

## Molecular Orbital Theory.

Proposed and developed by Mulliken, Leonard-Jones and Hückel.

There are two well-known methods of developing the molecular orbitals - i) Linear Combination of Atomic Orbitals (LCAO) method, and  
ii) United Atom Method.

### LCAO - technique.

Molecular orbitals can be visualised as being made up of appropriate atomic orbitals provided by the atoms joined together in the molecule. It is assumed that AOs of constituents combine in a linear additive fashion to form MOs.

- Consider two atoms A and B each possessing a single valence electron.
- Let  $\psi_A$  and  $\psi_B$  represent the wave functions of atoms A and B, and the atomic orbitals accommodating valence electrons overlap.
- The valence electrons will be in regions where the orbitals overlap and therefore they can be associated with either nucleus.
- Consequently the valence  $e^-$  have a much larger volume available for their movement as compared with that available in each isolated atom.

By: AG Nam

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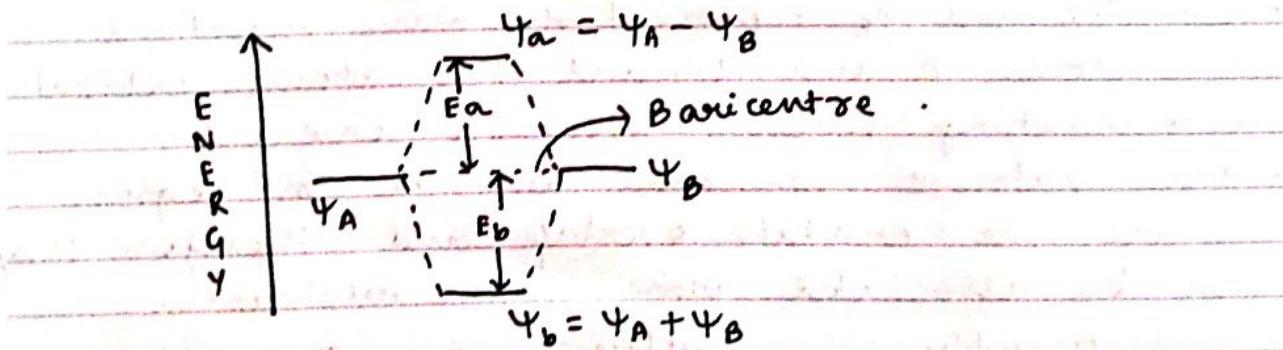
- The electrons can be thought of as moving in a MO whose total volume is approx. equal to the sum of the volume of AOs of A and B.
- thus MO can be expressed as a linear combination of AOs.

Wave function of MO,  $\Psi_{AB} = C_A \Psi_A + C_B \Psi_B$

$C_A$  and  $C_B$  are mixing coefficients and their values are so chosen as to get a MO of lowest energy.

For bonding in two similar atoms (Homonuclear) magnitude of the coefficients  $C_A$  and  $C_B$  must be same.  $C_A^2 = C_B^2$  or  $C_A = \pm C_B$ .

Thus one MO ( $\Psi_b$ ) can be obtained by addition of wave fn. of two AOs =  $\Psi_A + \Psi_B$  and other MO ( $\Psi_a$ ) can be obtained by subtraction of wave fn. of two AOs =  $\Psi_A - \Psi_B$



Acc. to Baricentre rule the extent of stabilization of bonding MO should be equal to extent of destabilization or energization of anti-bonding MO.

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Conditions for effective overlap of AOs to form MO :-

- i) Energy (E) - The combining AOs should be close in energy in order to undergo linear combination.
- ii) Orientation ( $\alpha$ ) - The combining AOs should be properly oriented in order to form bonding and anti-bonding MO.
- iii) Symmetry ( $S$ ) - The combining AOs should have more or less similar symmetry.

The main points of MOT are :-

- i) Electrons belonging to two bonding atoms are controlled by the entire molecule. The  $e^-$  will occupy MO that are analogous to AOs.
- ii) In an atom there are s, p, d . . . AOs determined by various values of Q. No. In a molecule we have a set of MOs  $\sigma, \pi, \delta, \dots$  determined by various Q. No.
- iii) Just as an AO can contain a max. of  $2e^-$ , MOs can also accommodate a max. of two  $e^-$  as Pauli's exclusion principle.
- iv) The various  $e^-$  occupy diff. orbitals according to Hund's rule of maximum multiplicity as in the case of AOs.

