

# Unit 3 Review 2

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VALENCE BOND, MOLECULAR ORBITAL THEORY, IMF'S

# Valence Bond vs. Molecular Orbital Theory

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- **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

- **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

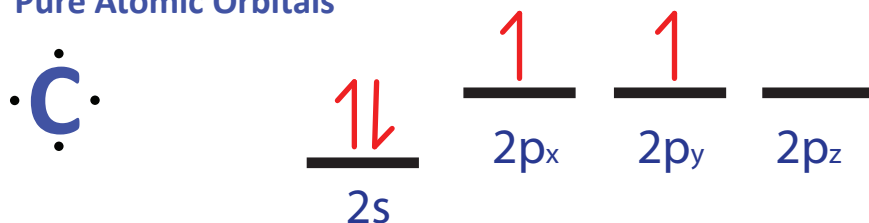
# Valence Bond Theory

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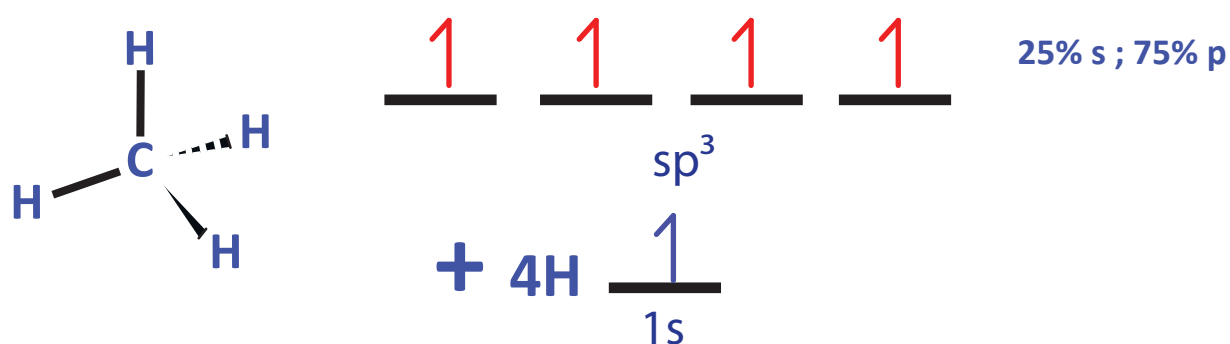
- **Valence Bond Theory** explains the behavior of the valence orbitals of bonding atoms by suggesting that pure atomic orbitals can form energetically favorable hybrid orbitals
- The conclusions of Valence Bond Theory are:
  1. The hybridization of a bonding atom depends on the number of electron regions (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-by-side)

# Valence Bond Theory

Pure Atomic Orbitals



Valence Bond Hybrid Orbitals

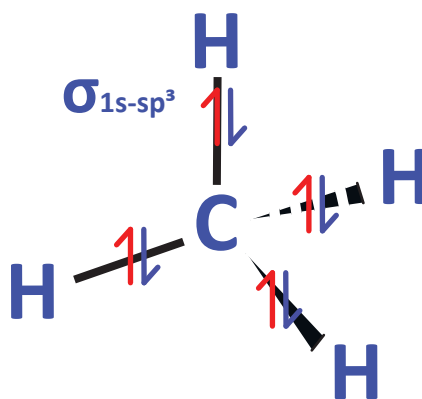


What you form:

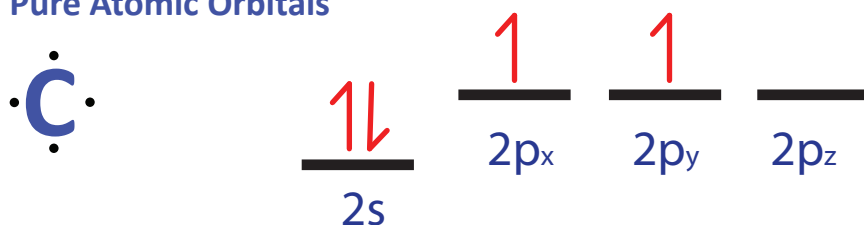
4 End-on-End overlaps (sigma bonds) between the pure 1s of H and the hybrid  $sp^3$  of C



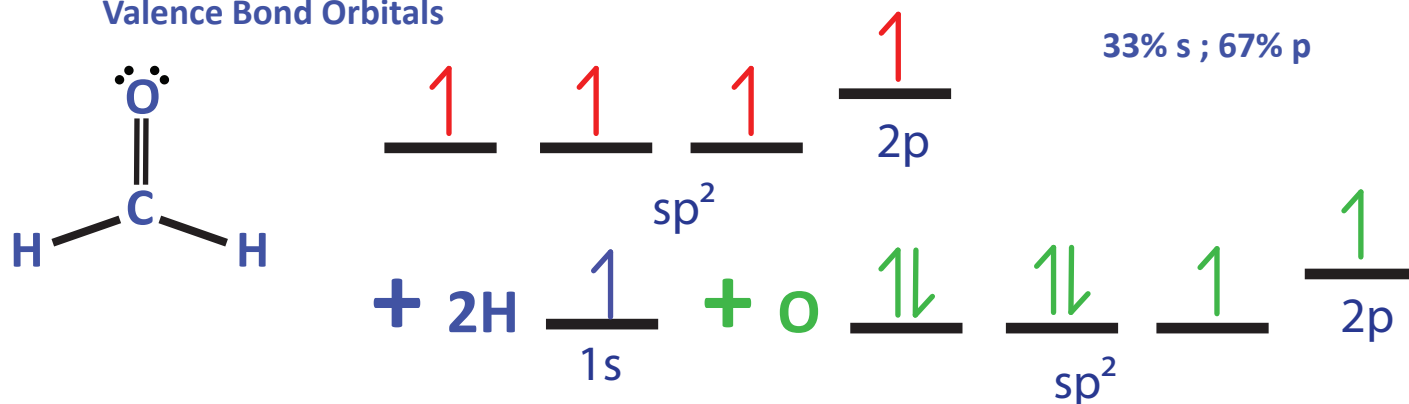
Your hybrid orbital shape ( $sp^3, sp^2, sp$ , etc.) absolutely depends on the molecule / surrounding atoms



### Pure Atomic Orbitals

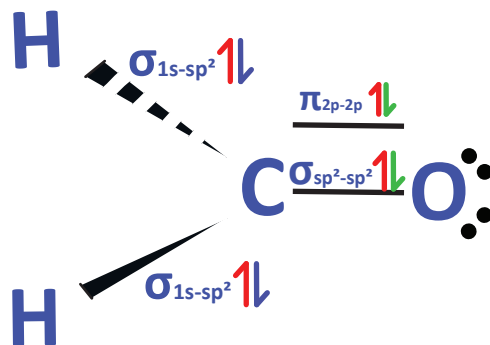
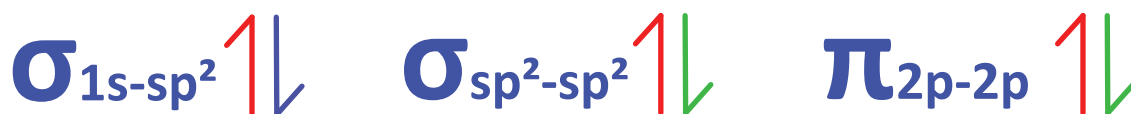


