

4.7.3 Types of Molecular Orbitals

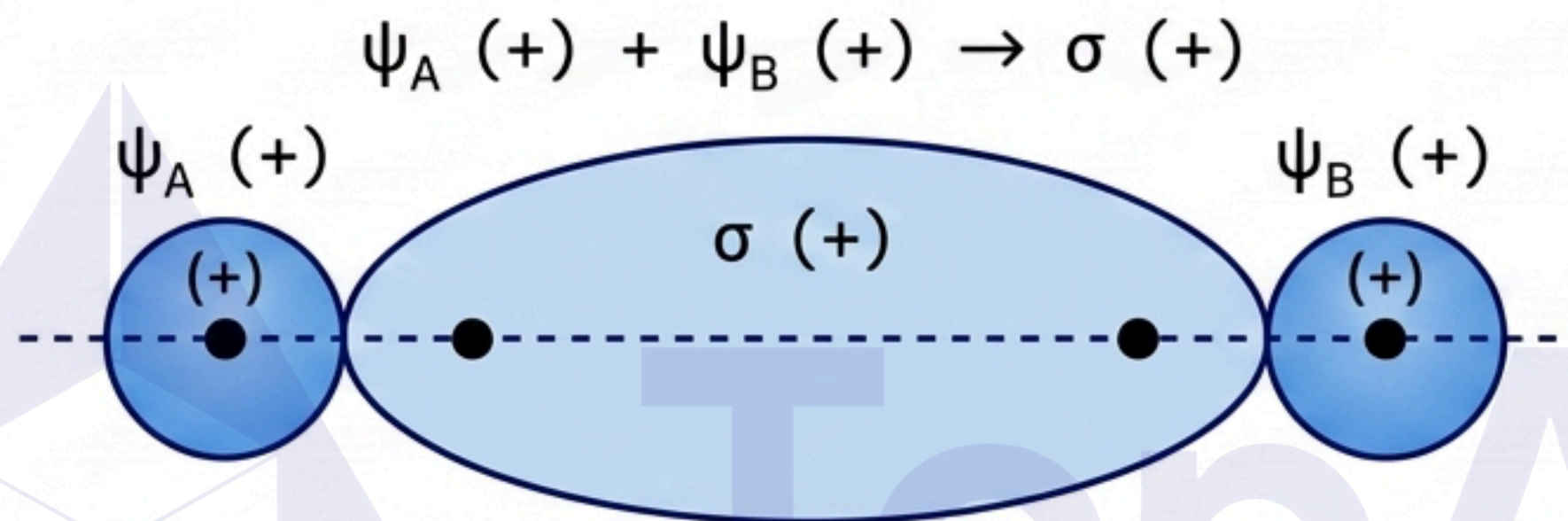
Linear Combination of Atomic Orbitals (LCAO): Sigma (σ) and Pi (π) **Formations**

[Exam-Smart Summary]

[LCAO Theory]

[Nodal Geometry]

Sigma Bonding MO (σ)



Symmetry

Symmetrical around the internuclear bond axis. (Cylindrical symmetry).

Electron Density

Concentrated directly between the two bonded nuclei. Shields nuclei from **mutual repulsion**.

Energy & Stability

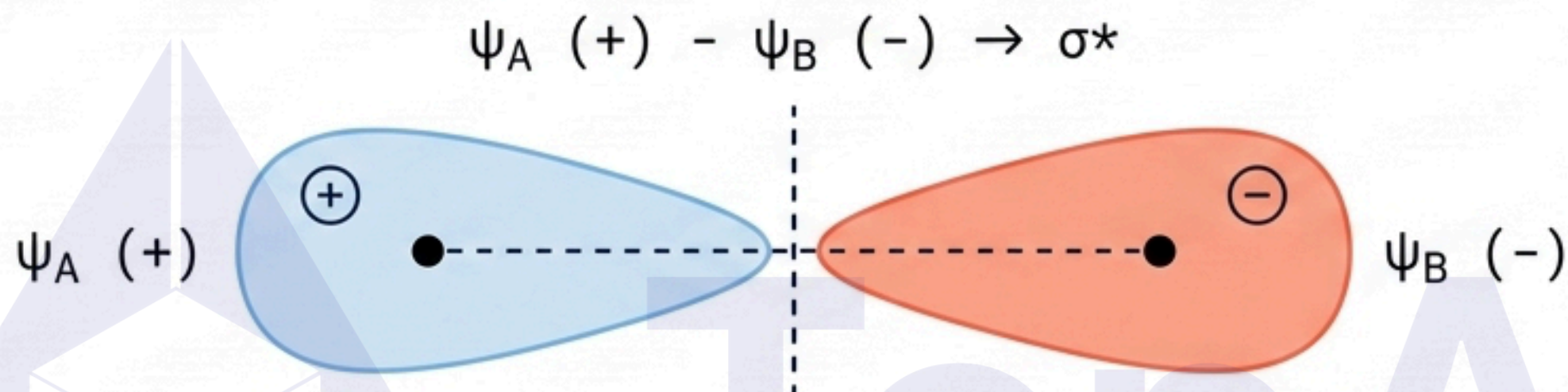
Lower energy than the parent atomic orbitals. Creates a highly stable bond.

