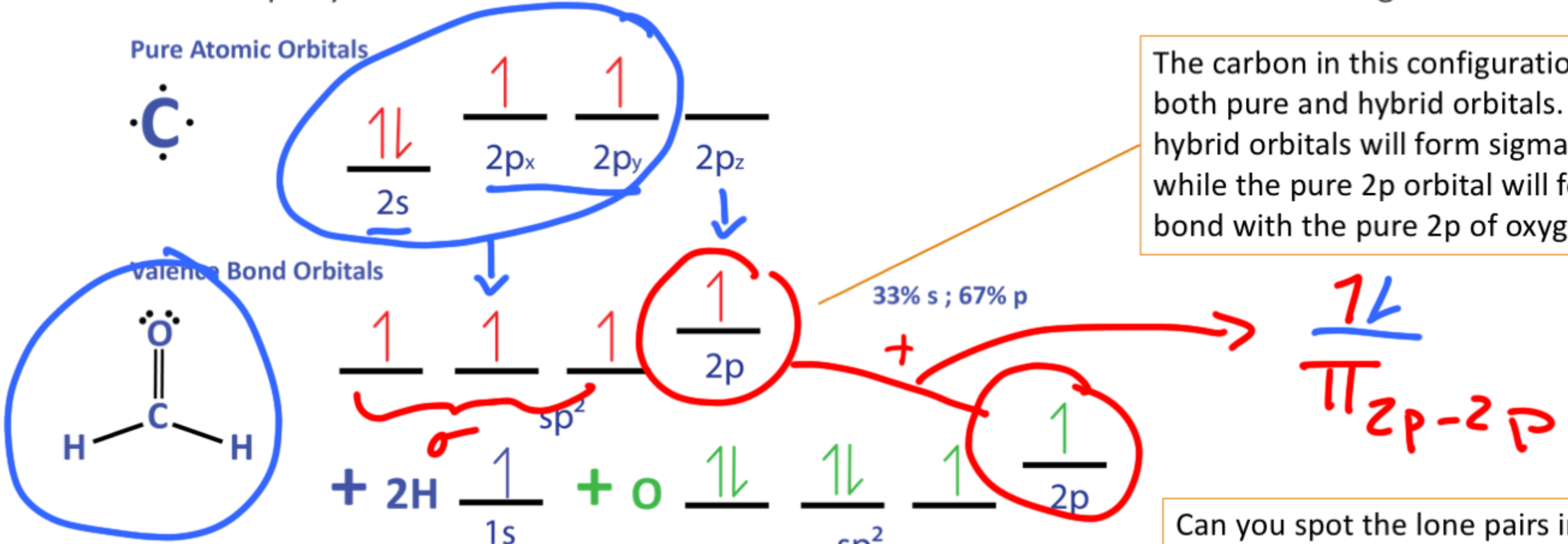
Lone pair in the hybrid sp^3 orbital

Valence Bond Example: Water



Valence Bond: sp^2

- The sp^2 hybridization is observed when a central atom has 3 electron-dense regions



The carbon in this configuration has both pure and hybrid orbitals. The hybrid orbitals will form sigma bonds, while the pure 2p orbital will form a pi bond with the pure 2p of oxygen

Can you spot the lone pairs in oxygen in the valence bond orbitals?

Valence Bond: sp^2

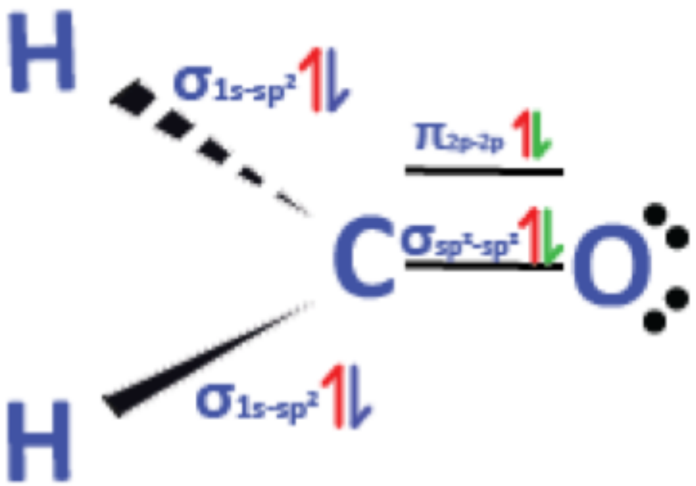
What you form:

End-on-End overlap (sigma bonds) between the pure 1s of H and the hybrid sp^2 of C

End-on-End overlap (sigma bond) between the hybrid sp^2 of O and the hybrid sp^2 of C