### Valence Bond Orbitals

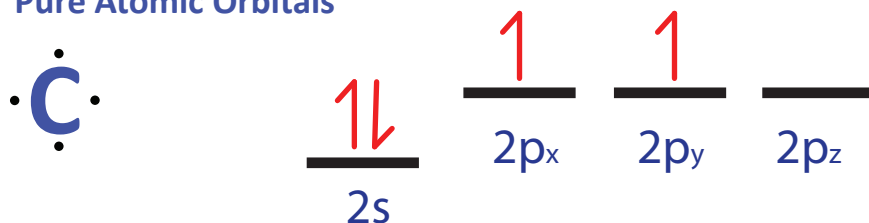


### What you form:

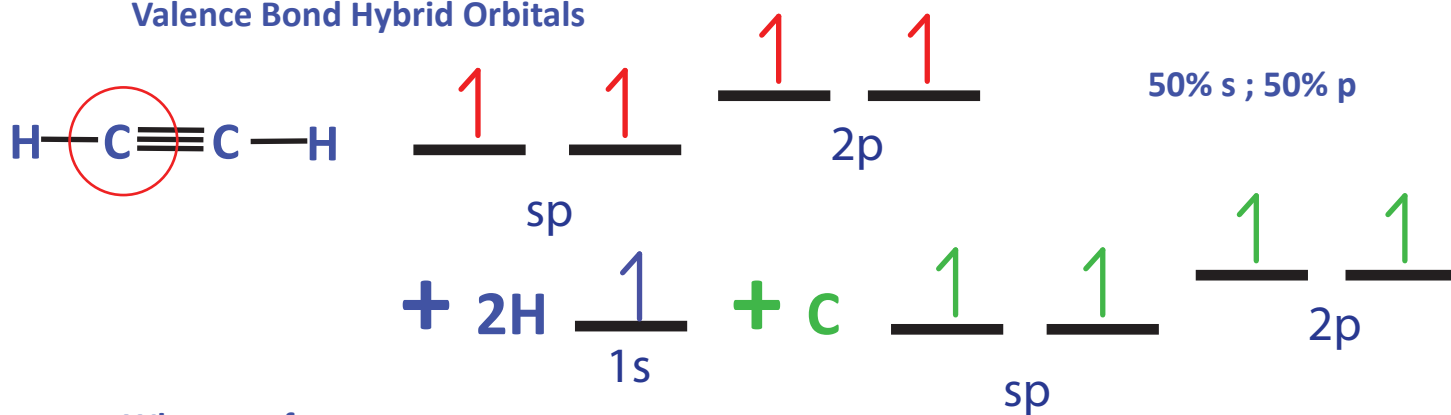
- End-on-End overlap (sigma bonds) between the pure 1s of H and the hybrid  $sp^2$  of C
- End-on-End overlap (sigma bond) between the hybrid  $sp^2$  of O and the hybrid  $sp^2$  of C
- Side-by-Side overlap (pi bond) between the pure 2p of O and the pure 2p of C



### Pure Atomic Orbitals

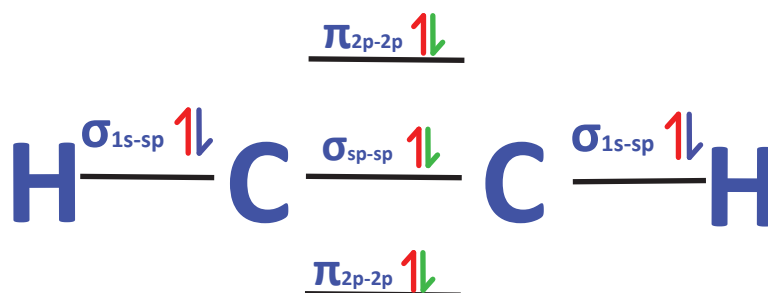


### Valence Bond Hybrid Orbitals

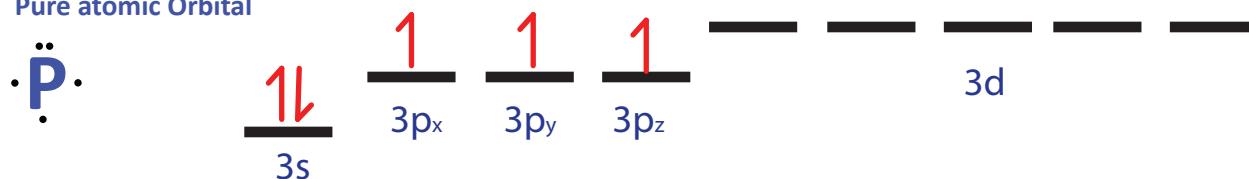


What you form:

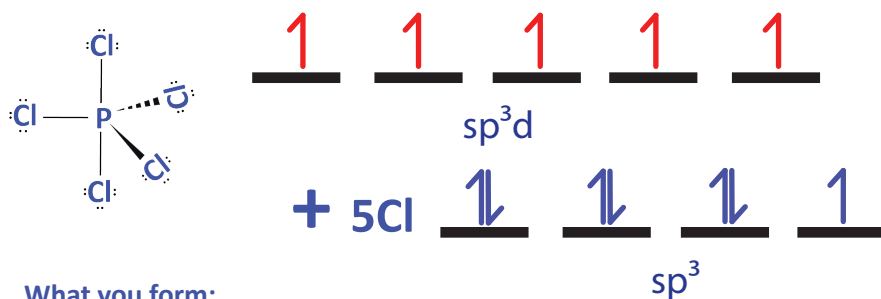
- 1 End-on-End overlap (sigma bond) between the pure 1s of H and the hybrid sp of C
- 1 End-on-End overlap (sigma bond) between the hybrid sp of C and the hybrid sp of C
- 2 Side-on-Side overlaps (pi bonds) between the pure 2p of C and the pure 2p of C



Pure atomic Orbital



Valence Bond Orbitals

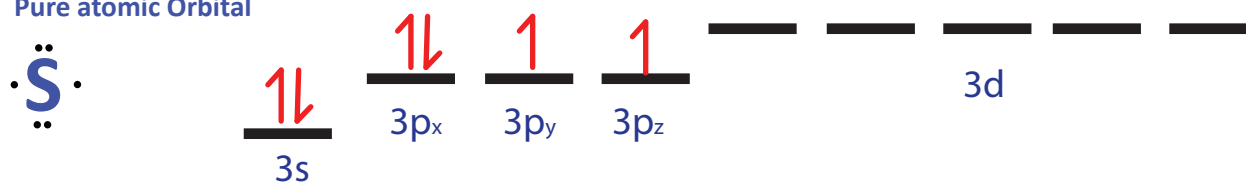


What you form:

