

Chapter 4: Chemical Bonding & Molecular Structure

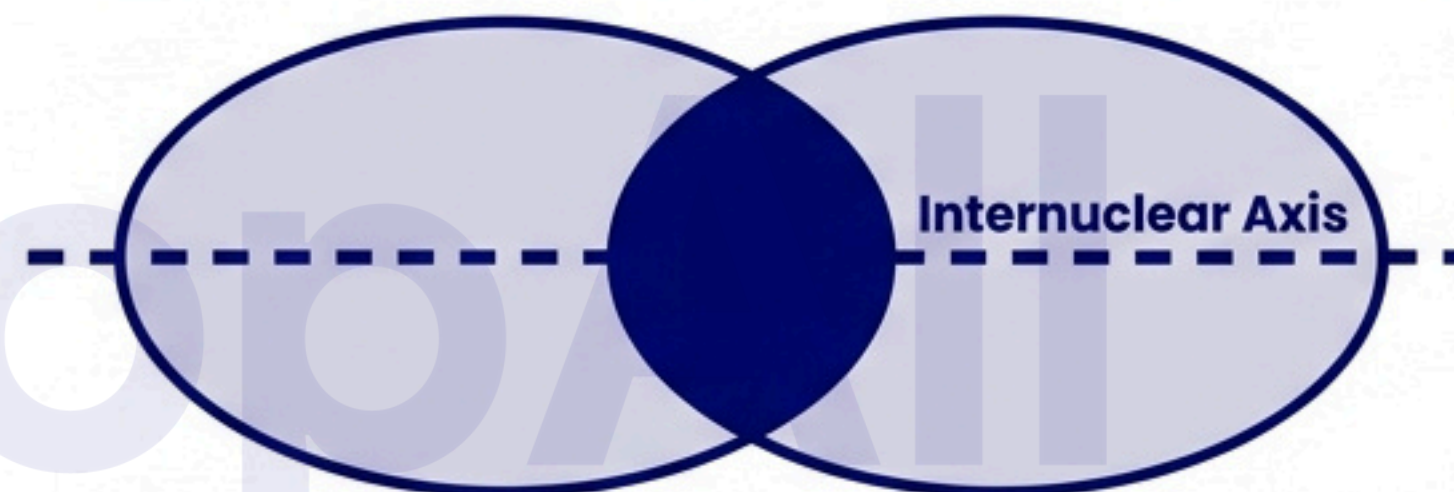
Sigma and Pi Bonds

Understanding Orbital Overlap in
Covalent Bonding

Sigma (σ) Bond: Axial Overlap

The Foundation of Covalent Bonds

- Formed by the **end-to-end (head-on) overlap** of bonding orbitals.
- Occurs directly along the **internuclear axis**.
- **High Strength:** Stronger than a π bond due to a larger extent of overlapping.
- **Symmetry:** Electron density is symmetrical around the bond axis.





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$$E=mc^2$$



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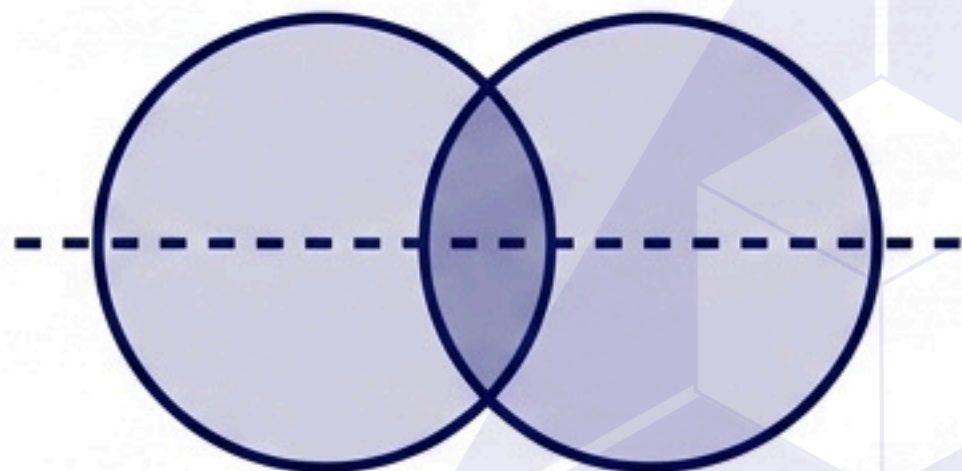
Key Highlights