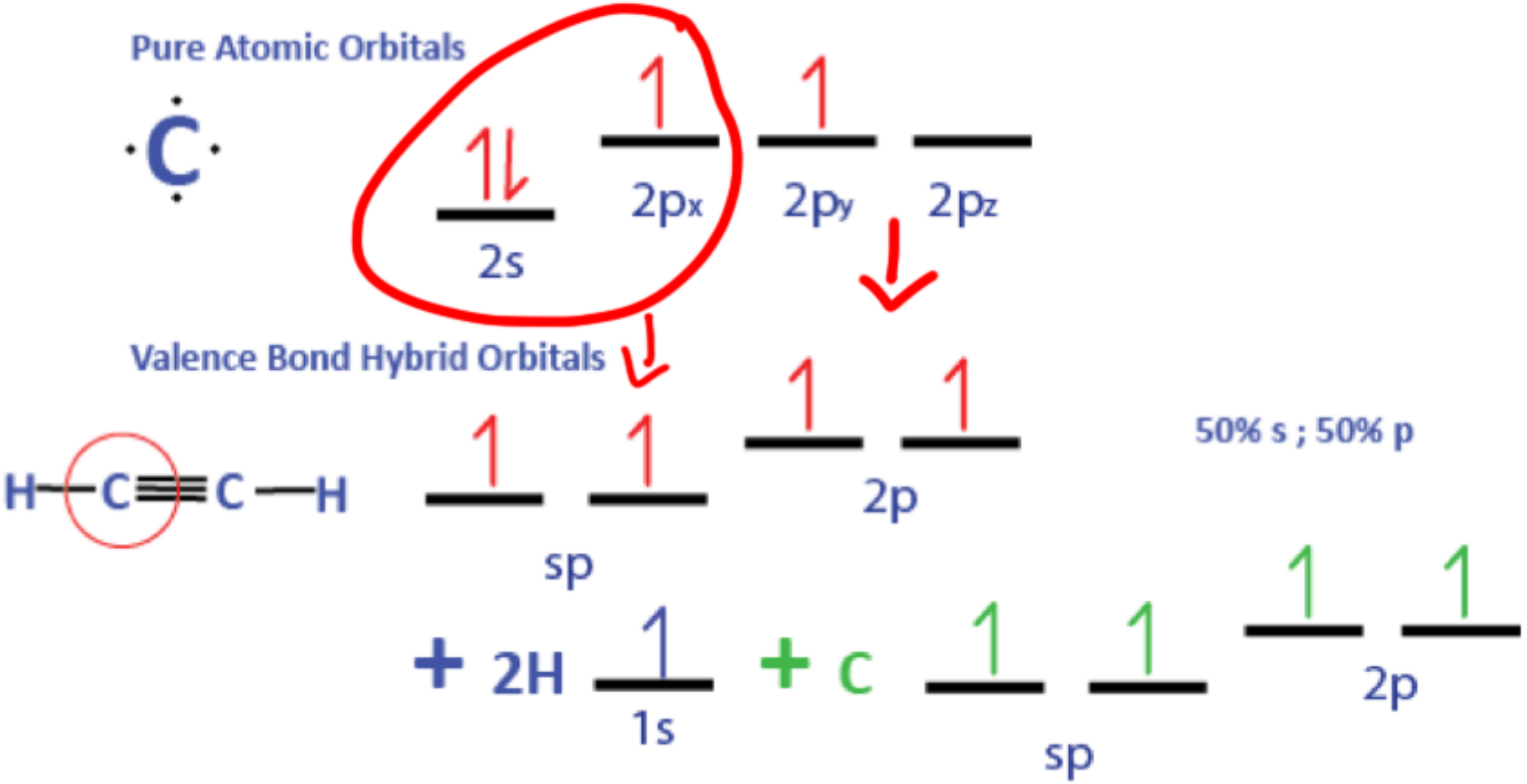
Side-by-Side overlap (pi bond) between the pure 2p of O and the pure 2p of C

$\sigma_{1s\text{-}sp^2}$ ↑↓ $\sigma_{sp^2\text{-}sp^2}$ ↑↓ $\pi_{2p\text{-}2p}$ ↑↓



Valence Bond: sp

- The sp hybridization is observed when a central atom has 2 electron-dense regions



Pure Atomic Orbitals

Valence Bond Hybrid Orbitals

50% s ; 50% p

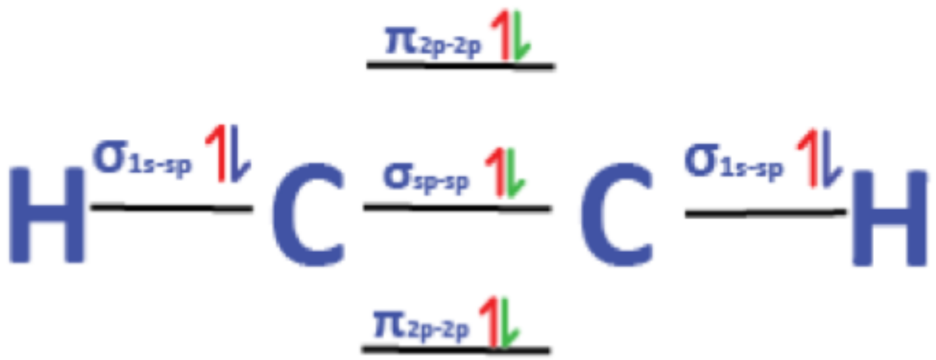
Valence Bond: sp

- The sp hybridization is observed when a central atom has 2 electron-dense regions

What you form:

