Unit 4 Review 1

VALENCE BOND AND MOLECULAR ORBITAL THEORIES

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** (Unit 2)
  - Practical, but not fully accurate especially when it comes to physical properties and delocalized electrons

Hybrids

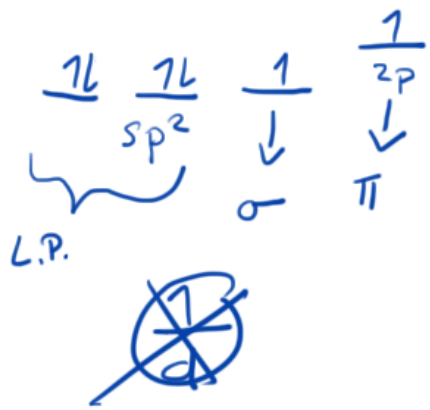
- Molecular Orbital Theory
  - Diagrams
  - Answers three fundamental questions regarding your molecule: bond order, magnetism, HOMO-LUMO gap
  - Sigma and pi orbitals
  - Focuses on the electrons as "waves"
  - Depends on the number of electrons
  - Accurate, but very complex for polyatomic molecules; important for physical properties and delocalization of electrons

Bonds, Antibonds

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)

Dr. B's Rules



Valence Bond Summary

Hybrids

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

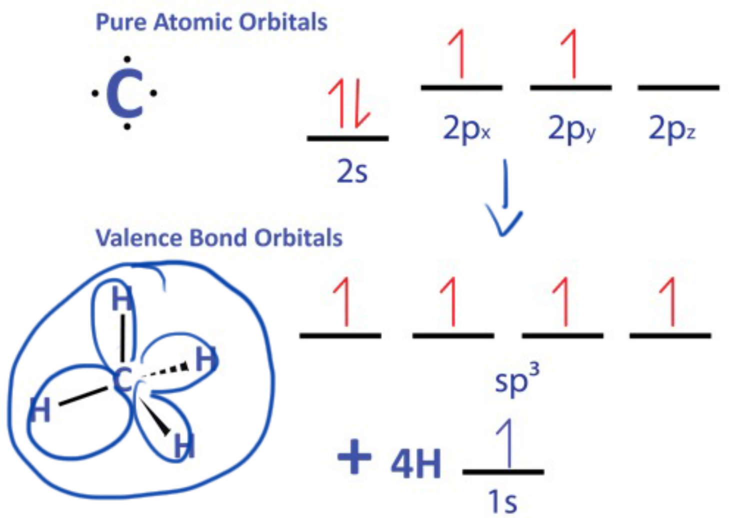
1. Sigma bonds are almost always overlapping hybrid orbitals (with the exception of hydrogen's pure 1s)
2. Pi bonds are always overlapping valence p-orbitals.

σ: rotation

π: Can delocalize

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

25% s ; 75% p

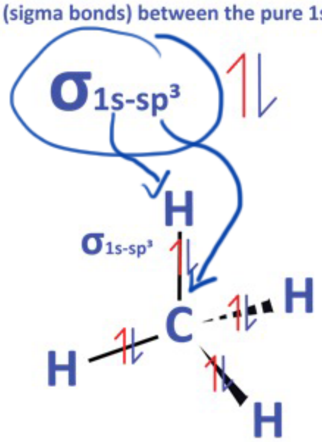
This looks better for forming four sigma (end-on-end) bonds

Valence Bond: sp^3

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

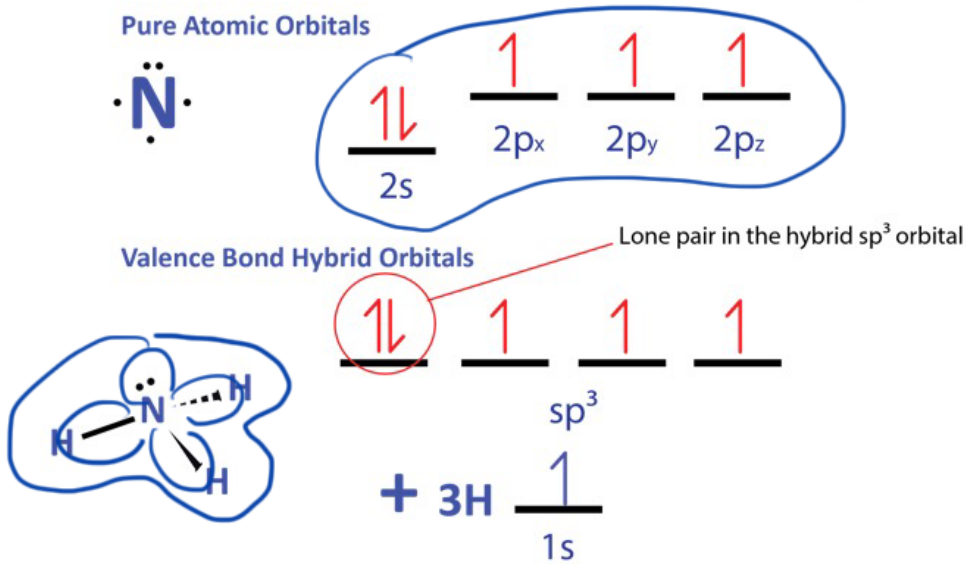
What you form:

