



PONDICHERRY UNIVERSITY

पाण्डिच्चेरी विश्वविद्यालय புதுவைப் பல்கலைக்கழகம்

# LINEAR COMBINATION OF ATOMIC ORBITALS (L.C.A.O).

**COURSE:** REVIEW OF QUANTUM MECHANICS AND E.M.T

**CODE:** 612

**COURSE INSTRUCTOR:** ASSISTANT PROFESSOR DR. P. THANGADURAI.

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M.Tech 1st YEAR , sem -1.

# Introduction

- If an electron can be found in an atomic orbital belonging to atom A and also in an atomic orbital belonging to atom B, then the overall wave function is a superposition of the two orbitals.

$$\psi_{\pm} = N(A \pm B)$$

- The technical term for superposition in the above equation is a **linear combination of atomic orbitals**.
- The approximate molecular orbital formed from a linear combination of atomic orbitals is called a **LCAO-MO**.

A molecular orbital that has cylindrical symmetry around the internuclear axis, such as the one we are discussing, is called a  $\sigma$  orbital because it resembles an s orbital when viewed along the axis and, more precisely, because it has zero orbital angular momentum around the internuclear axis.

## Normalizing a molecular orbital

- Normalize the molecular orbital  $\psi_+$
- To proceed, substitute the LCAO into this integral, and make use of the fact that the atomic orbitals are individually normalized.
- When we substitute the wavefunction in the following normalization condition, we find

$$\begin{aligned}\int \psi \psi^* d\tau &= 1 \\ \int \psi \psi^* d\tau &= N^2 \left( \int A^2 d\tau + \int B^2 d\tau + 2 \int AB d\tau \right) \\ &= N^2 (1 + 1 + 2S)\end{aligned}$$