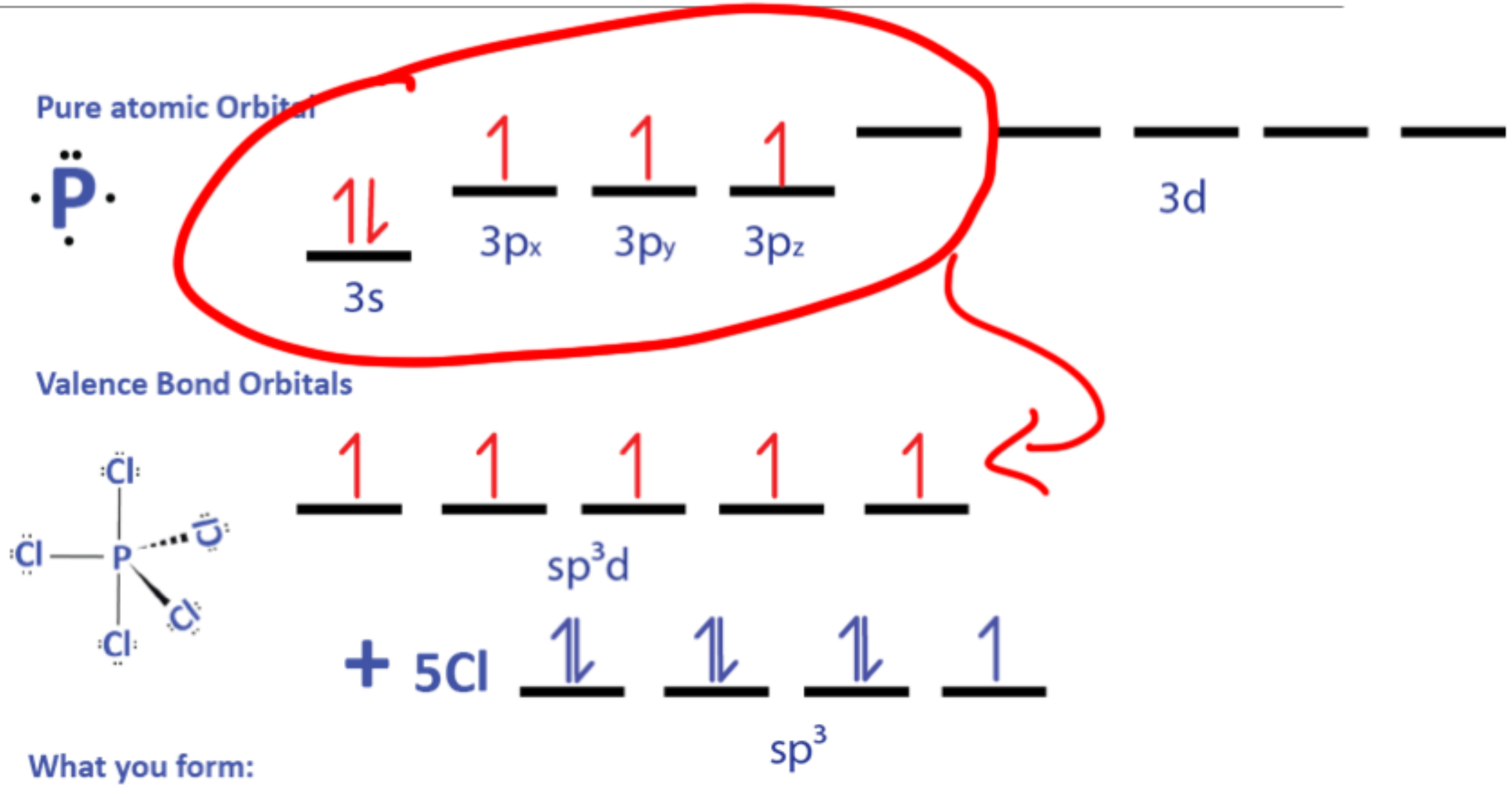
1 End-on-End overlap (sigma bond) between the pure 1s of H and the hybrid sp of C
1 End-on-End overlap (sigma bond) between the hybrid sp of C and the hybrid sp of C
2 Side-on-Side overlaps (pi bonds) between the pure 2p of C and the pure 2p of C

$\sigma_{1s\text{-}sp}$ ↑↓ $\sigma_{sp\text{-}sp}$ ↑↓ $\pi_{2p\text{-}2p}$ ↑↓



Valence Bond: sp^3d

- The sp^3d hybridization is observed when a central atom has 5 electron-dense regions
- This can **only** occur on central atoms with 3p or greater electrons – the same rules apply for expanded valence Lewis Structures