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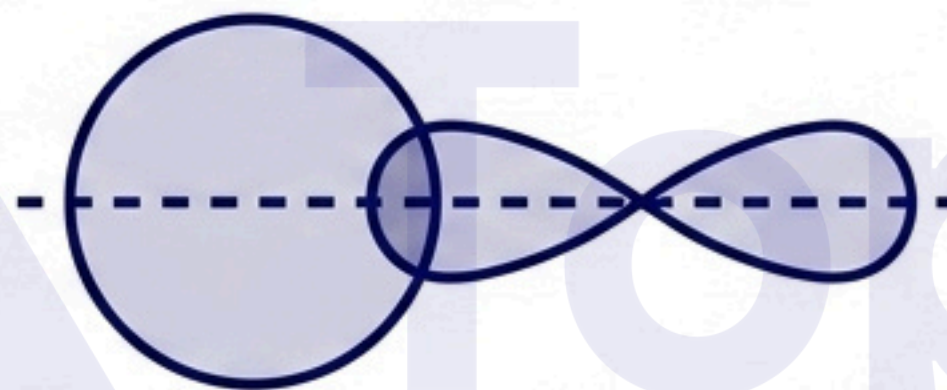
Three Combinations for σ Overlap

s-s Overlap



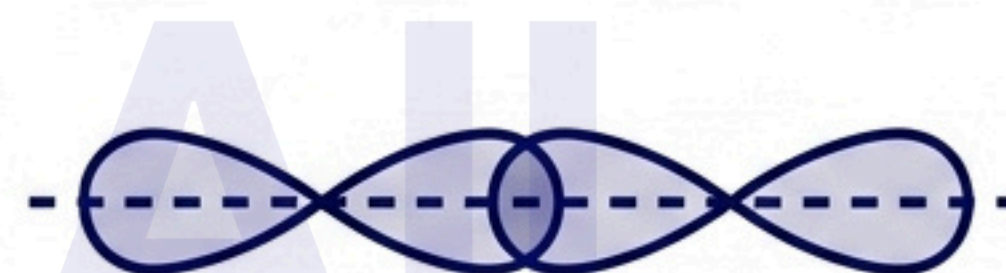
Overlap of two half-filled s-orbitals.
(e.g., H_2 molecule).

s-p Overlap



Half-filled s-orbital of one atom merges with a half-filled p-orbital of another.

p-p Overlap

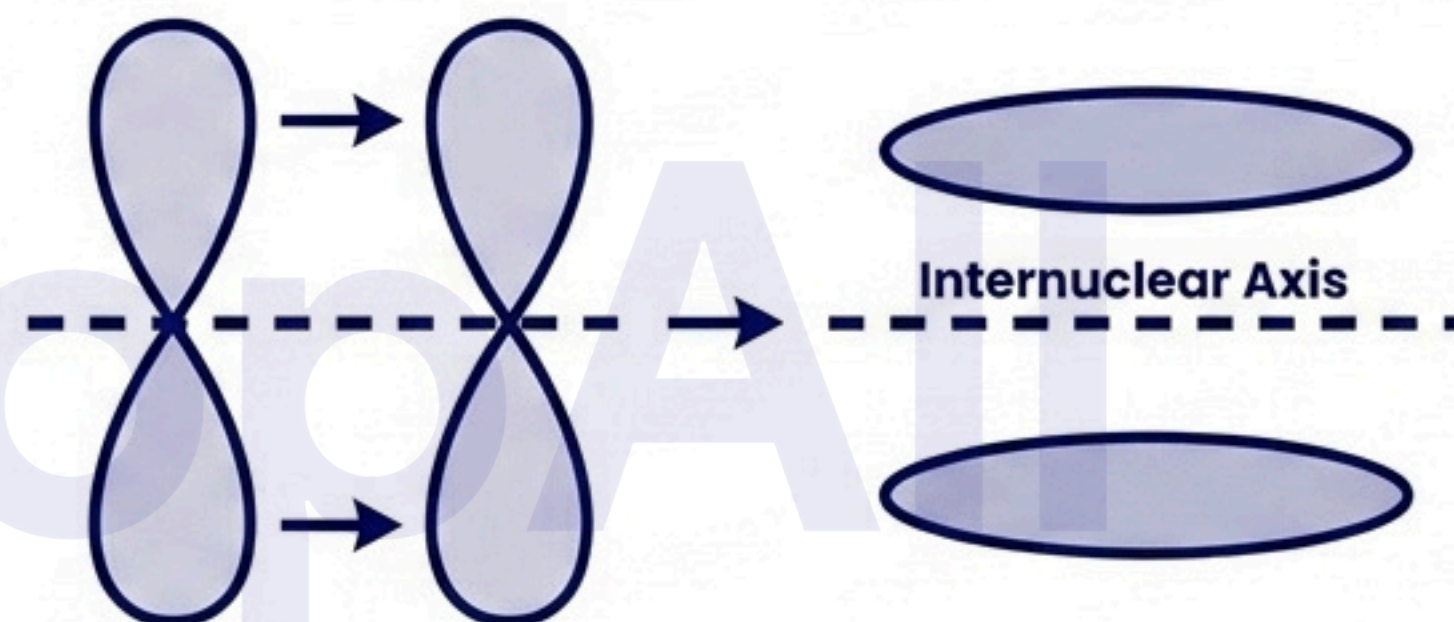


Two half-filled p-orbitals approaching each other head-on.