where,  $S = \int AB d\tau$ . For the integral to be equal to 1, we require

$$N = \frac{1}{\{2(1+S)\}^2}$$

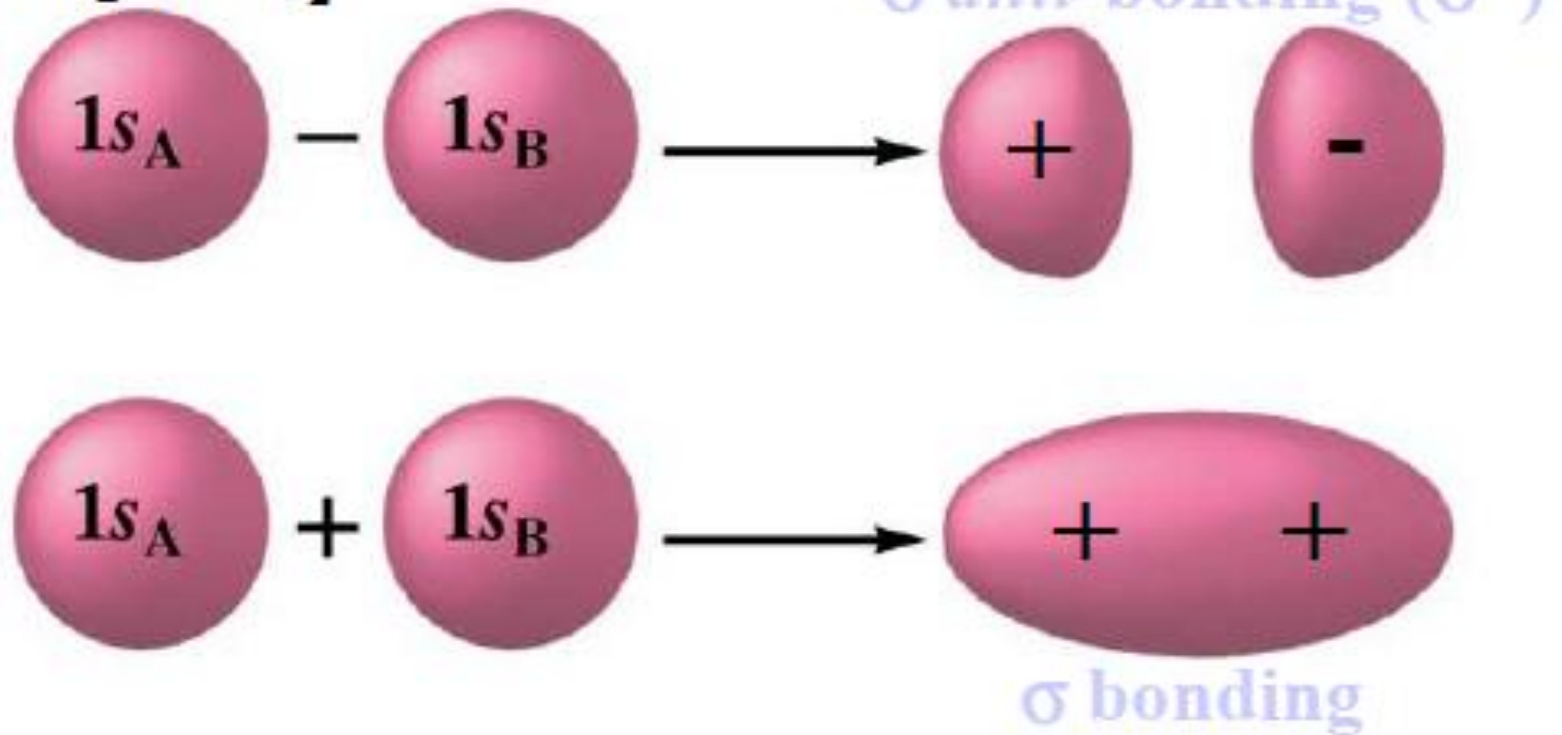
In  $H_2^+$ ,  $S=0.59$ , so  $N=0.56$

First and second terms are atomic orbitals and they are individually normalized.

- The lower-energy orbital, which has the form  $\psi_+ = \phi_A + \phi_B$  is called a bonding orbital.
- The higher energy orbital, which has the form  $\psi_- = \phi_A - \phi_B$  is called Anti bonding orbital
- An anti bonding orbital is more anti bonding than a bonding orbital is bonding.

# Molecular Orbitals are simply Linear Combinations of Atomic Orbitals ("L.C.A.O.-M.O.s")

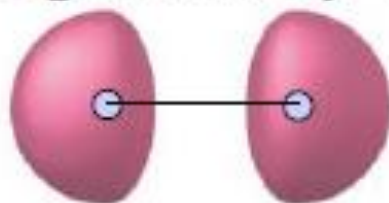
Example:  $H_2$



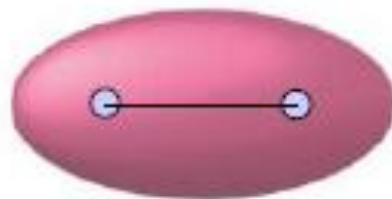
Next Question: *Why* does this work?