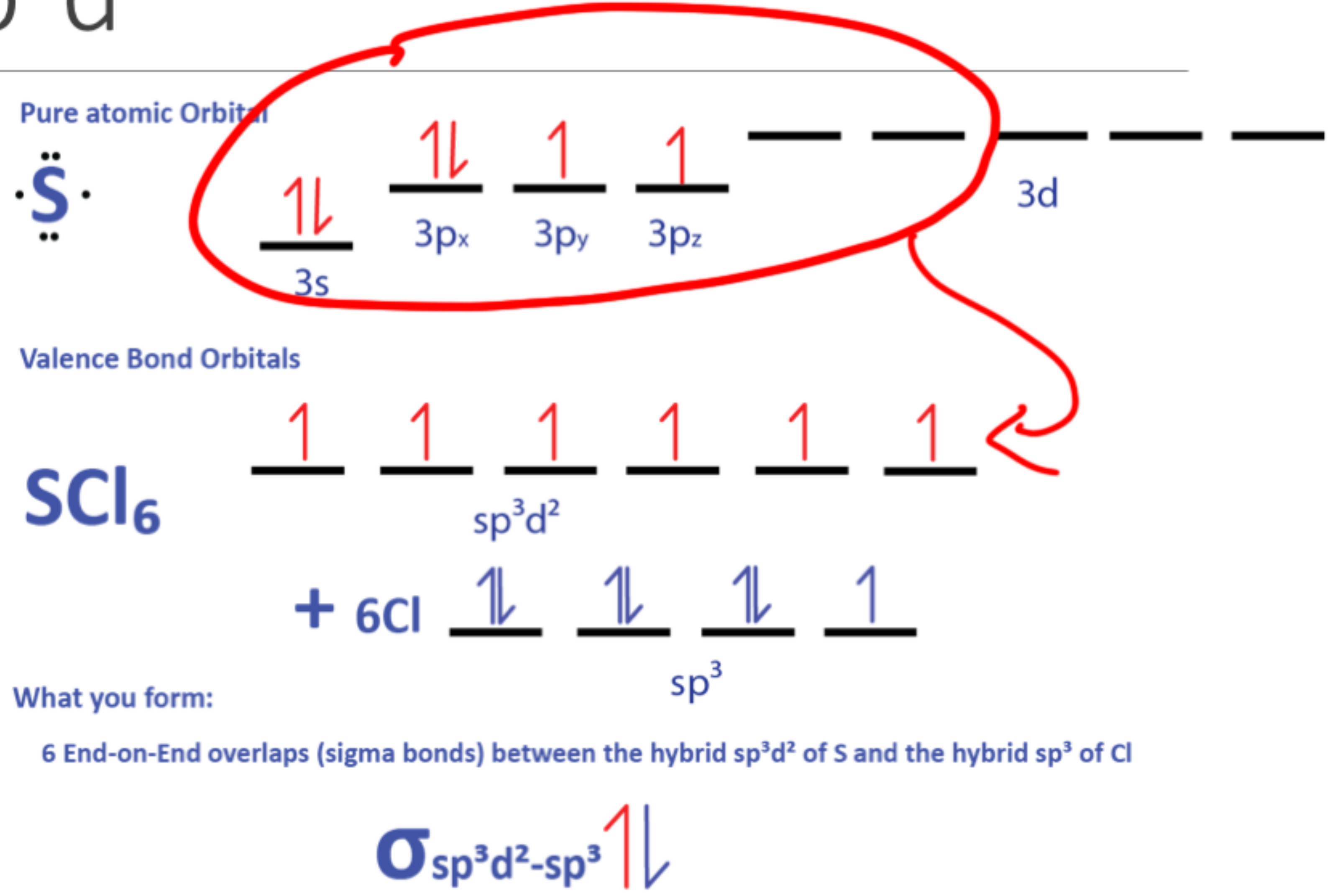
What you form:

5 End-on-End overlaps (sigma bonds) between the hybrid sp^3d of P and the hybrid sp^3 of Cl

$\sigma_{sp^3d\text{-}sp^3}$ $\uparrow\downarrow$

Valence Bond: sp^3d^2

- The sp^3d^2 hybridization is observed when a central atom has 6 electron-dense regions
- This can **only** occur with central atoms with 3p or greater electrons – the same rules apply for expanded valence Lewis Structures



6 End-on-End overlaps (sigma bonds) between the hybrid sp^3d^2 of S and the hybrid sp^3 of Cl

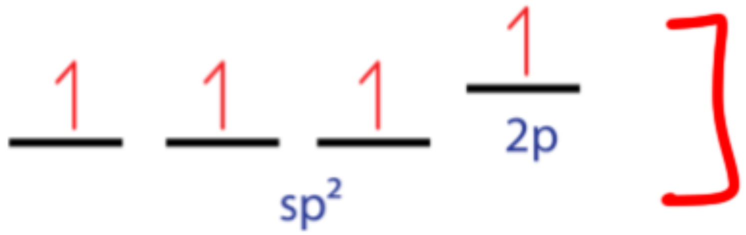
$\sigma_{sp^3d^2\text{-}sp^3}$ ↑↓

VB Challenge Question

$3\ \sigma$ bonds

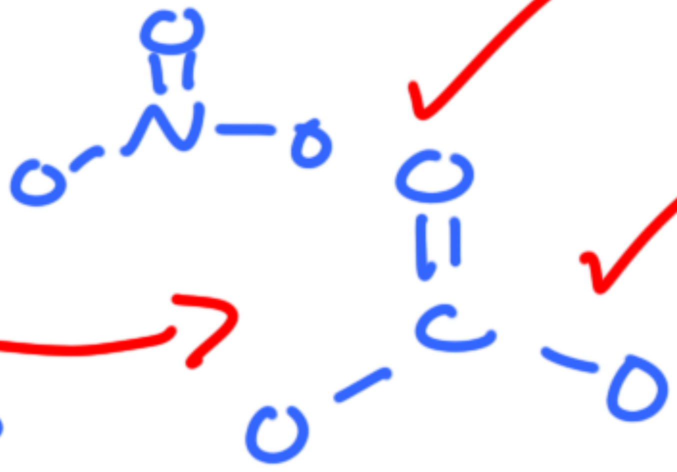
$1\ \pi$ bond

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:

- ~~HCN~~ → $H-C\equiv N:$ $2\sigma, 2\pi$
- ✓ NO_3^- →
- ✓ CO_3^{2-} →
- ~~CO_2~~



$\boxed{NO_3^-, CO_3^{2-}}$

Valence Bond Question

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

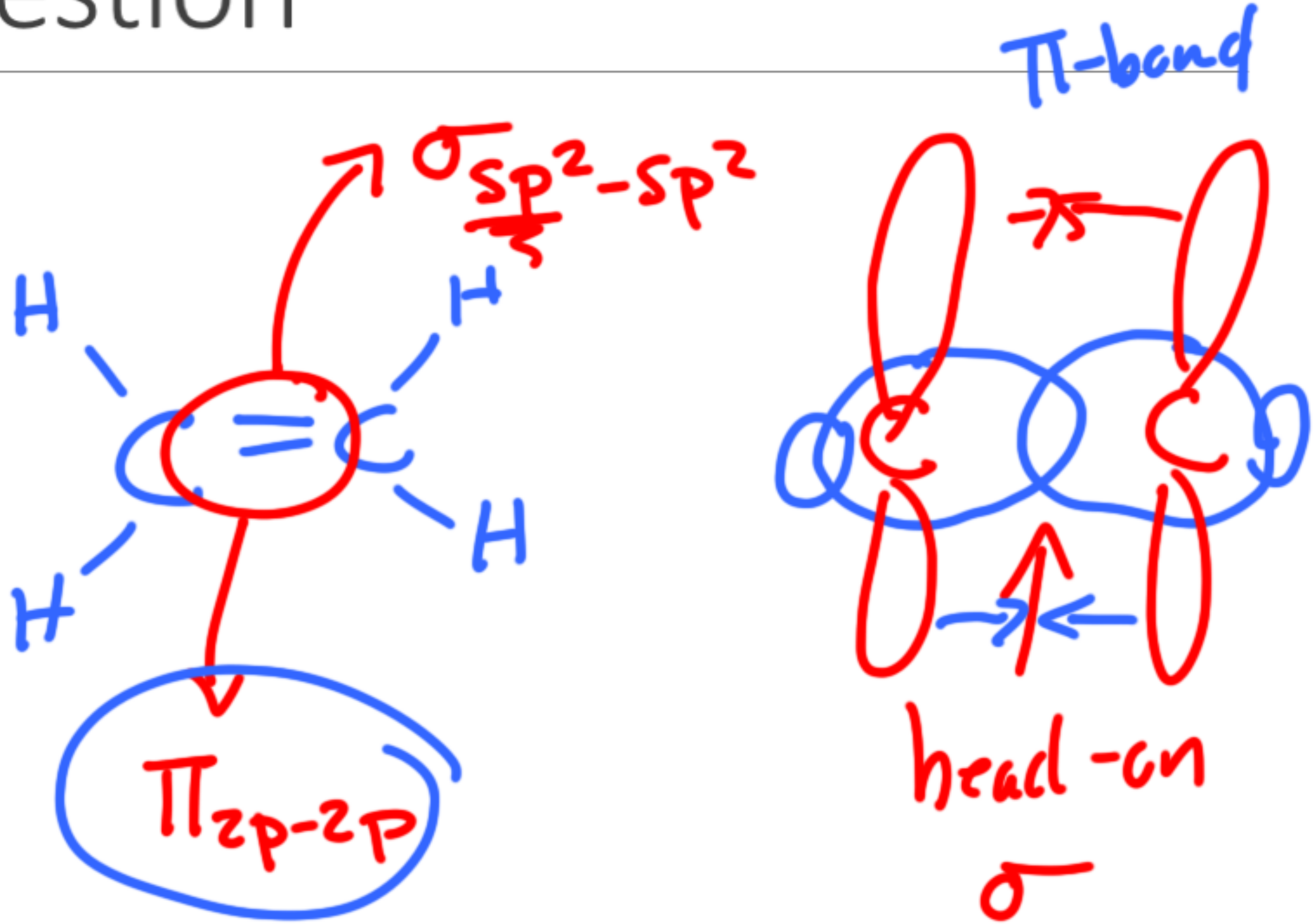
2. π; $1p$

[✓ **3.** π; $2p$]