LCAO Equation: $\sigma = \psi_A + \psi_B$ (Addition of wave functions)

HEAD-ON OVERLAP | DESTRUCTIVE INTERFERENCE



Sigma Antibonding MO (σ^*)



[Key Feature: 1 Nodal Plane perpendicular to bond axis]

Symmetry

Still symmetrical around the bond axis, but split by a node.

Electron Density

Pushed away from the space between nuclei. Zero density exactly between the nuclei.

Energy & Stability

Higher energy than parent atomic orbitals. Destabilizes the molecule.

LCAO Equation: $\sigma^* = \psi_A - \psi_B$ (Subtraction of wave functions)



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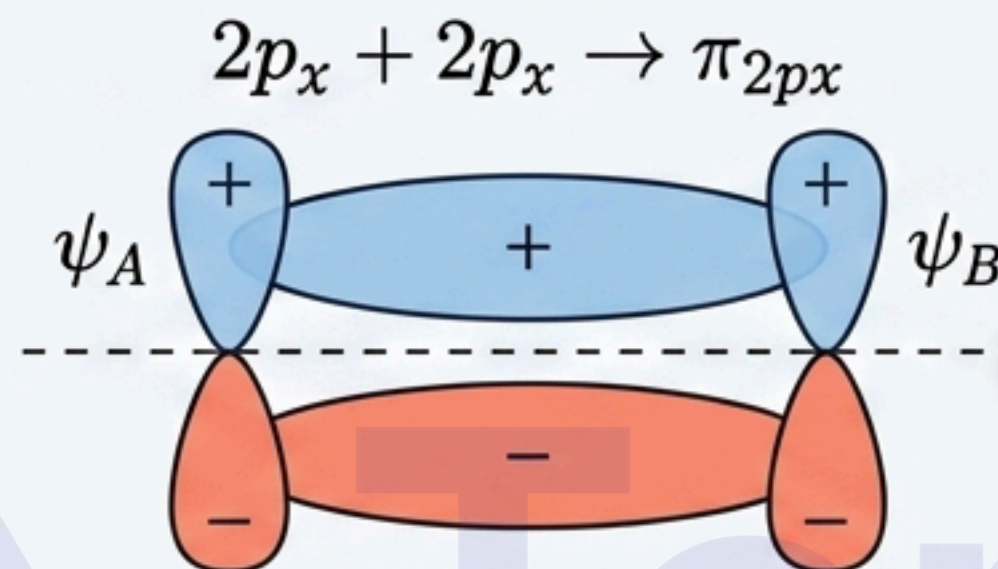
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Pi Bonding MO (π)



[Node Logic: Zero density ON the internuclear axis]

Symmetry

Not symmetrical around the bond axis.