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



Valence Bond: sp^3 with 3 bonding regions

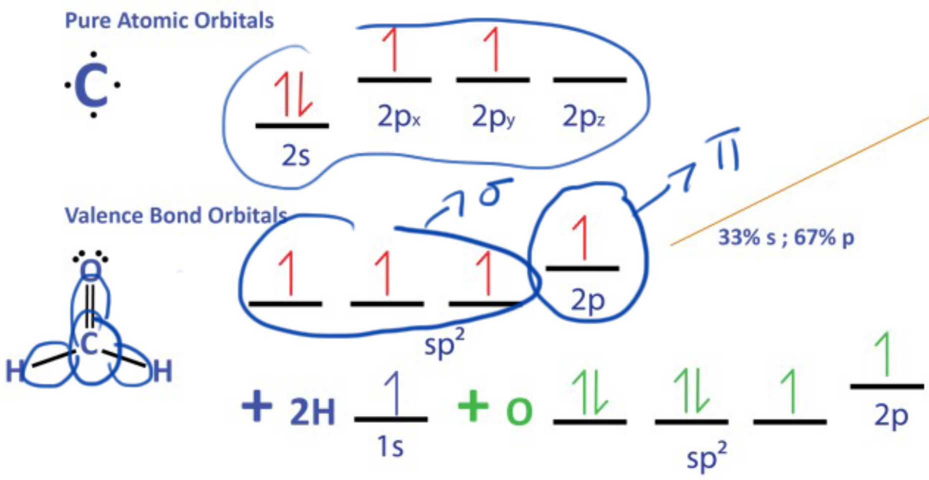
- Ammonia has sp^3 hybridization with only 3 bonding regions
- This is because ammonia still has a tetrahedral electronic geometry, resulting in paired electrons in one of the sp^3 orbitals



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

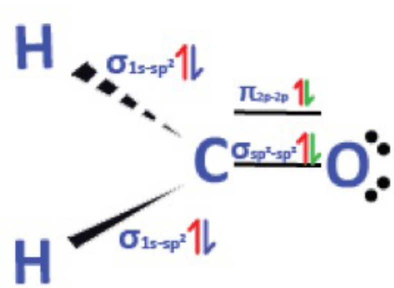
Can you spot the lone pairs in oxygen in the valence bond orbitals?

Valence Bond: sp^2

What you form:

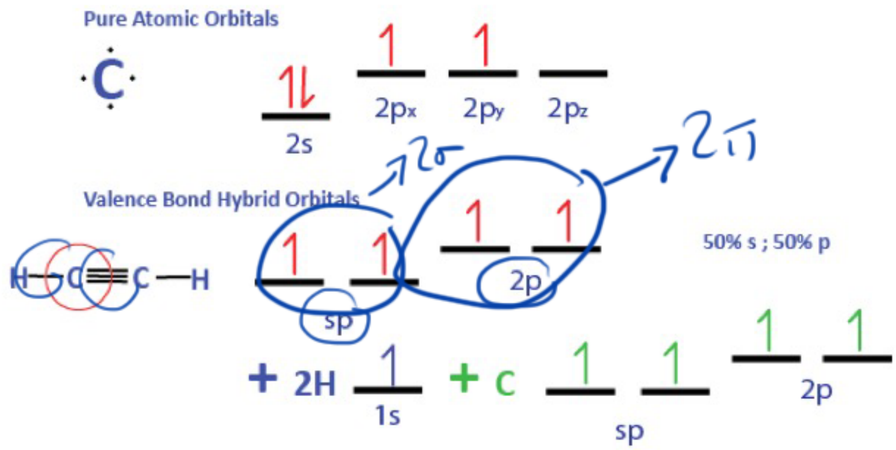
End-on-End overlap (sigma bonds) between the pure 1s of H and the hybrid sp^2 of C
End-on-End overlap (sigma bond) between the hybrid sp^2 of O and the hybrid sp^2 of C
Side-by-Side overlap (pi bond) between the pure 2p of O and the pure 2p of C

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



Valence Bond: sp

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



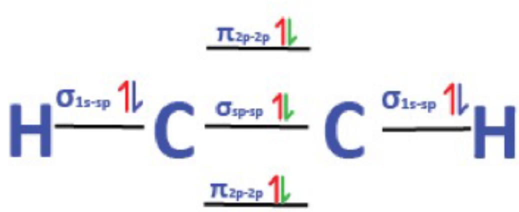
Valence Bond: sp

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

What you form:

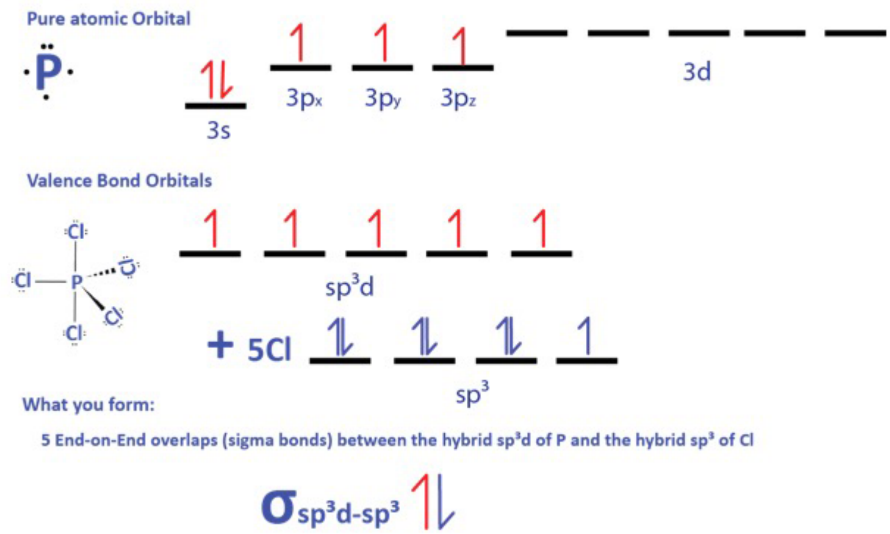
- 1 End-on-End overlap (sigma bond) between the pure 1s of H and the hybrid sp of C
- 1 End-on-End overlap (sigma bond) between the hybrid sp of C and the hybrid sp of C
- 2 Side-on-Side overlaps (pi bonds) between the pure 2p of C and the pure 2p of C