4. σ; sp^2

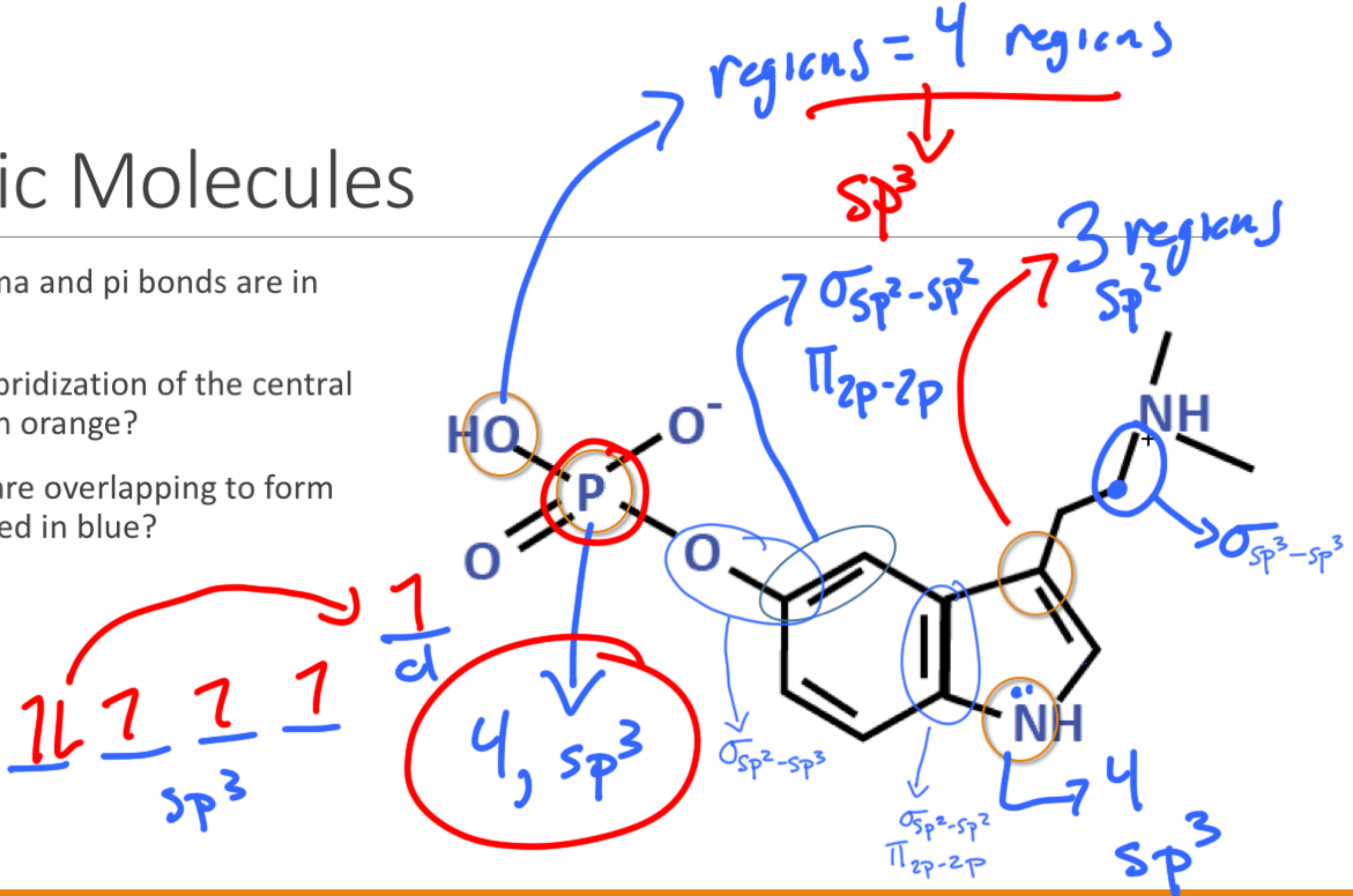
5. σ; sp^3

π



Organic Molecules

- How many sigma and pi bonds are in this structure?
- What is the hybridization of the central atoms circled in orange?
- What orbitals are overlapping to form the bonds circled in blue?



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 not fully accurate especially 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