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Bonding orbitals - MO that is obtained by the addition overlap of two AOs.

Features -

- i) It possesses lower energy than the AOs from which it is formed.
- ii) It has high  $e^-$  density in the region between the two nuclei and this accounts for stability of bond.
- iii) It is formed when lobes of combining AOs have been same sign.
- iv) Every  $e^-$  in a bonding MO contributes to attraction between two atoms.

Antibonding orbitals - MO obtained by subtraction overlap of two AOs.

Features -

- i) It possesses higher energy than the AOs from which it is formed.
- ii) The probability of finding the  $e^-$  in between the nuclei is negligible. The  $e^-$  density is concentrated only on one nucleus at any particular moment.
- iii) It is formed only when the lobes of combining AOs have opposite signs.
- iv) Every  $e^-$  in an ABMO contributes to repulsion b/w two atoms.

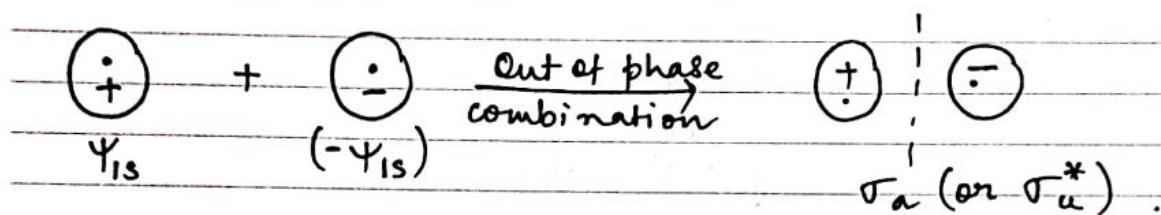
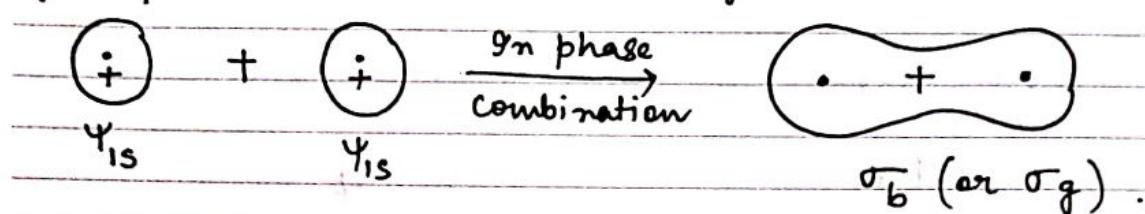
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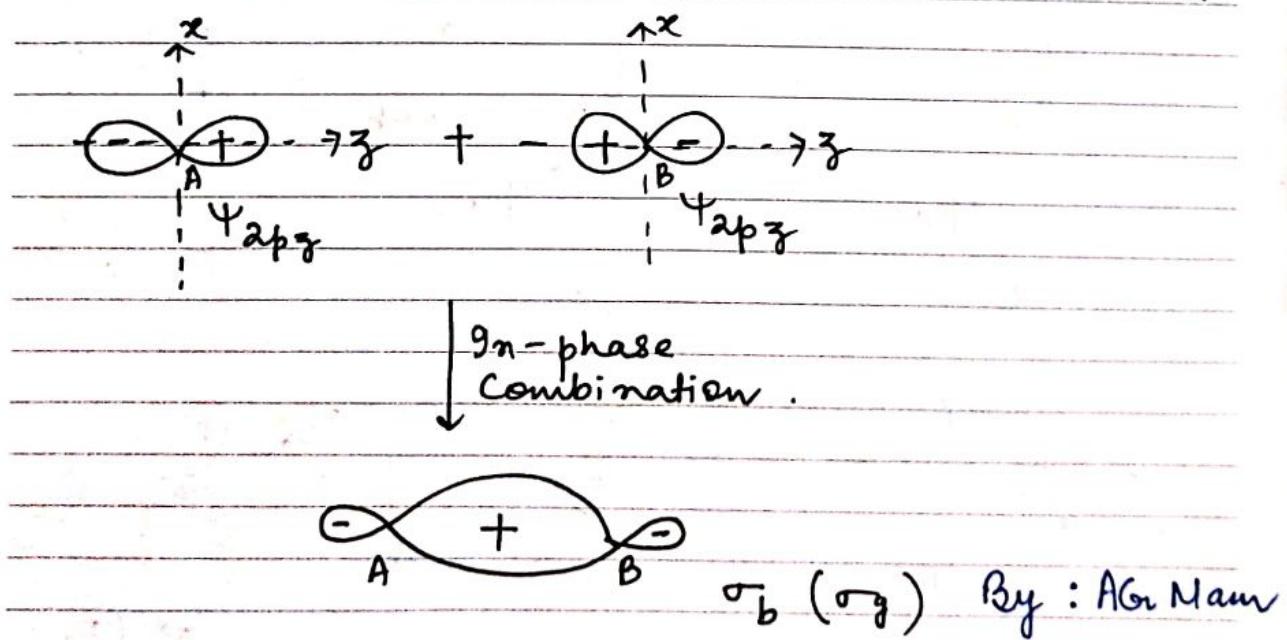
- Formation of sigma-type & pi-type MOs from AOs through LCAO.