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



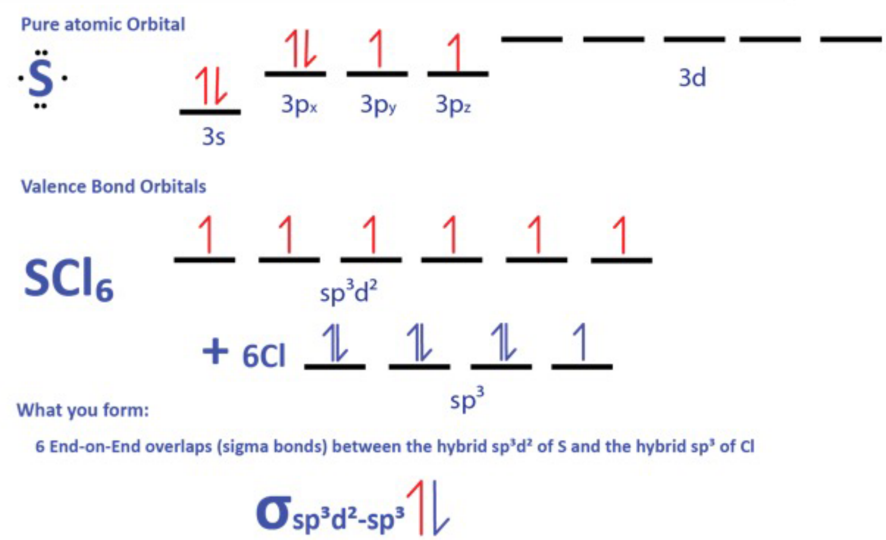
Valence Bond: sp^3d

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



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

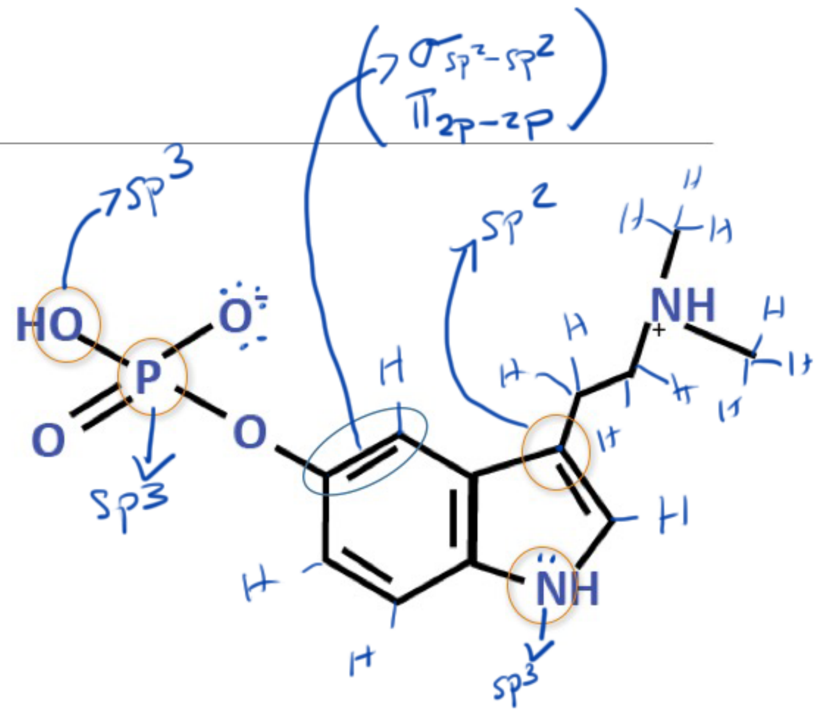


Organic Molecules

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?



Organic Molecules

What is the hybridization of the circled central atoms?

Oxygen – sp^3

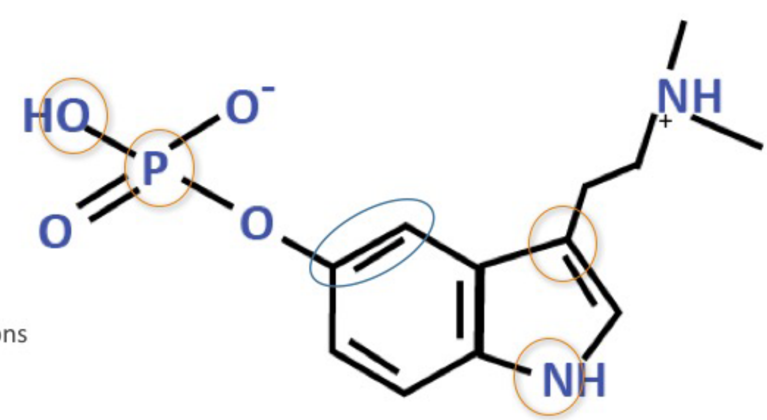
Nitrogen – sp^3

Carbon – sp^2

Phosphorus – sp^3

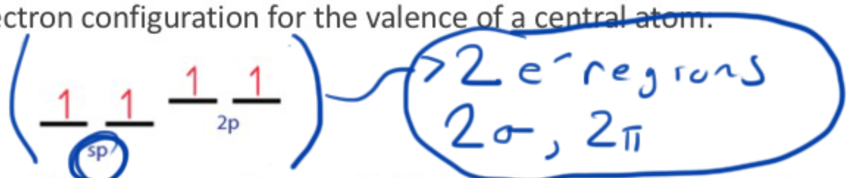
Overlapping double bond is:

- Head on overlap of sp^2 of carbons
- Side-by-side overlap of the pure 2p of the carbons



VB Challenge Question

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



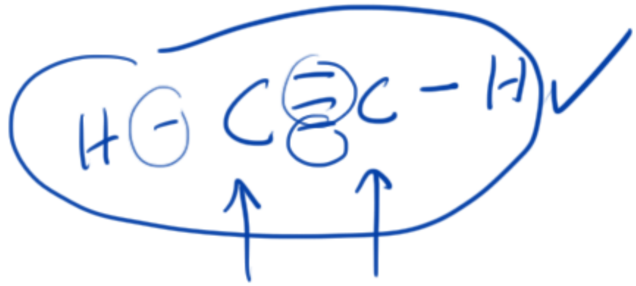
This configuration could be the central atom of which of the following molecules:

CN^- → sp   :C≡N

NO_2 → sp²   O–N̈=O

CO_3^{2-} → sp²

CO_2 → O=C=O ✓



Valence Bond Question

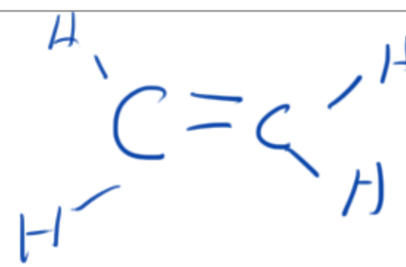
pi bond formation
011 3.0 points

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.