Molecular Orbital Theory

ATOMIC ORBITALS COMBINE TO FORM MOLECULAR ORBITALS

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**

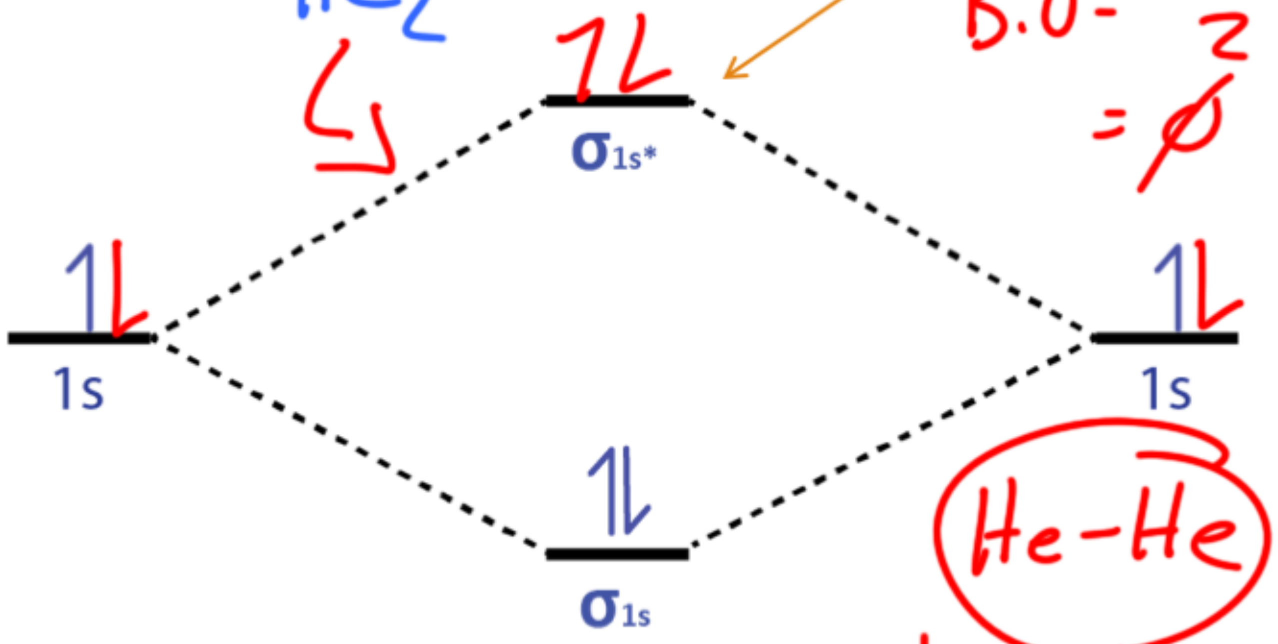
Molecular Orbital Theory

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

- Molecular Orbital Theory looks at individual electrons as “waves.”
- This 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 H_2