Overlapping of the lobes with same sign gives bonding interaction while overlapping of lobes with opp. sign produces an antibonding interaction.



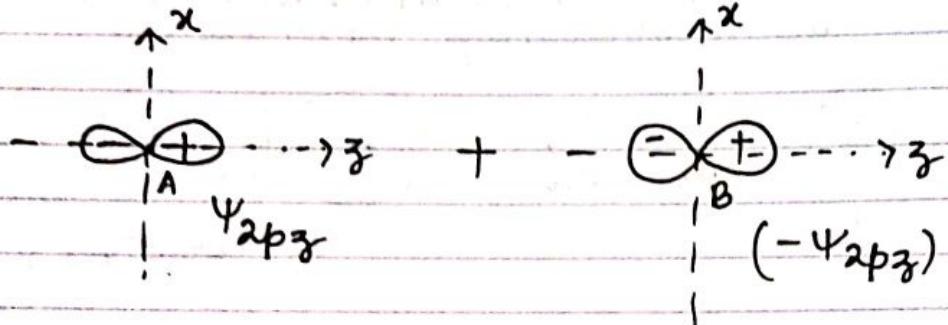
'g' → gerade → centre of symmetry.  
 'u' → ungerade → no centre of symmetry.

Head on combination of AOs is designated by 'σ'  
 Parallel      "      "      "      "      "      " : π