→ π   2p

1. π; sp^2
2. π; $1p$
3. π; $2p$
4. σ; sp^2
5. σ; sp^3

π_{2p-2p}

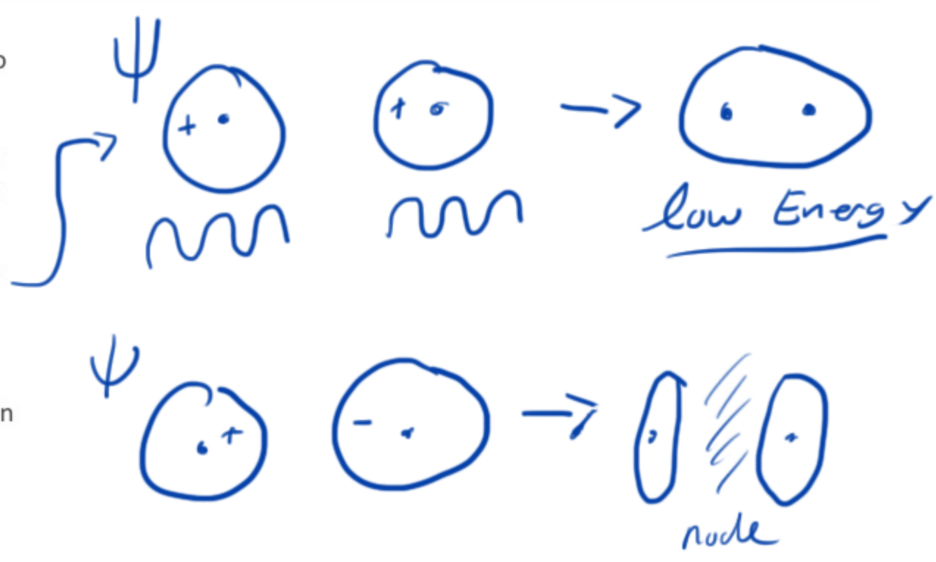


Molecular Orbital Theory

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**

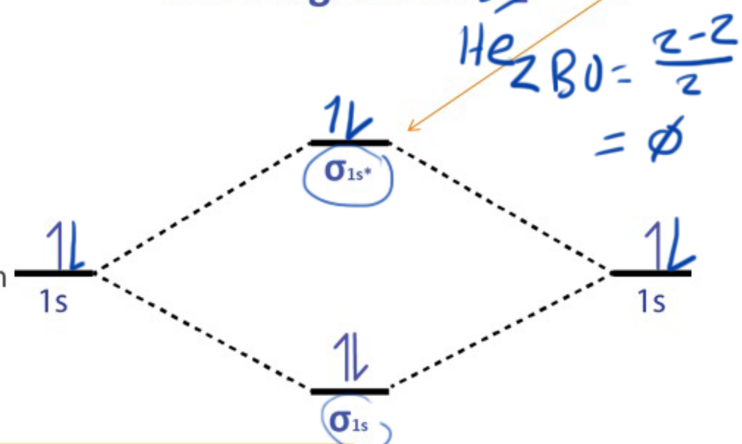


For every bonding orbital, there is a higher energy anti-bonding orbital

Molecular Orbital Theory

- 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**

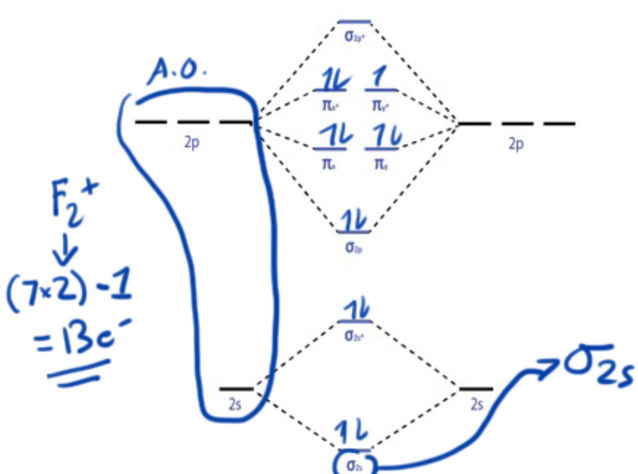
MO Diagram for ~~H_2~~



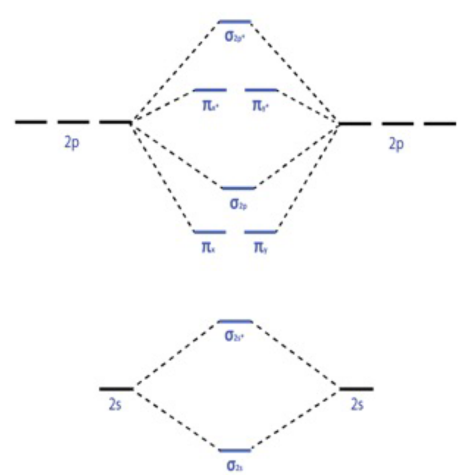
Note: our focus in this class will be on Hydrogen, Helium, row 2 diatomics, and their ions