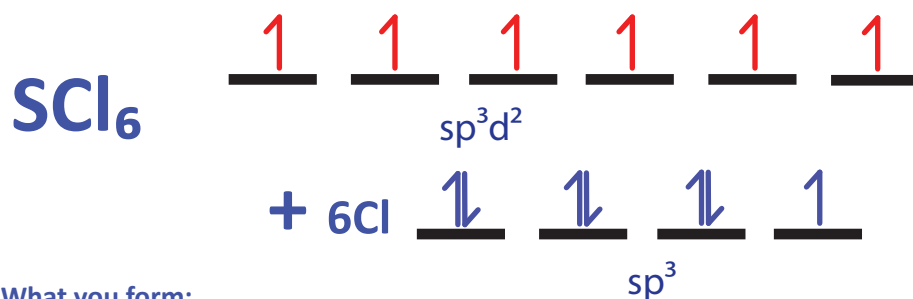
5 End-on-End overlaps (sigma bonds) between the hybrid sp<sup>3</sup>d of P and the hybrid sp<sup>3</sup> of Cl



Pure atomic Orbital



Valence Bond Orbitals



What you form:

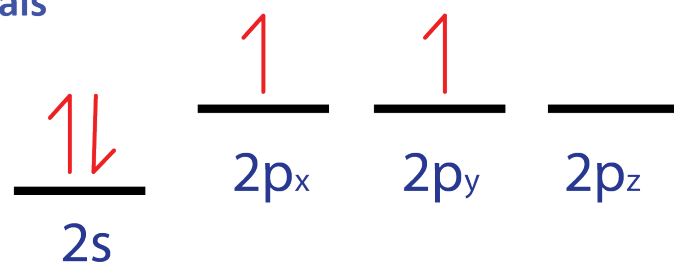
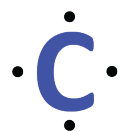
6 End-on-End overlaps (sigma bonds) between the hybrid sp<sup>3</sup>d<sup>2</sup> of S and the hybrid sp<sup>3</sup> of Cl



# Valence Bond: $sp^3$

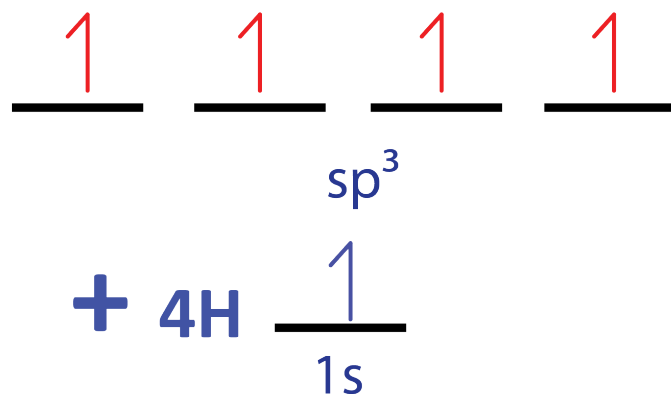
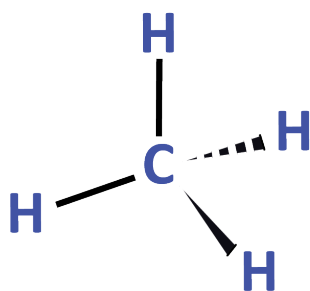
- The  $sp^3$  hybridization is observed when a central atom has 4 electron-dense regions

Pure Atomic Orbitals



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

Valence Bond Orbitals



25% s ; 75% p

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



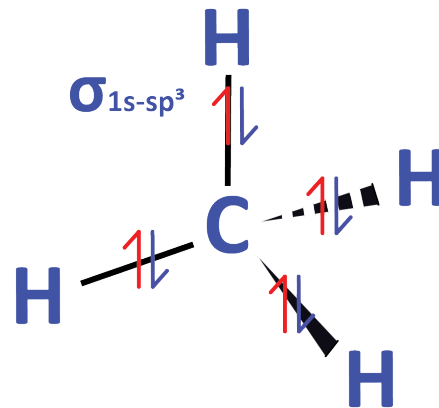
# Valence Bond: $sp^3$

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

What you form:

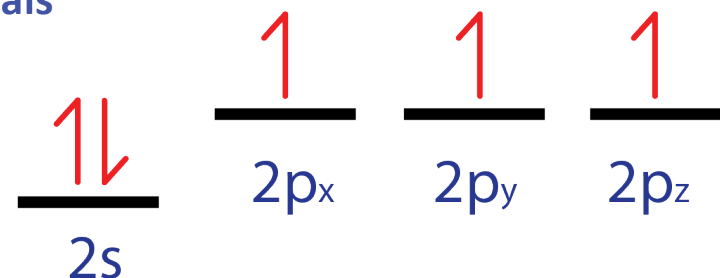
4 End-on-End overlaps (sigma bonds) between the pure 1s of H and the hybrid  $sp^3$  of C



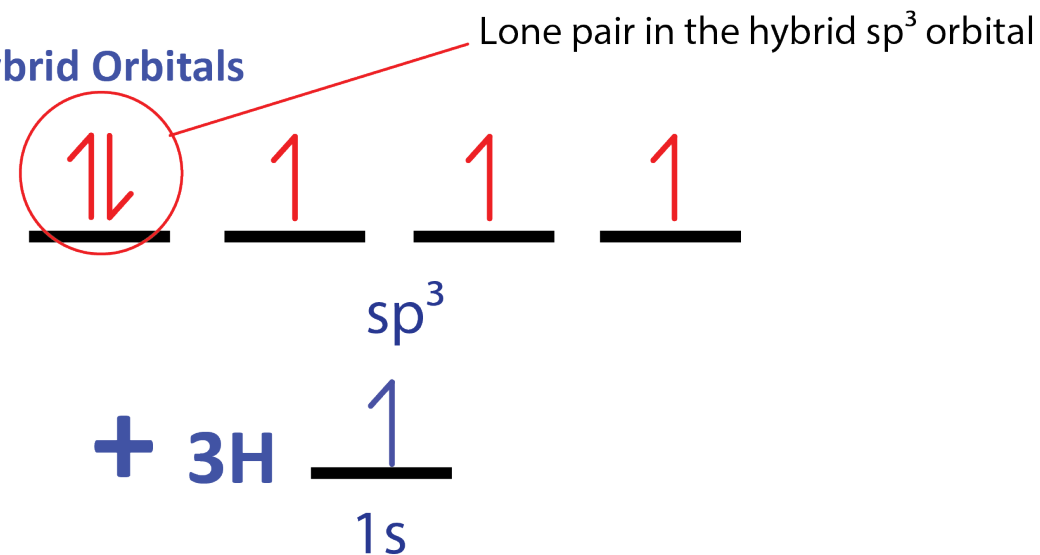
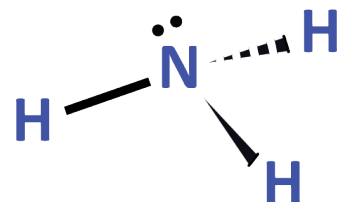
# Valence Bond: $sp^3$ with 3 bonding regions