Electron Density

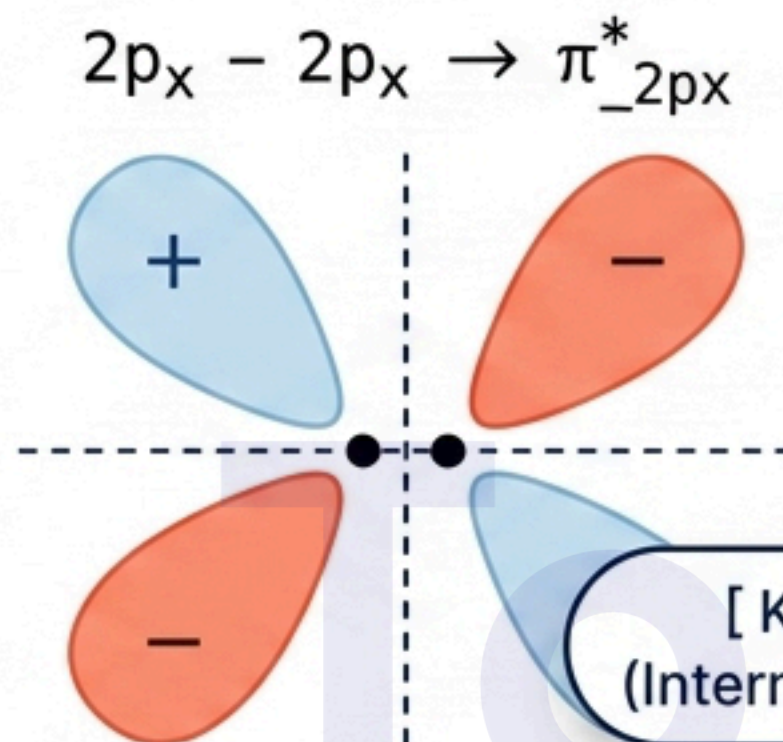
Two saucer-type clouds located above and below the plane of the participating nuclei.

Energy & Stability

Lower energy than parent p -orbitals, but generally higher energy (weaker bond) than a sigma bonding orbital.

LCAO Equation: $\pi = \psi_A + \psi_B$ (Parallel axis addition)

Pi Antibonding MO (π^*)



[Key Feature: 2 Nodal Planes
(Internuclear axis + Between nuclei)]

Symmetry

Asymmetrical. Axes remain parallel, but phases are inverted across the vertical node.

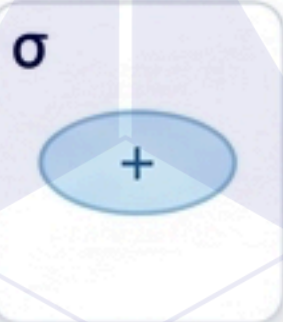
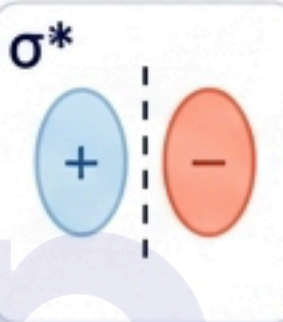
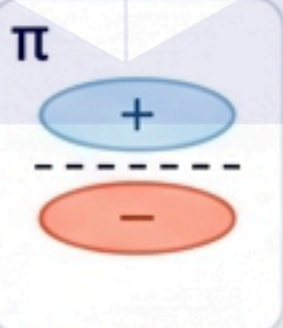
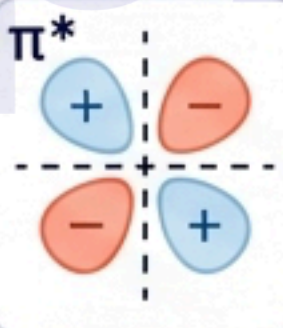
Electron Density

Pushed entirely away from both the internuclear axis and the plane between the atoms.

Energy & Stability

Highest energy state. Strongly destabilizes the molecular structure.

Nodal Structure and Symmetry Differences

	Column 1 Bonding (Addition)	Column 2 Antibonding (Subtraction)
Row 1 Sigma (σ) Types (Axial Overlap)	 Symmetrical around axis. 0 perpendicular nodes. Electron density centered.	 Symmetrical around axis. 1 perpendicular node. Electron density outward.
Row 2 Pi (π) Types (Sideways Overlap)	 Asymmetrical. 1 internuclear node (along the axis). Density above/below.	 Asymmetrical. 2 nodes (along axis + perpendicular). Density pushed to 4 quadrants.

The Golden Rule: Bonding MOs place electron density between nuclei to hold them together (lower energy). Antibonding MOs create nodes between nuclei, pulling them apart (higher energy).



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