Molecular Orbital Theory

O_2 and F_2

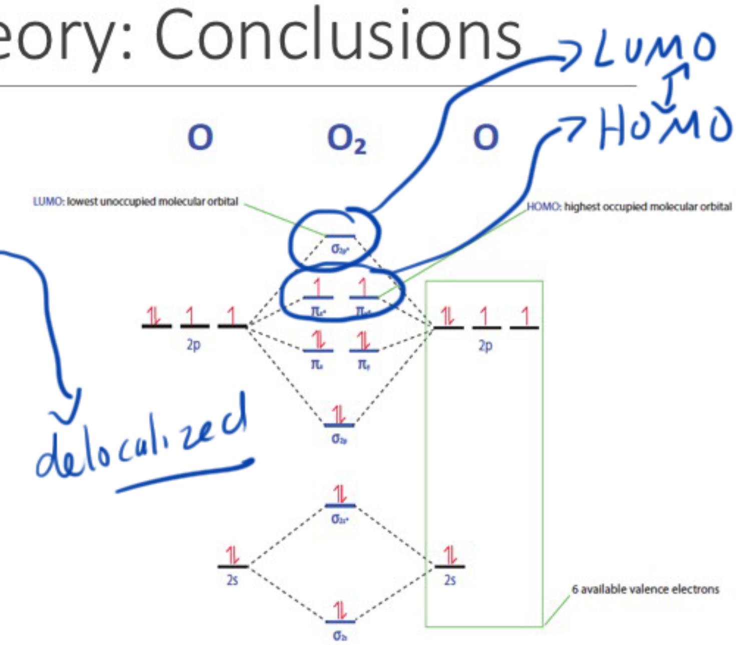


B_2, N_2, and C_2



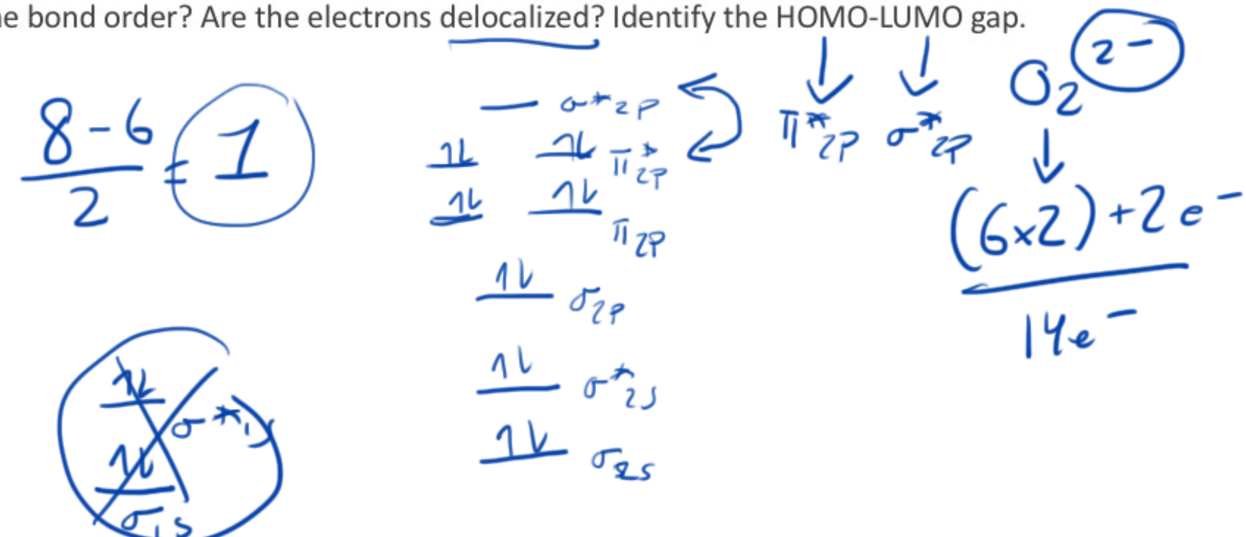
Molecular Orbital Theory: Conclusions

- 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)



MO Theory Question

What is the molecular orbital electron configuration for O_2^{2-}? Does this molecule exist? What is the bond order? Are the electrons delocalized? Identify the HOMO-LUMO gap.

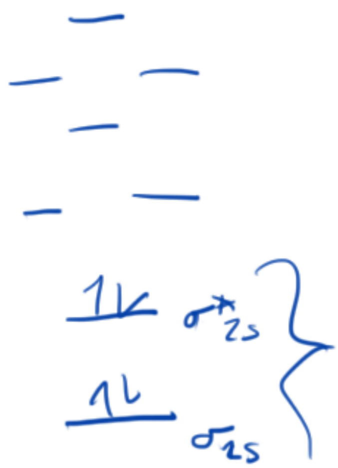


MO Theory Question

Does Be_2 exist? How does molecular orbital theory prove this?

↓

NO!



Be_2

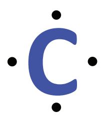
↓

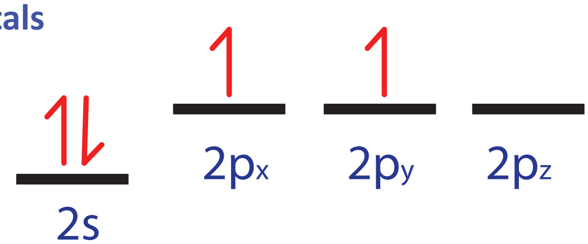
$2(2) = 4e^-$

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

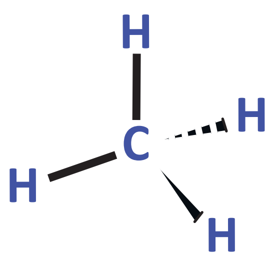
Valence Bond Theory

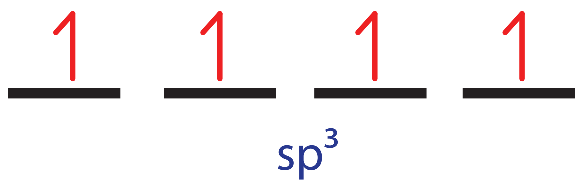
Pure Atomic Orbitals



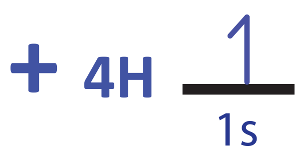


Valence Bond Hybrid Orbitals



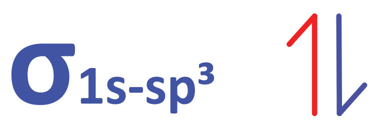


25% s ; 75% p

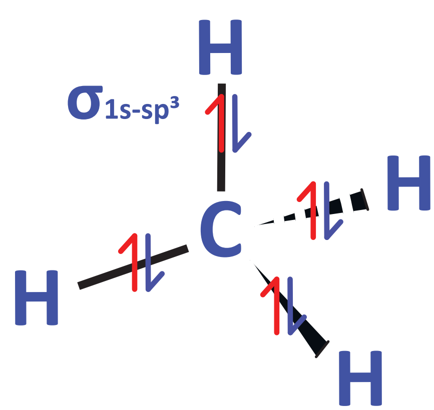


What you form:

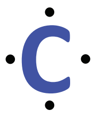
4 End-on-End overlaps (sigma bonds) between the pure 1s of H and the hybrid sp^3 of C

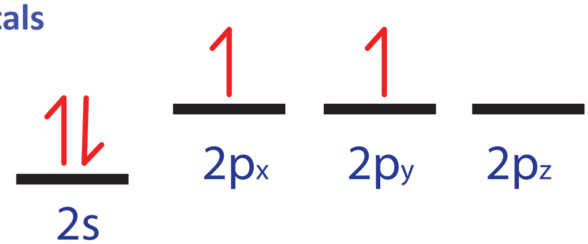


Your hybrid orbital shape (sp3,sp2,sp,etc.) absolutely depends on the molecule / surrounding atoms

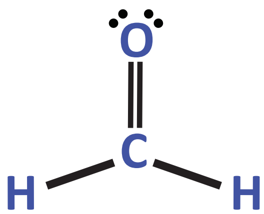


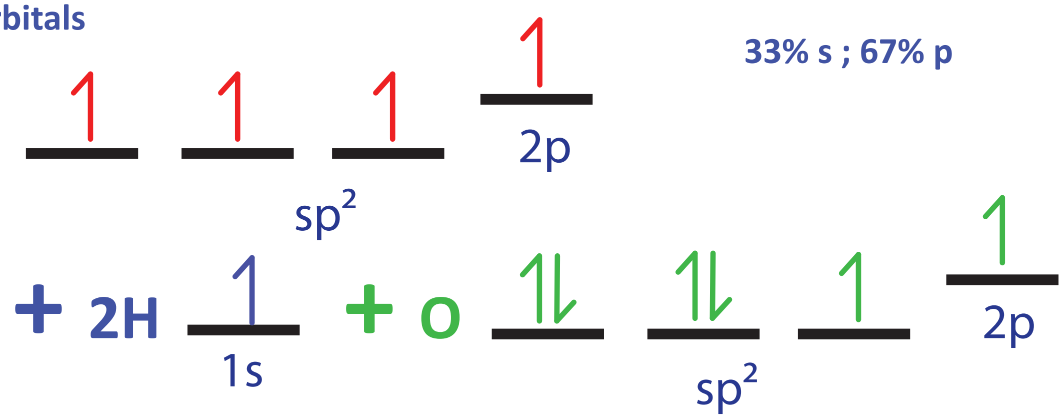
Pure Atomic Orbitals





Valence Bond Orbitals



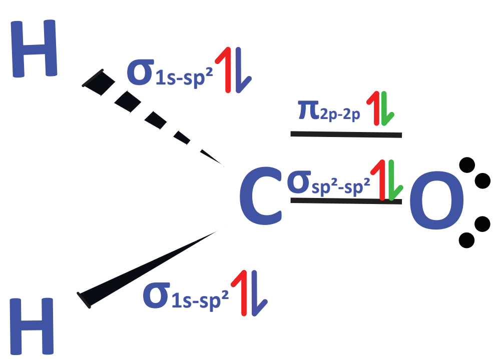


33% s ; 67% p

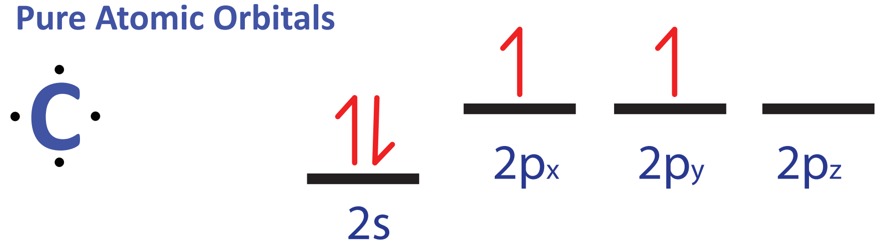
What you form:

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

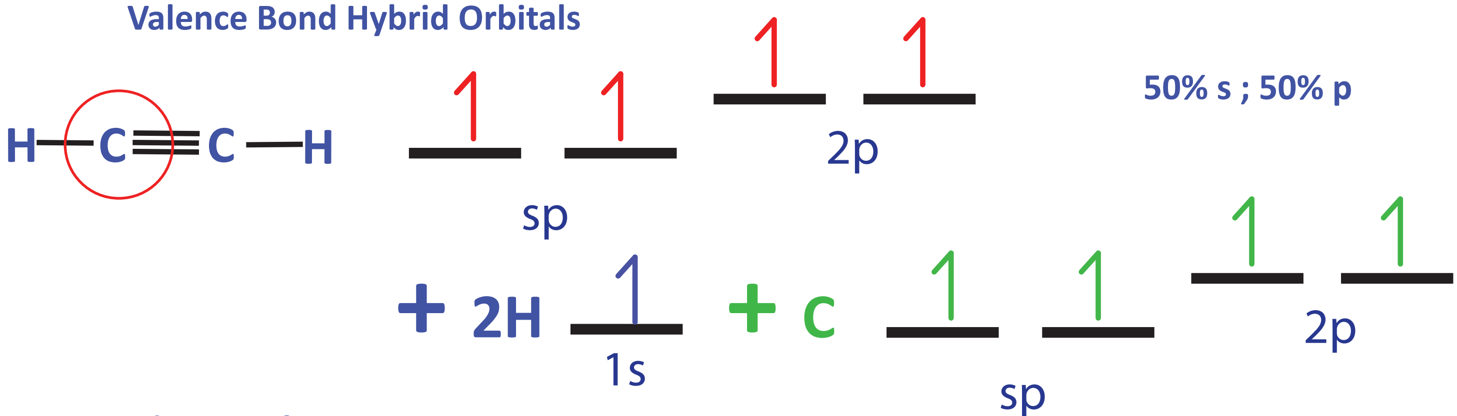
$\sigma_{1s\text{-}sp^2}$ ↑↓ $\sigma_{sp^2\text{-}sp^2}$ ↑↓ $\pi_{2p\text{-}2p}$ ↑↓