## Bonding is driven by stabilization of electrons

- Electrons are negatively charged
- Nuclei are positively charged



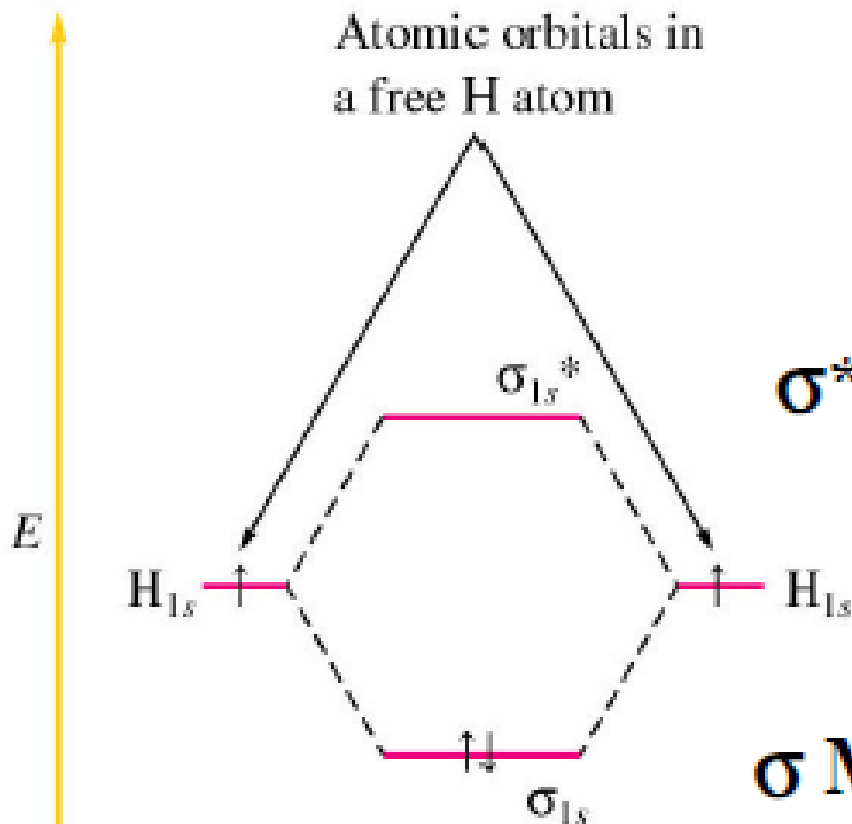
○ = ⊕ = nucleus



The bonding combination puts electron density between the two nuclei - **stabilization**

The antibonding combination moves electron density away from the nuclei - **destabilization**

Atomic orbitals in  
a free H atom



**$\sigma^*$  M.O. is raised in energy**

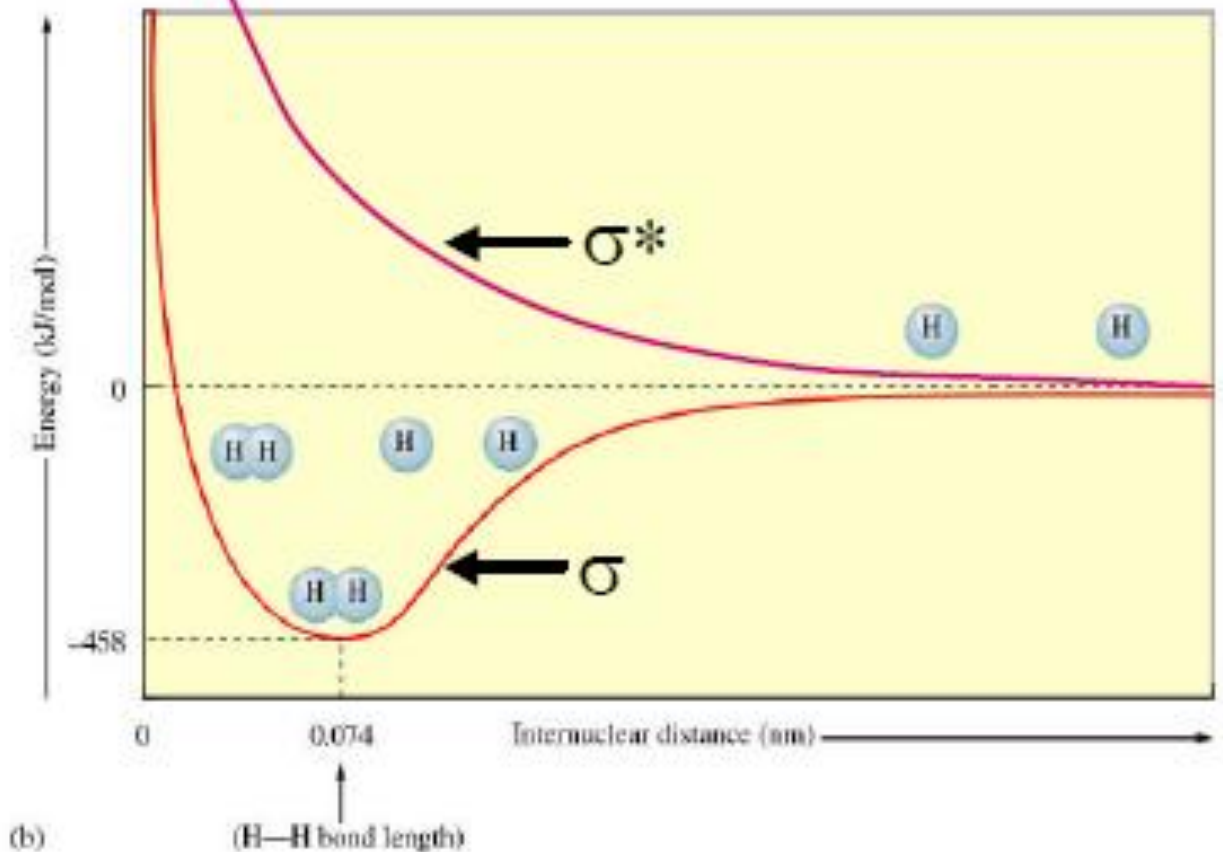
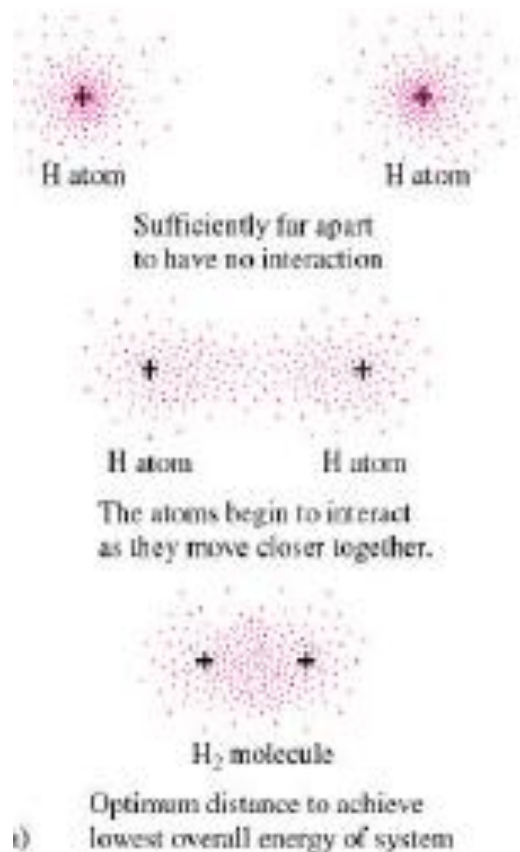
**$\sigma$  M.O. is lowered in energy**