Pi (π) Bond: Lateral Overlap

The Secondary Bond

- Orbitals remain **parallel to each other** and **perpendicular to the internuclear axis**.
- **Sidewise Overlap:** Orbitals merge laterally rather than head-on.
- **Lower Strength:** Weaker than a σ bond because the extent of overlapping is smaller.
- **Electron Cloud:** Forms two saucer-type charged clouds located **above and below** the plane of the atoms.



Molecule Architecture: Bond Composition

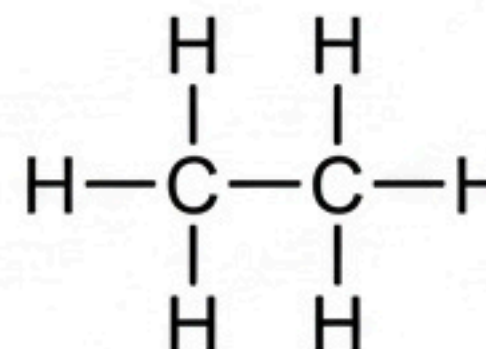


Multiple bonds between atoms are always formed by adding π bonds to a foundational σ bond.

Single Bond

1 σ bond

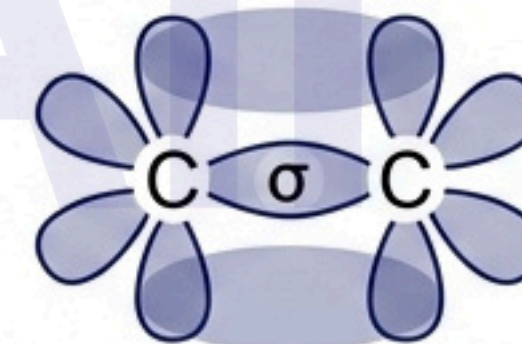
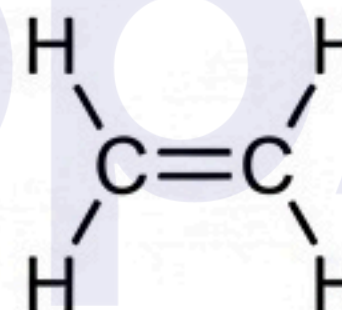
Formed purely by head-on axial overlap.



Double Bond

1 σ bond + 1 π bond

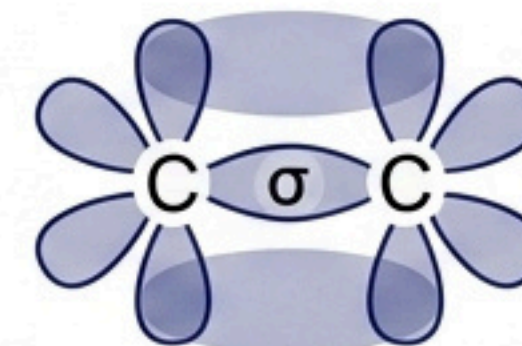
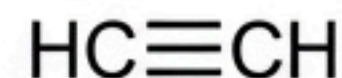
Unhybridized p -orbitals overlap sidewise above and below the σ framework.



Triple Bond

1 σ bond + 2 π bonds

One foundational axial overlap surrounded by two perpendicular sidewise overlaps.



Diagnostic Comparison: σ vs. π

Parameter	Sigma (σ) Bond	Pi (π) Bond
Overlap Type	Head-on / Axial	Sidewise / Lateral
Bond Strength	Stronger (larger extent of overlap)	Weaker (smaller extent of overlap)
Symmetry	Symmetrical around the internuclear axis	Asymmetrical (saucer electron clouds above & below axis)
Formation Sequence	Formed independently (foundation of all single bonds)	Formed only after a σ bond exists
Orbital Types	s-s, s-p, or p-p overlapping	Only p-p (or p-d, d-d) overlapping

Key Takeaways



Overlap Dictates Strength: The extent of atomic orbital overlap determines covalent bond strength. σ bonds are inherently stronger than π bonds because head-on overlap covers a larger physical area than sidewise overlap.



Sigma is the Foundation: Every single covalent bond is a σ bond. Multiple bonds cannot mathematically or physically exist without a foundational σ bond acting as the axis.



Pi Brings Multiplicity: Double and triple molecular geometries are created strictly by adding one or two π bonds to the pre-existing σ bond framework.



Spatial Geometry: σ electron density maps directly onto the internuclear axis, whereas π bonds hover as parallel saucer clouds above and below the axis.



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