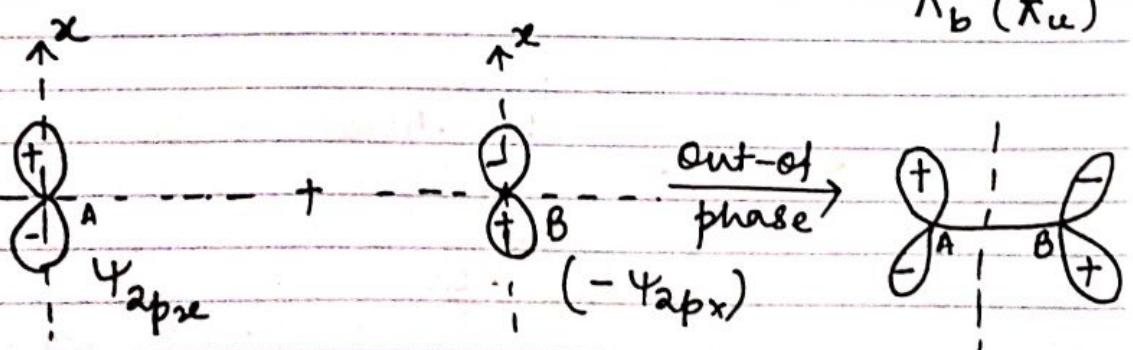
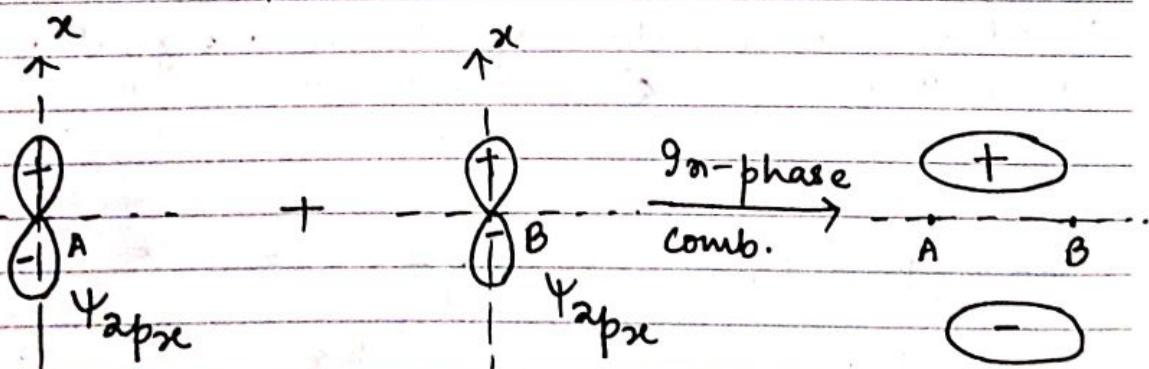
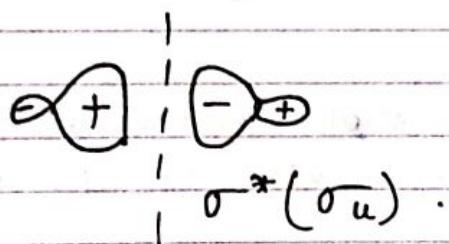


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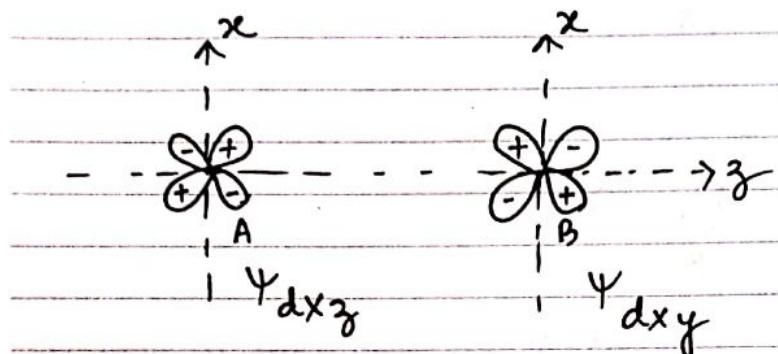
↓  
 Out of  
 phase  
 combination.



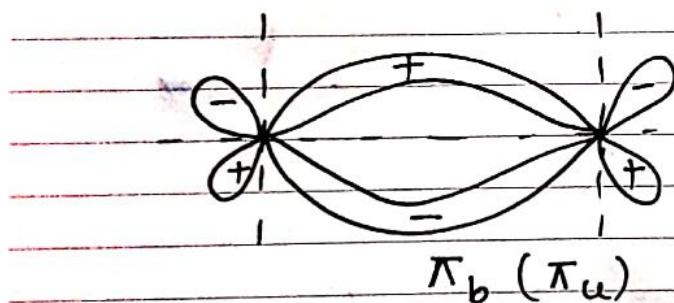
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$d_{xz} + d_{x^2}$ .