$\sigma_{1s}^*$  and  $\sigma_{1s}$  are  
molecular orbitals  
in the  $H_2$  molecule.

**H atom:  $(1s)^1$  electron configuration**

**$H_2$  molecule:  $(\sigma_{1s})^2$  electron configuration**

# Same as previous description of bonding





# Bond Order

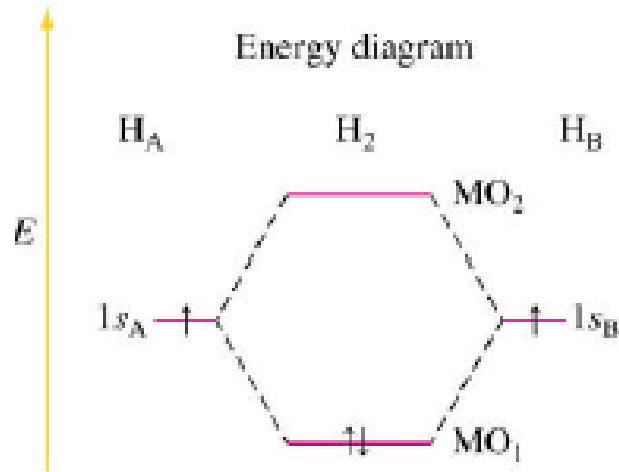
$$\text{Bond Order} = \frac{\# \text{ bonding electrons} - \# \text{ antibonding electrons}}{2}$$