He_2



$$B.O = \frac{2-2}{2} = 0$$

He-He

does not exist

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

O_2^+

$\frac{8-4}{2} = 2$

$\frac{8-3}{2} = 2.5$

Molecular Orbital Theory

1) Magnetism
2) HOMO-LUMO Gap

diamagnetic

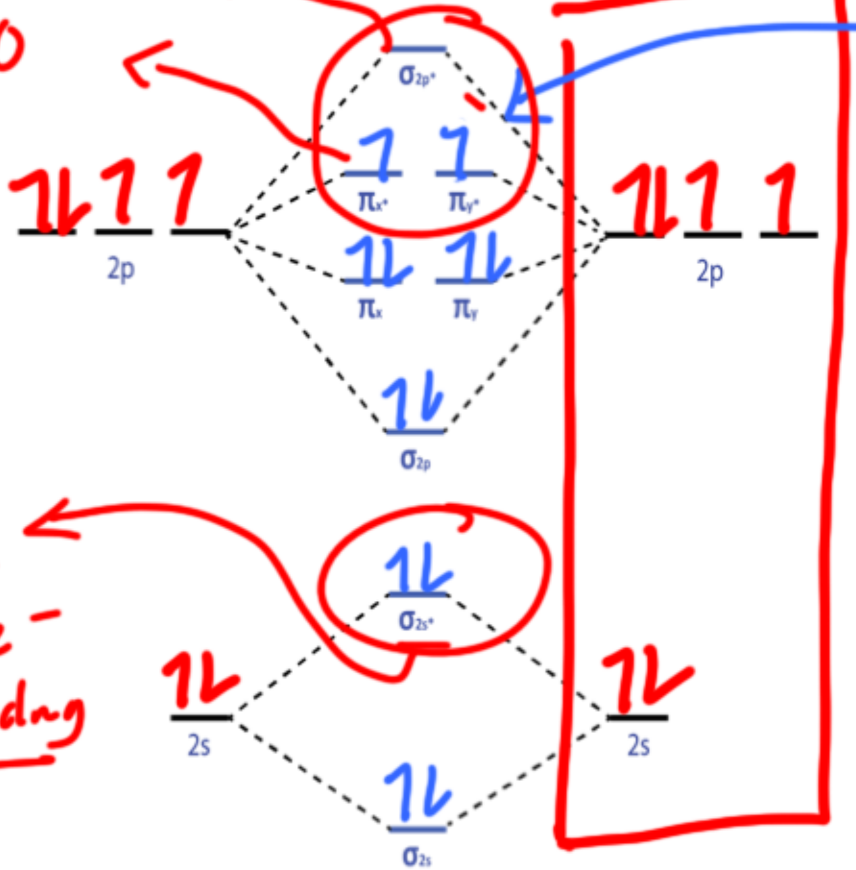
paramagnetic

O_2 and F_2

MO diagram

LUMO

HOMO

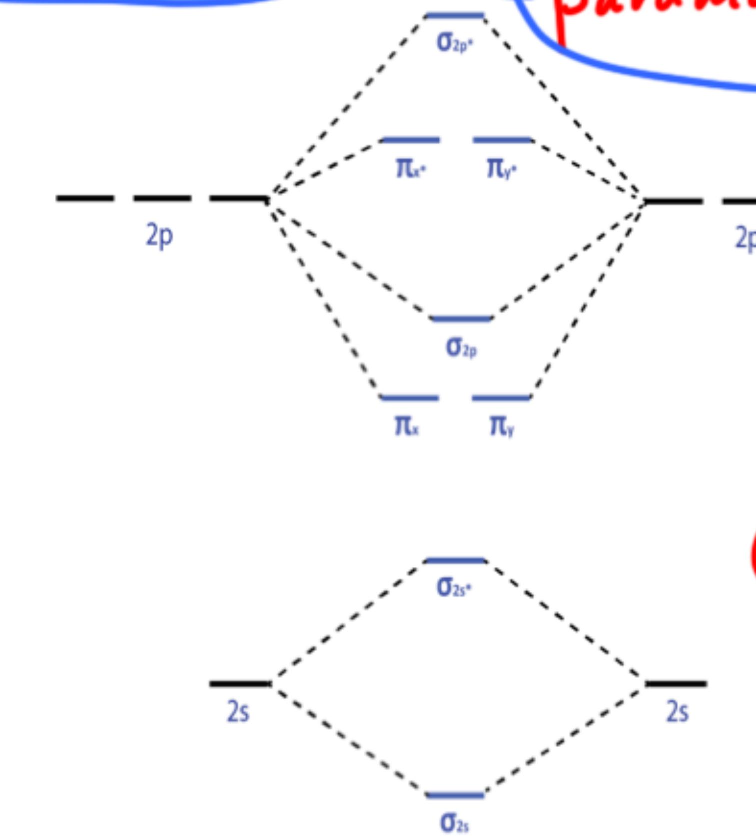


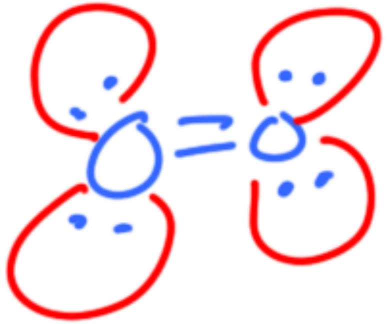
B.O.

antibond

B.O. = $\frac{\text{bonding } e^- - \text{antibonding}}{2}$

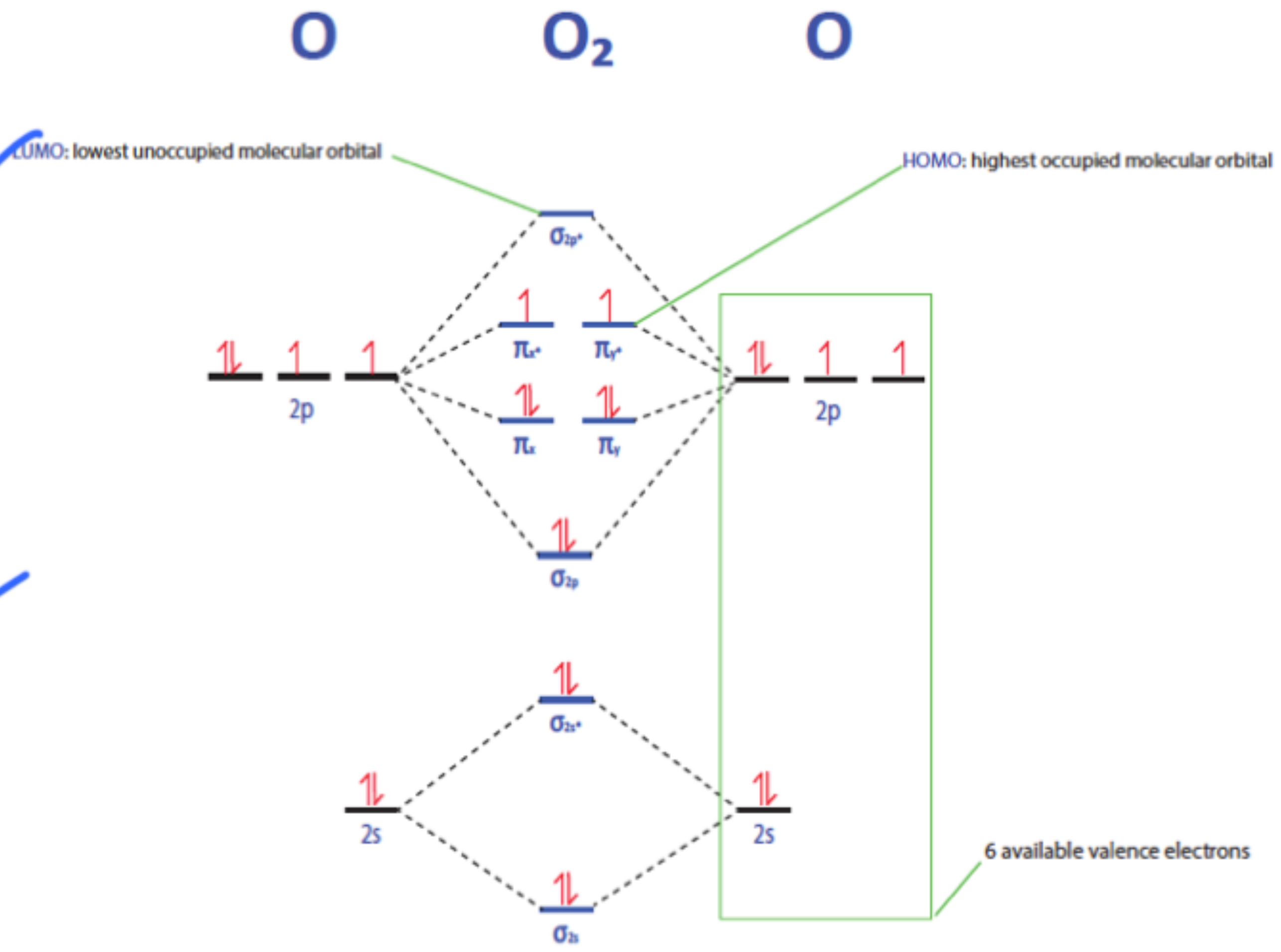
B_2, N_2, and C_2





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)



LUMO: lowest unoccupied molecular orbital

HOMO: highest occupied molecular orbital

6 available valence electrons