- 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



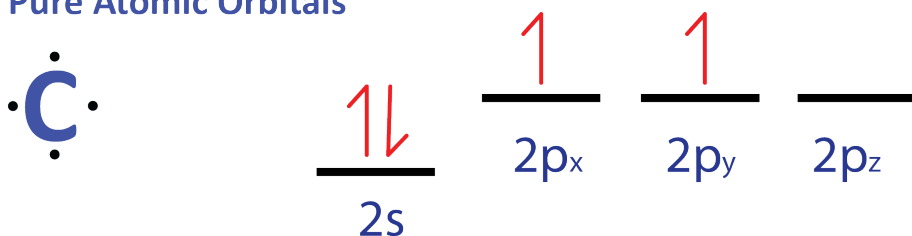
Valence Bond Hybrid Orbitals



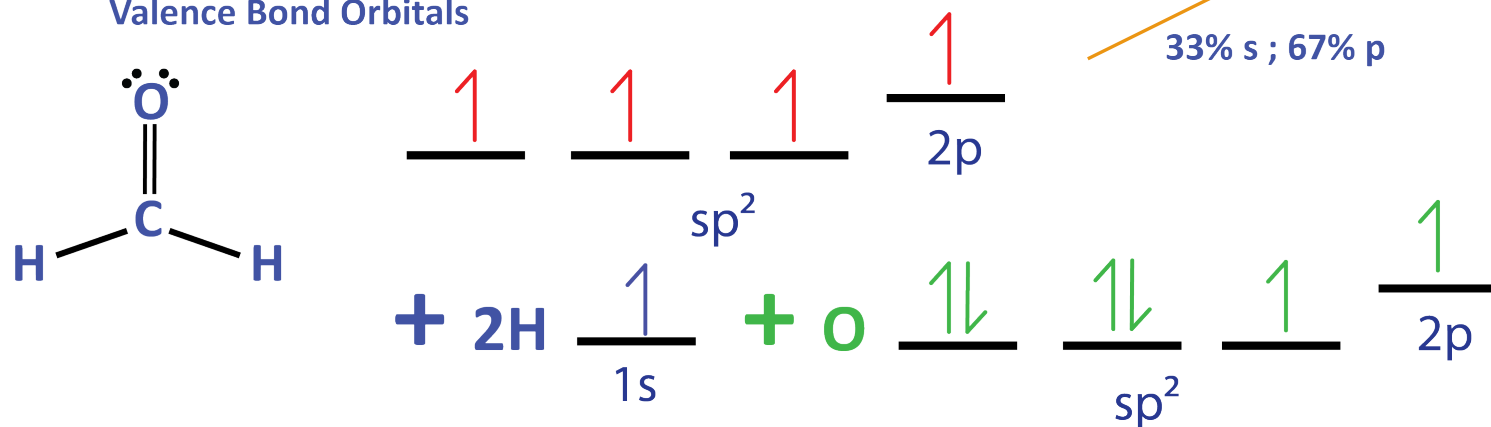
# Valence Bond: $sp^2$

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

Pure Atomic Orbitals



Valence Bond Orbitals



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: $sp^2$

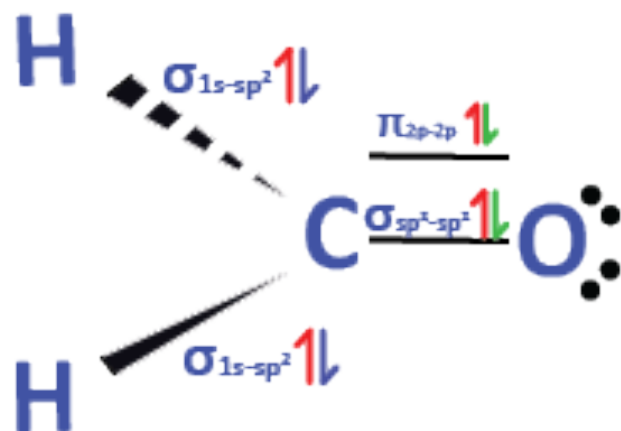
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What you form:

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

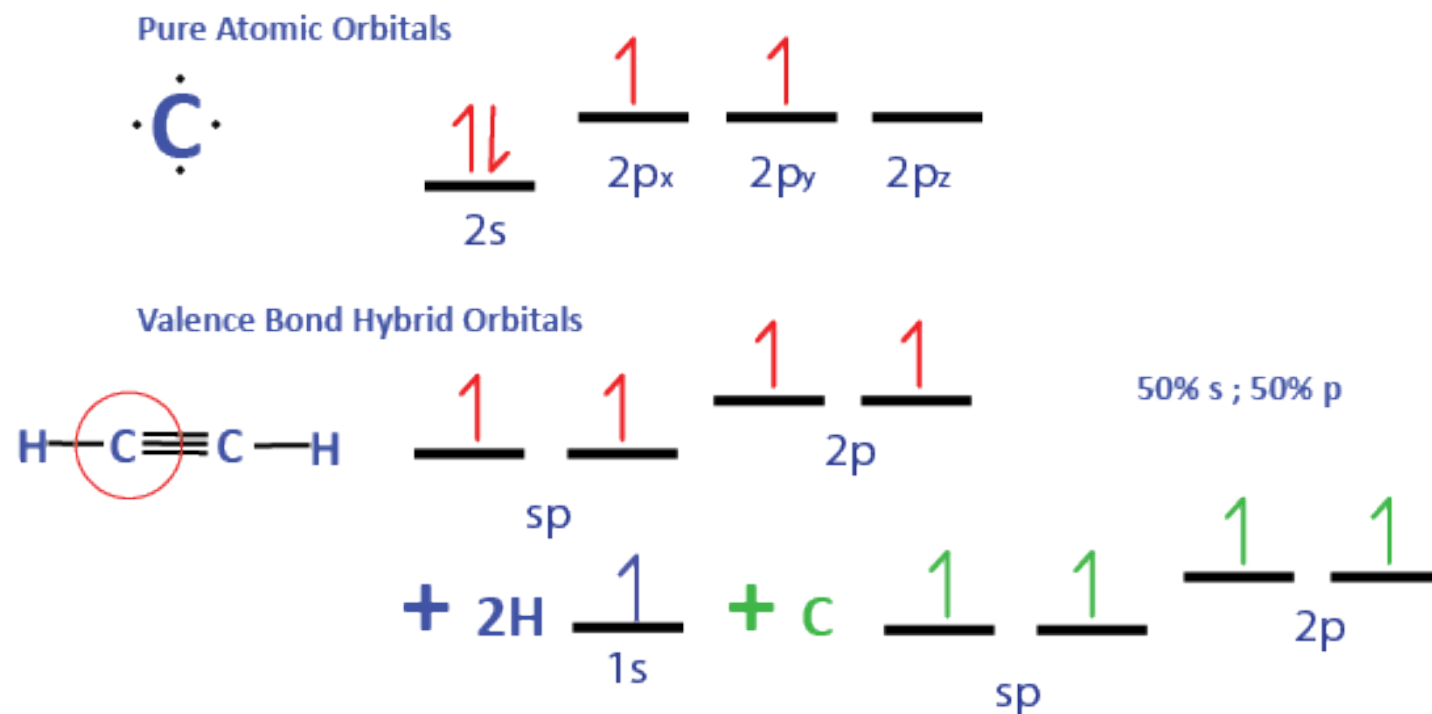
End-on-End overlap (sigma bond) between the hybrid  $sp^2$  of O and the hybrid  $sp^2$  of C