The bond order is an indication of bond strength

Greater bond order  Greater bond strength

# Bond Order: Examples

$\text{H}_2$



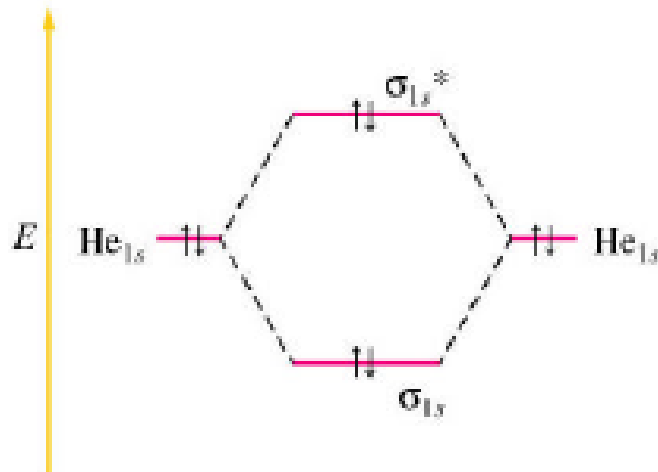
$$\text{Bond order} = (2-0)/2 = 1$$

Single bond

Stable molecule

(450kJ/mol bond)

$\text{He}_2$



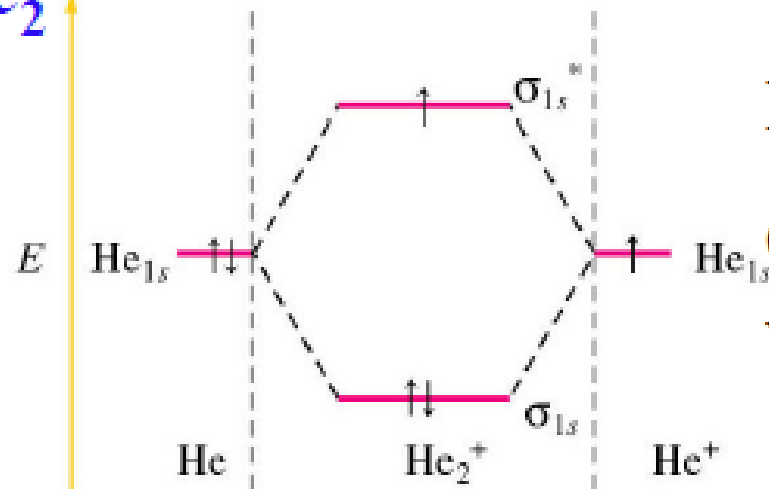
$$\text{Bond order} = (2-2)/2 = 0$$

No bond!

Unstable molecule

(0kJ/mol bond)

$\text{He}_2^+$



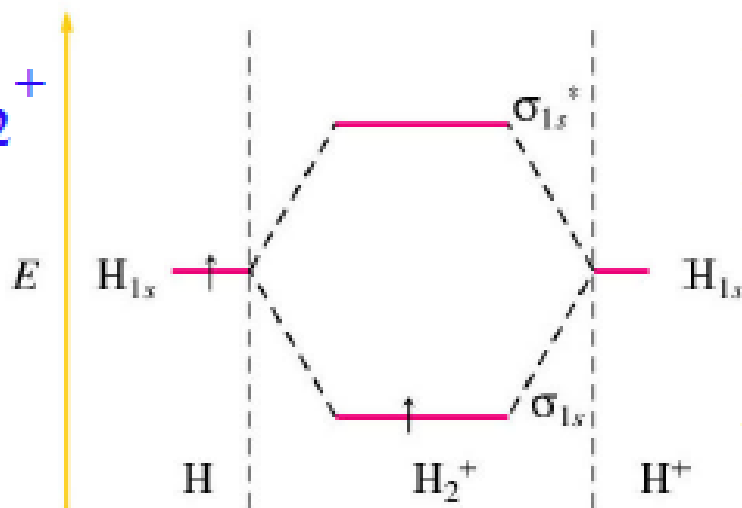
$$\text{Bond order} = (2-1)/2 = 1/2$$

Half of a single bond

Can be made, but its not very stable

(250kJ/mol bond)

$\text{H}_2^+$



$$\text{Bond order} = (1-0)/2 = 1/2$$

Half of a single bond

Can be made, but its not very stable

(255kJ/mol bond)

**Thank you..!**