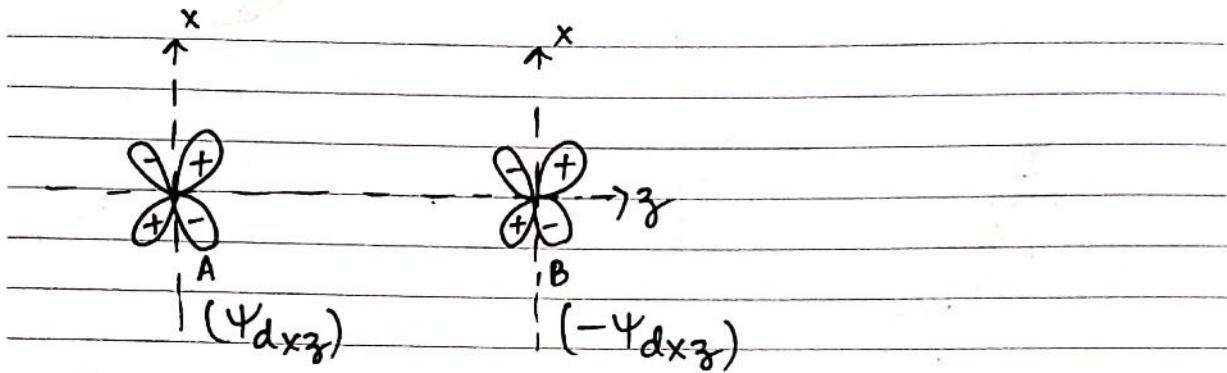


↓  
In-phase  
Combination

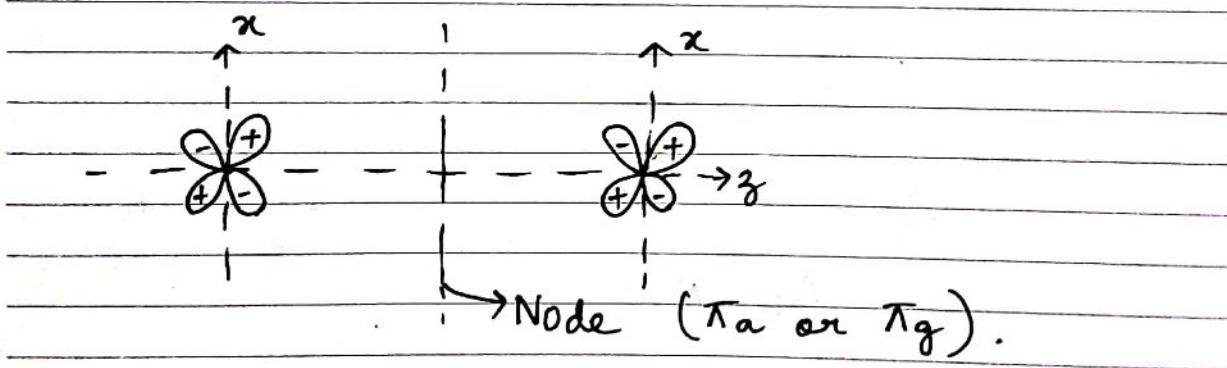


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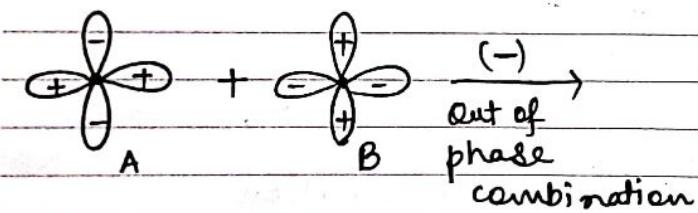
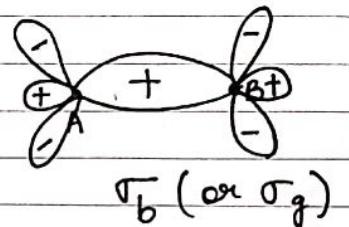
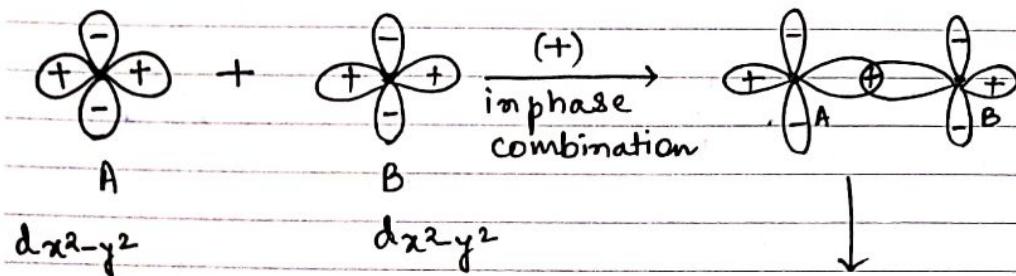


↓ Out of phase combination.