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



# Valence Bond: sp

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



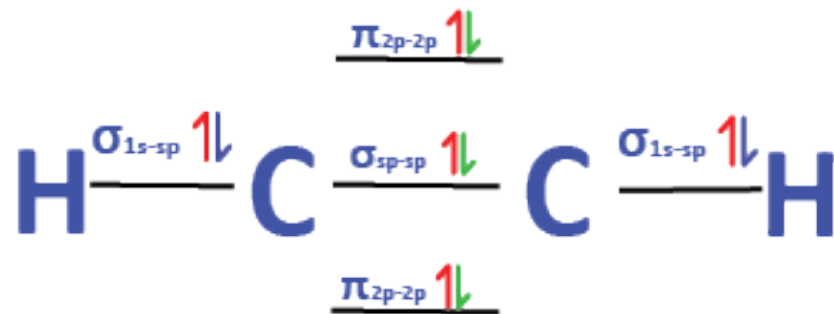
# Valence Bond: sp

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

What you form:

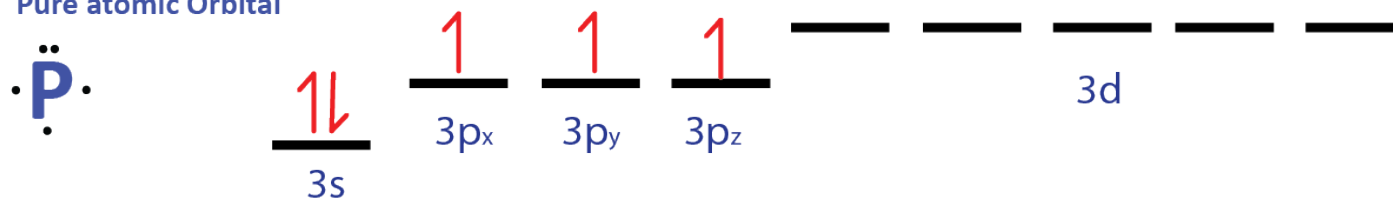
- 1 End-on-End overlap (sigma bond) between the pure 1s of H and the hybrid sp of C
- 1 End-on-End overlap (sigma bond) between the hybrid sp of C and the hybrid sp of C
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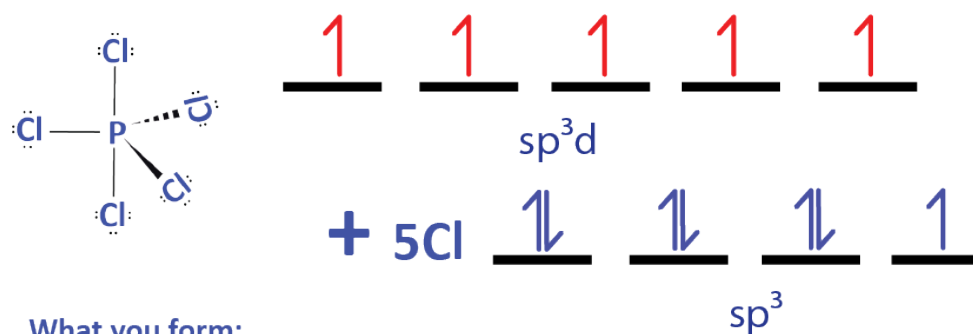
# Valence Bond: $sp^3d$

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

Pure atomic Orbital



Valence Bond Orbitals



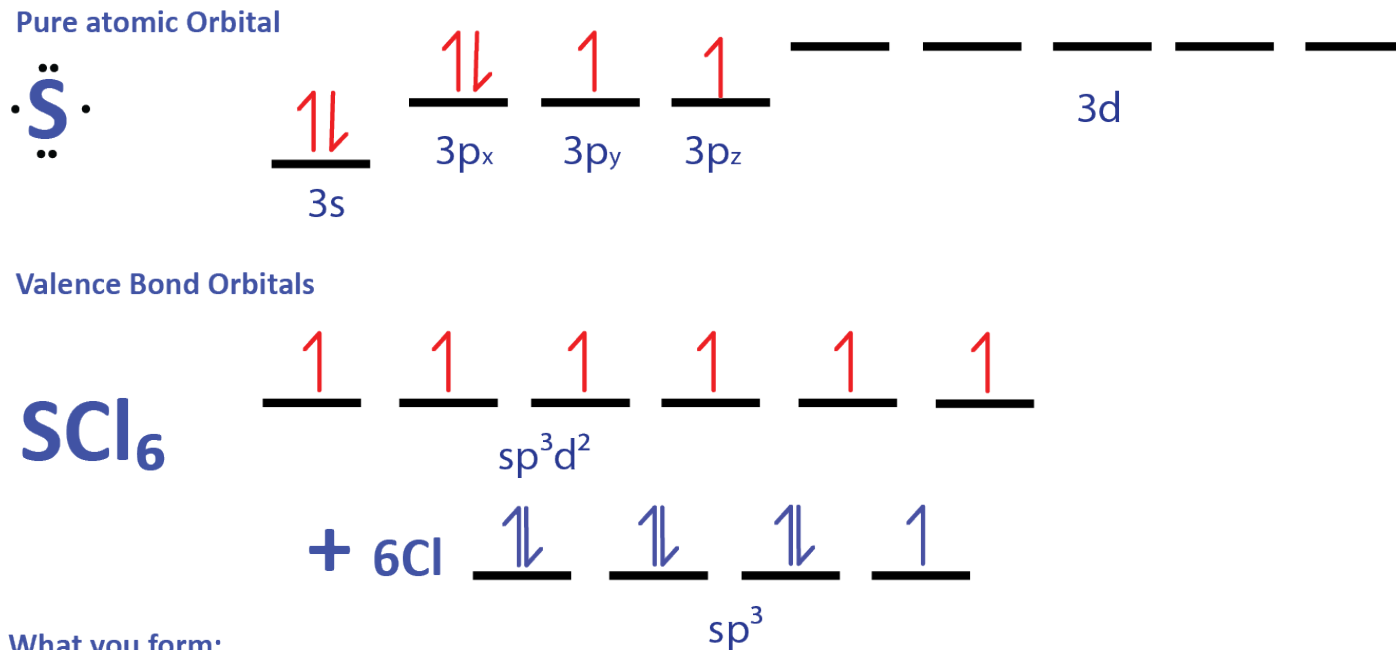
What you form:

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

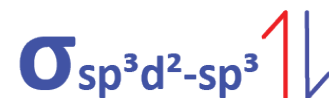


# Valence Bond: $sp^3d^2$

- 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





# Valence Bond Summary

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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>

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

Note: is necessary to memorize this trend with bonds but not necessarily sufficient for the exam. Be able to determine the types of orbitals (pure, hybrid) that go into making the particular bond.