Pure Atomic Orbitals

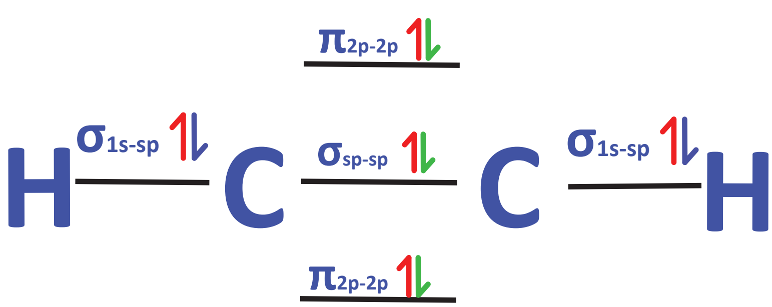


Valence Bond Hybrid Orbitals

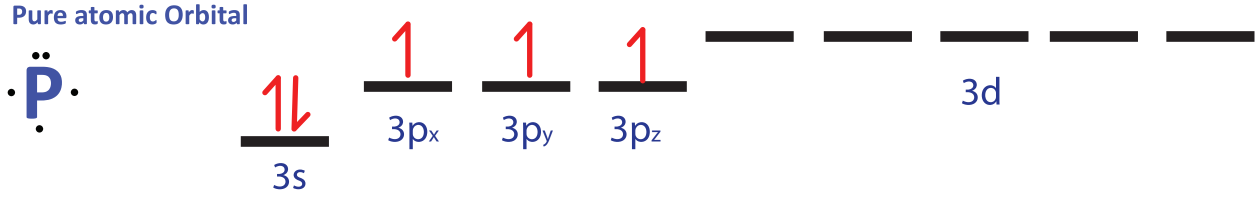


What you form:

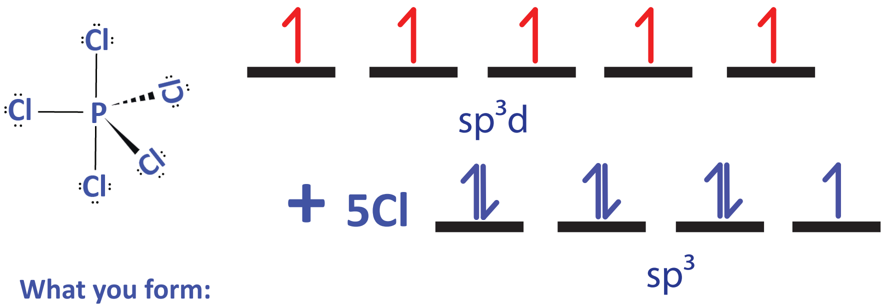
1 End-on-End overlap (sigma bond) between the pure 1s of H and the hybrid sp of C
1 End-on-End overlap (sigma bond) between the hybrid sp of C and the hybrid sp of C
2 Side-on-Side overlaps (pi bonds) between the pure 2p of C and the pure 2p of C



Pure atomic Orbital



Valence Bond Orbitals

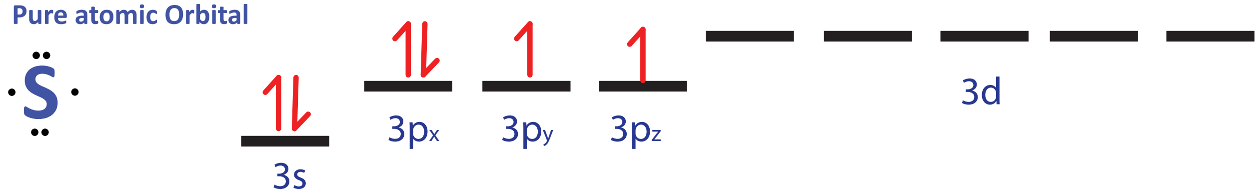


What you form:

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

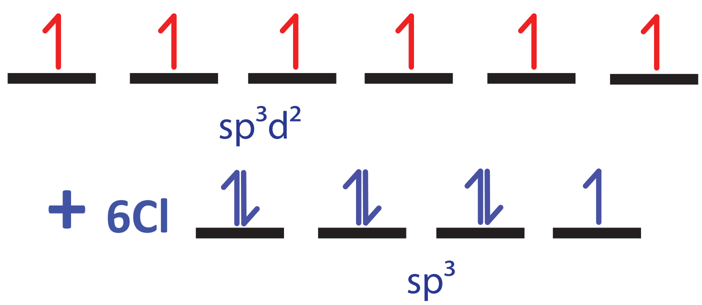
$\sigma_{sp^3d-sp^3}$ ↑↓

Pure atomic Orbital



Valence Bond Orbitals

SCl_6



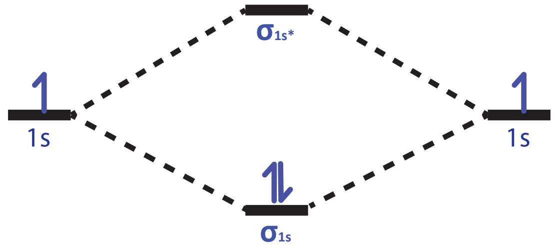
What you form:

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

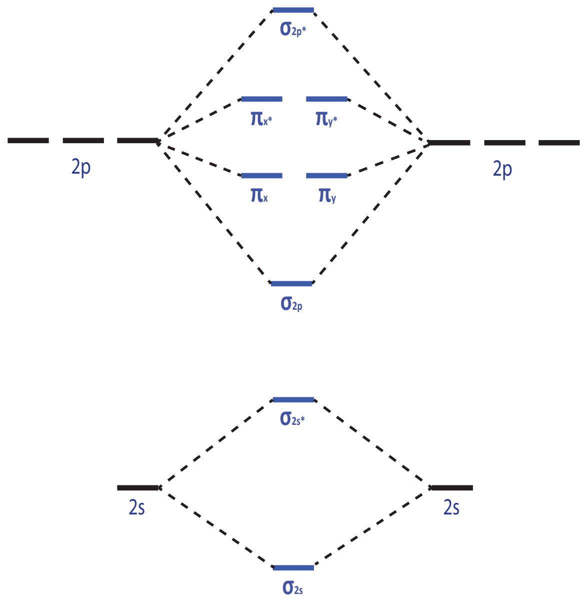
$\sigma_{sp^3d^2-sp^3}$ ↑↓

Molecular Orbital Theory

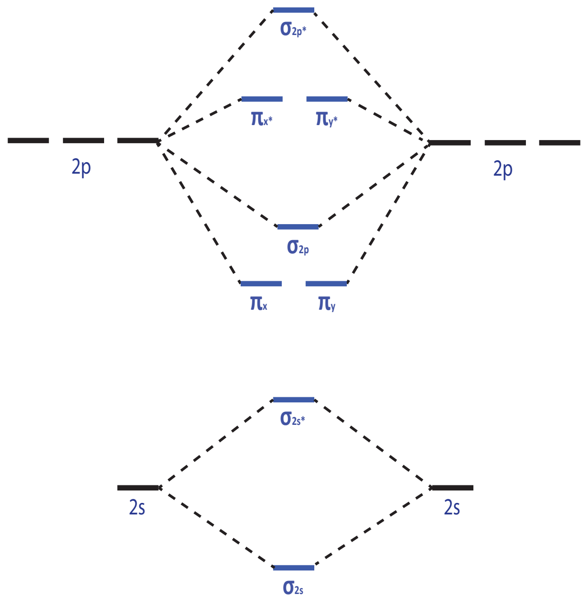
MO Diagram for H_2

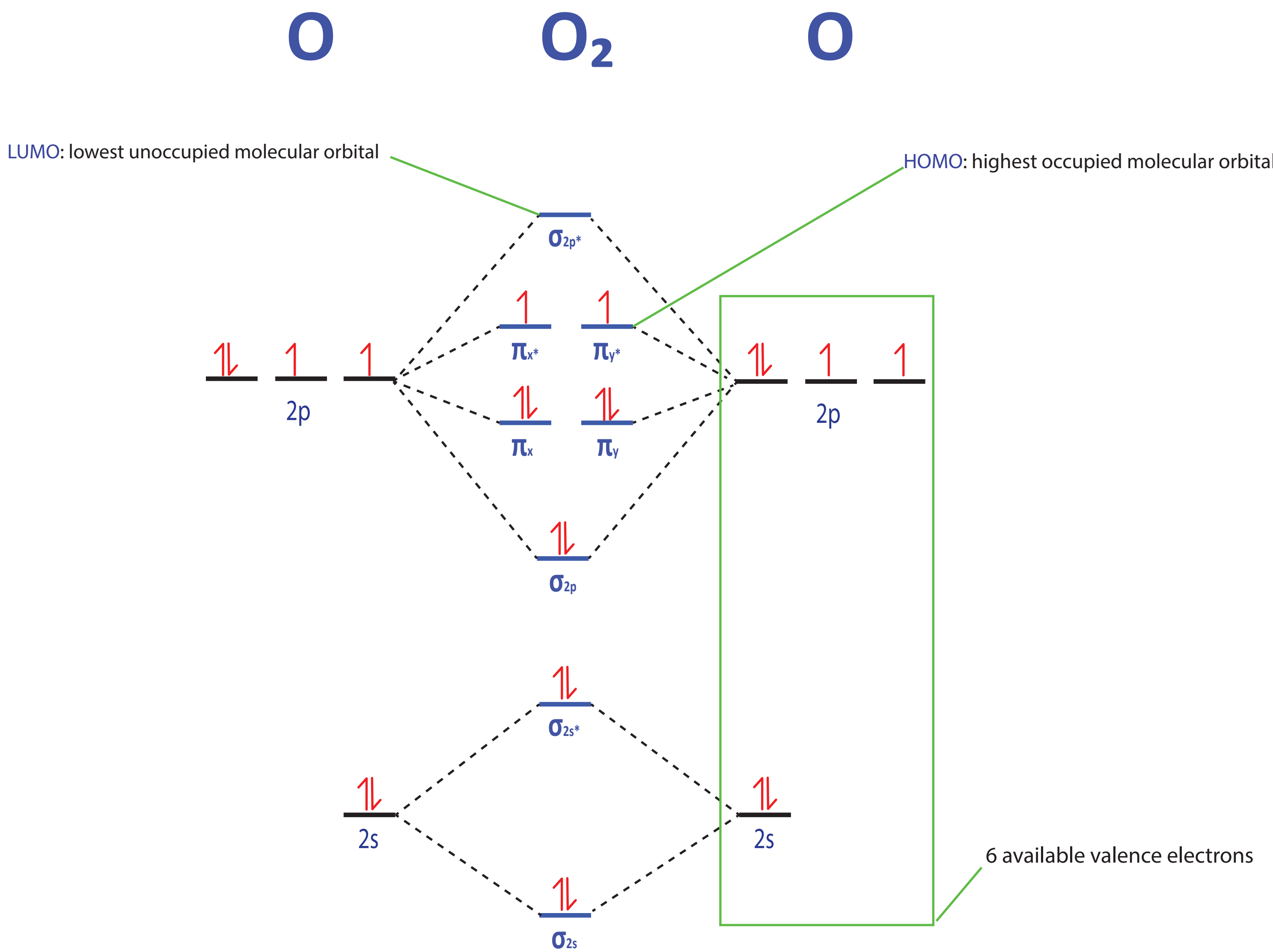


O_2 and F_2



B_2, N_2, and C_2





Conclusions from this diagram:

Bond Order = ½ (Bonding electrons - Anti-bonding electrons)
Bond Order = ½ (8 - 4) = 2

Oxygen is paramagnetic, meaning it contains unpaired electrons.
Paramagnetic compounds are attracted to a magnetic field.