Atomic orbitals: orbitals on an atom

Molecular orbitals: orbitals in a molecule where two or more atoms come together to form a bond.

Bonding: The overlap of two orbitals
- Orbitals have wave properties
  - Constructive & destructive interference occurs with waves: constructive & destructive interference also occurs with orbitals.

In-phase combination of orbitals → constructive interference

Out-of-phase combination of orbitals → destructive interference

Summation of two waves results in doubling of amplitude

Summation of two waves results in canceling out: zero amplitude
- **destructive:**
  - \( \text{C} \) \( \downarrow \) \( \text{sp}^3 \) + - \( \text{H} \) \( \downarrow \) → - - - + -
  - \( \sigma^* = \text{antibonding (higher in } \varepsilon \text{ than } \text{SM}) \)

- **constructive:**
  - \( \text{C} \) \( \downarrow \) \( \text{sp}^3 \) + + + \( \mu \) → - - + +
  - \( \sigma = \text{bonding (lower in energy than individual atomic orbitals)} \)

- +/- denotes amplitude NOT charge
- In Hydrogen 1s orbitals, + & - amplitude exists at the same time & the sign depends on which atom it is reacting with. *This is true for all atomic orbitals*

- Every bond has a bonding & an antibonding orbital
- For every stable molecule, the bonding orbital is filled & the antibonding orbital is empty.

- Atomic orbitals:
  - \( H - N : \) \( \rightarrow \) \( H - Cl : \) \( \rightarrow \) \( H - N - H + : Cl : \)
  - filled orbital (\( \sigma^* H - Cl \))
  - empty orbital

*Arrows represent interaction of lone pair (filled orbital) w/ the empty antibonding (\( \sigma^* \)) orbital on the hydrogen atom (electrons overlap w/ the empty orbital to populate the \( \sigma^* \) of \( H - Cl \) & cleaves the \( H - Cl \) bond*
H - Cl:

- Electronegativity is a measure of orbital energy.
  - More electronegativity = lower energy orbitals (i.e., CNOF) for orbitals.
- \( \sigma^* \) antibonding combination
- \( \sigma \) bonding combination

- Lower energy empty orbitals are more reactive & higher energy filled orbitals are more reactive because the energy match is better.

\[ \text{E} \quad \text{poor match} \] \[ \text{better match} \]

- The closer these orbitals are to each other, the better the interaction.

"Energy match" = How close in energy two interacting orbitals are.
more basic lone pair

* In this example, the lone pair on N is more basic than the lone pair on O because N is less electronegative than O, meaning that it has higher energy orbitals than O, is a less stable lone pair, and is more reactive.

CH₃⁻ vs. NH₂⁻

more basic lone pair

(C is less electronegative than N)

carbonion = most basic compound known
Bonds have 2 components:

- **σ bond** = "head on bonding" cylindrically symmetrical
- **π bond** = "sideways bonding"

**σ** orbital (you want to be the lowest empty orbital)

**π** orbital (highest filled orbital)

π bond - you cannot rotate about π bonds

NO OVERLAP

π/C bonds are 90° to each other

orbital have less interaction than σ orbitals

- there is less lowering
- less raising for

π orbitals

most reactive combination

BIC BEST ENERGY MATCH
Two kinds of mechanisms:
1. Polar: $2e^-$, Nu: $\underline{\text{H}}^+$ or $\text{B}^-/\text{H}^+$
2. Radical: odd # of $e^-$ (i.e. $1e^-$, $3e^-$)

Rules for writing reaction mechanisms: (polar)
1. Attack w/ electrons
   - *arrows represent movement of electrons!*
   - never violated
   - arrows start from electrons on either Nu: or base
   - *Electrons attack empty orbitals (either nonbonding or antibonding*)
   - $\text{H}-\text{N}: \overset{\text{H}}{\rightarrow} \overset{\text{H}}{\text{O}}$
   - $\text{H}-\text{N}: \overset{\text{H}}{\rightarrow} \overset{\text{H}}{\text{O}}$
   - vs.
   - $\text{H}-\text{N}: \overset{\text{H}}{\rightarrow} \overset{\text{H}}{\text{O}}$
   - $\text{H}-\text{N}: \overset{\text{H}}{\rightarrow} \overset{\text{H}}{\text{O}}$
   - e\text{'s attacking nonbonding orbitals (i.e. H-Cl)}

2. Break bonds towards the more electronegative atom
   - $\text{H}-\text{N}: \overset{\text{H}}{\rightarrow} \overset{\text{H}}{\text{Cl}}$
   - sometimes violated
   - $\text{H}-\text{N}: \overset{\text{H}}{\rightarrow} \overset{\text{H}}{\text{Cl}}$
   - Better because electrons end up on Cl which is more electronegative than H.
   - $\text{H}-\text{N}: \overset{\text{H}}{\rightarrow} \overset{\text{H}}{\text{Cl}}$
   - NOT observed