# Question

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Which of the following shapes is possible with  $sp^3d$  hybridization (choose all that apply)?

a. square planar

b. bent

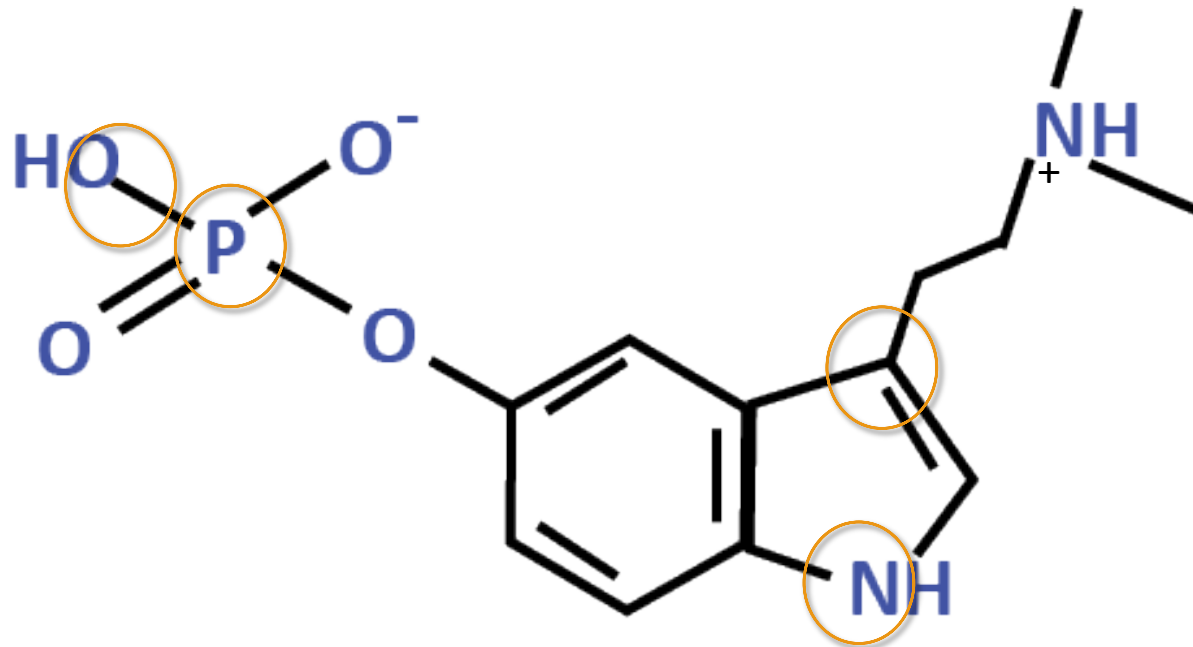
c. linear

d. see-saw

# Organic Molecules

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What is the hybridization of the circled central atoms?



# Organic Molecules

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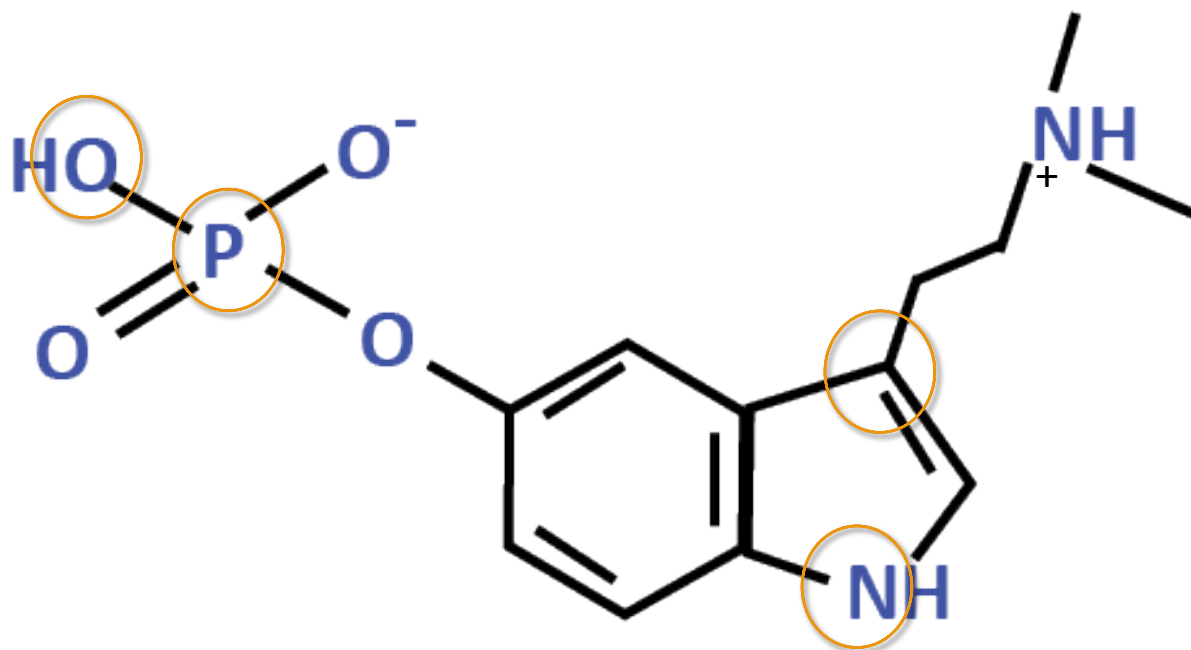
What is the hybridization of the circled central atoms?

Oxygen –  $sp^3$

Nitrogen –  $sp^3$

Carbon –  $sp^2$

Phosphorus –  $sp^3$



# Molecular Orbital Theory

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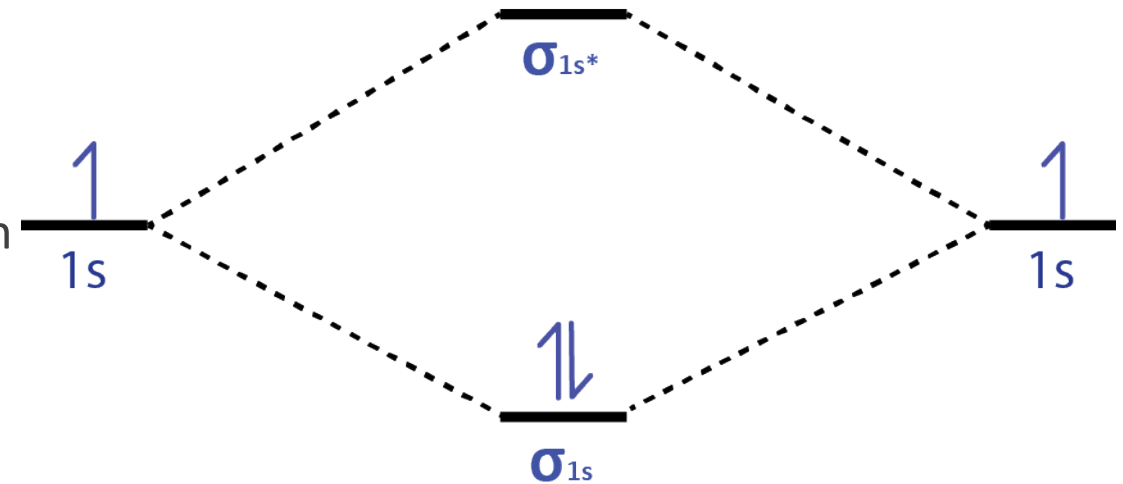
ATOMIC ORBITALS COMBINE TO FORM MOLECULAR ORBITALS

# 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**
  - **Stable**
- **Destructive interference** results in repulsion (zero electron density; anti-bond)
  - **High Energy**
  - **Unstable**

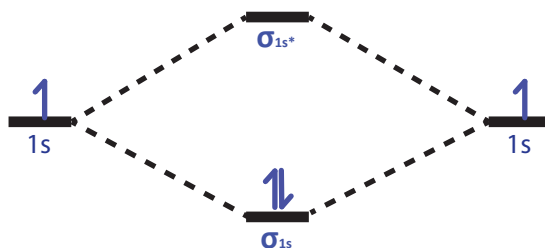
MO Diagram for H<sub>2</sub>



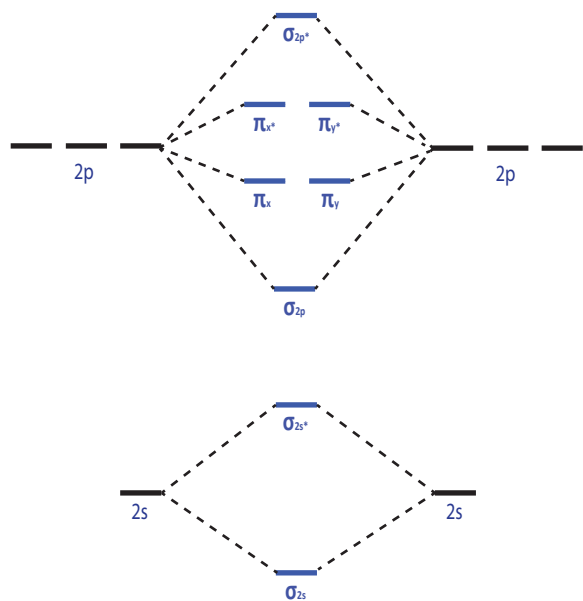
Note: our focus in this class will be on Hydrogen, Helium, row 2 diatomics, and their ions

# Molecular Orbital Theory

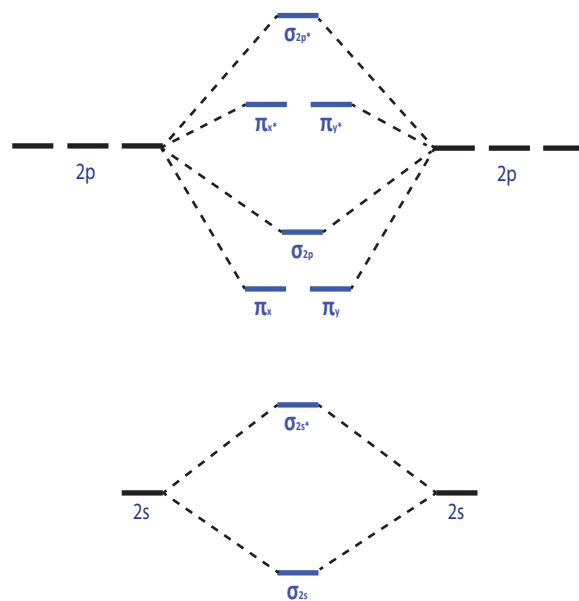
MO Diagram for H<sub>2</sub>



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



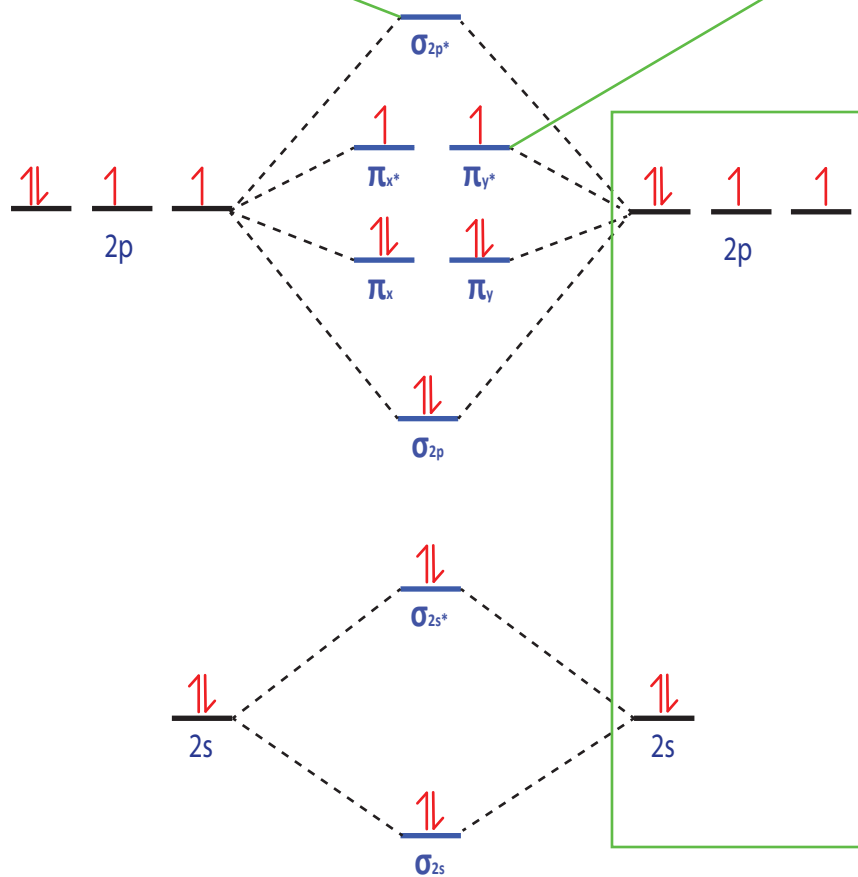
B<sub>2</sub>, N<sub>2</sub>, and C<sub>2</sub>





LUMO: lowest unoccupied molecular orbital

HOMO: highest occupied molecular orbital



## Conclusions from this diagram:

Bond Order =  $\frac{1}{2}$  (Bonding electrons - Anti-bonding electrons)

Bond Order =  $\frac{1}{2}$  (8 - 4) = 2

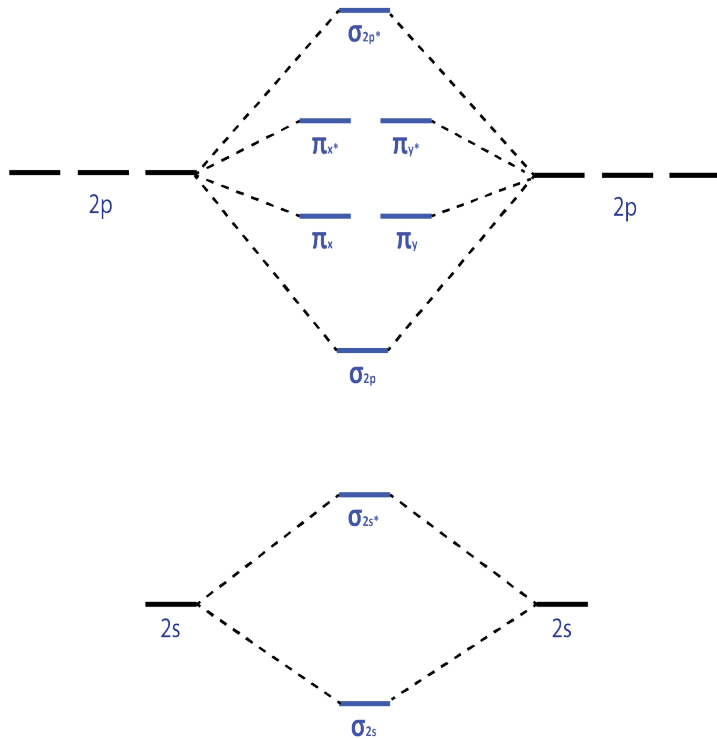
Oxygen is **paramagnetic**, meaning it contains unpaired electrons.

Paramagnetic compounds are **attracted** to a magnetic field.

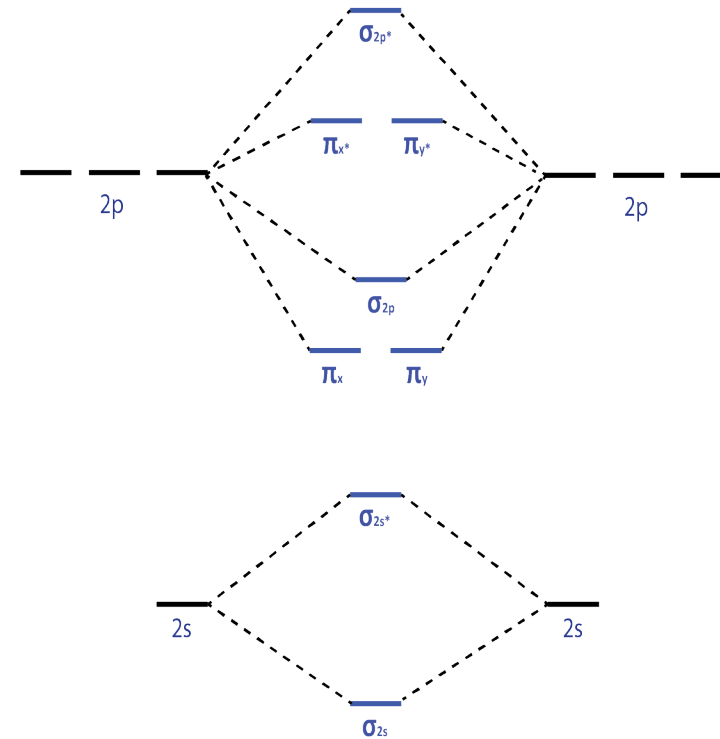


# Molecular Orbital Theory

$O_2$  and  $F_2$

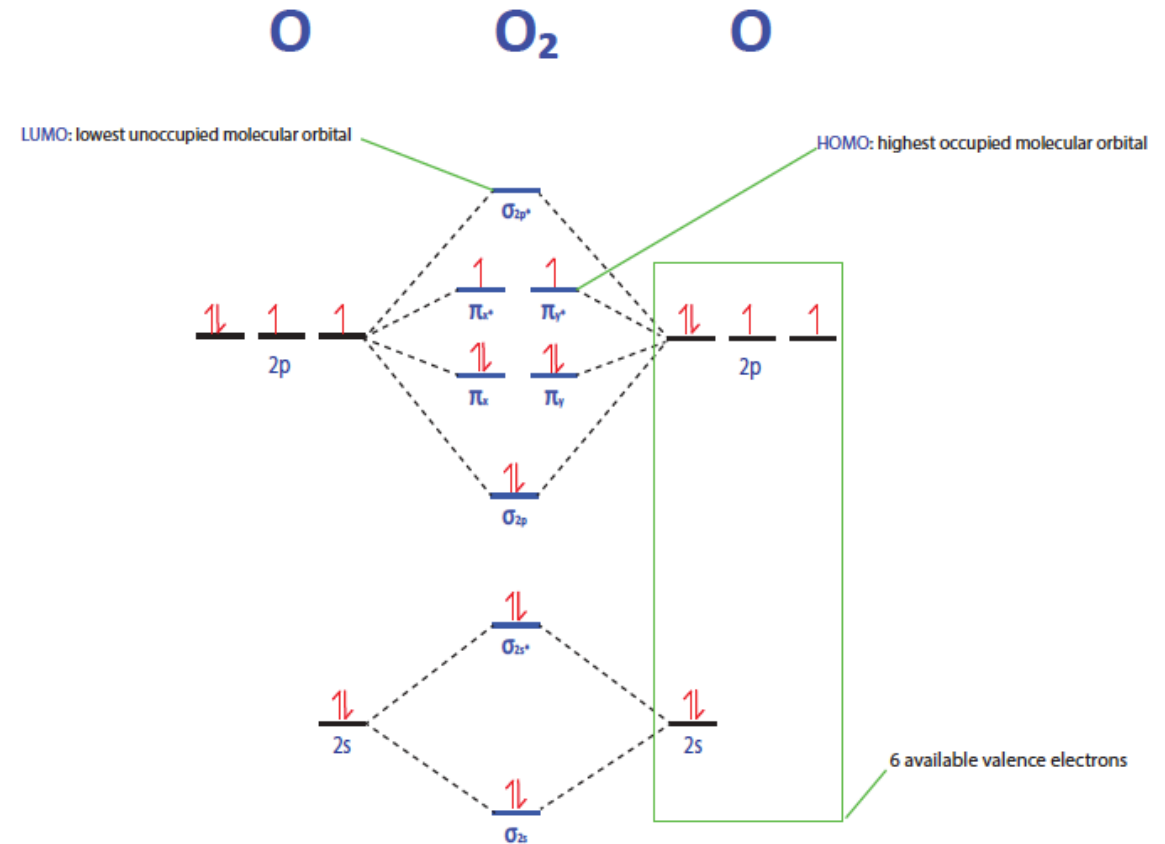


$B_2$ ,  $N_2$ , and  $C_2$



# Molecular Orbital Theory: Conclusions

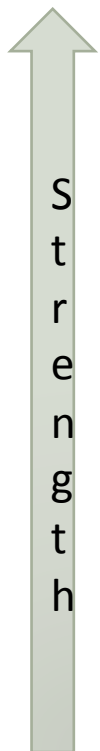
- Molecular Orbital Theory provides three conclusions that Valence Bond and VSEPR are unable to explain:
  1. MO Theory can describe fractional bond orders ascribed to charged molecules and resonance structures using anti-bonding and bonding orbitals
  2. MO Theory can identify the magnetic properties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



# Intermolecular Forces

# Intermolecular Forces

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- 3 main types of IMF's:
  - Hydrogen bonding (extra strong dipole-dipole)
    - Determine relative strength based on number of hydrogen bonds or electronegative difference (example: O-H vs. N-H)
  - Dipole-dipole
    - Determine relative strength based on electronegativity (Lewis Structures are important)
    - Consider polarity when comparing similar molecules in the same period
  - Dispersion forces (present in all molecules)
    - Determine relative strength based on MW, polarizability, shape/"stackability"
    - Consider polarizability when comparing similar molecules with atoms in the same group (ex. Halogen diatomics)

The name of the game for IMF's: Predict the dominant IMF's a molecule and compare relative physical properties