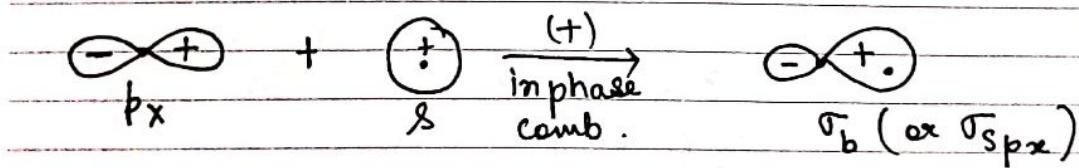


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$d_{x^2-y^2} + d_{x^2-y^2}$ 


→ Nodal Plane.

 $(p_x + \delta)$ 


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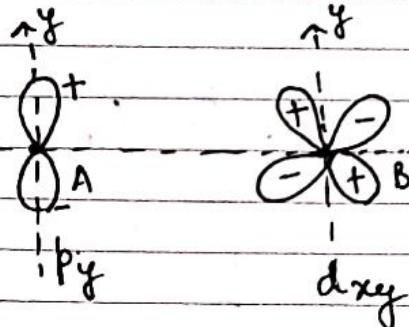
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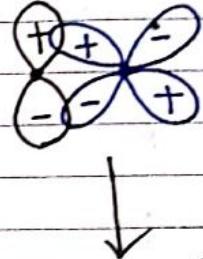


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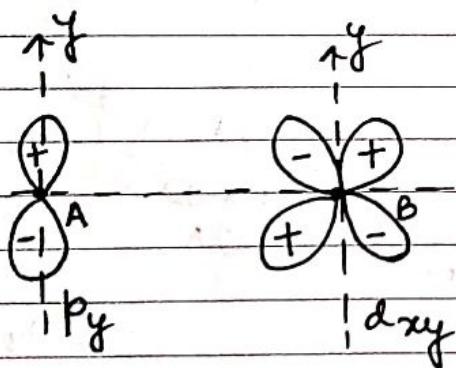
(p<sub>y</sub> + d<sub>xy</sub>)



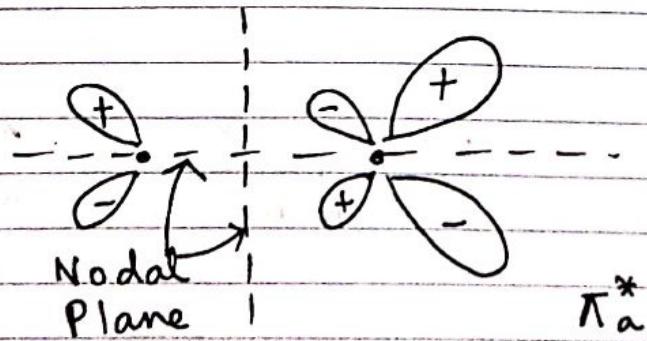
in-phase  
(+)  
combination



Nodal  
Plane.  
 $\pi_b (\pi_{pd})$



out of phase  
(-)  
combination



$\pi_a^* (\pi_{pd}^*)$

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- $\sigma$ ,  $\pi$ ,  $\delta$  and  $\phi$  MOS.

$\sigma$  bond arises by the overlap of '1 lobe + 1 lobe'

$\pi$  bond arises by the overlap of '2 lobes + 2 lobes'  
 $\delta$  " " " " " " " " 4 " + 4 "  
 $\phi$  " " " " " " " " 6 " + 6 "

The 's' orbital can show only  $\sigma$ -type interaction,  
 'p' orbital can show both  $\sigma$  and  $\pi$ -type interaction,  
 'd' orbital can show  $\sigma, \pi, \delta$  - type interaction,  
 'f' orbital can show  $\sigma, \pi, \delta, \phi$  - type interactions.

- (+) and (-) combinations of the AOs.

Here (+) or inphase combinations are always considered to give the BMOs and (-) give ABMOs. For this purpose, the combining  $p_x$  orbitals (taking z-axis as the bonding axis) are drawn in diff. way. i.e. w.r.t the nucleus, the left lobe of one orbital is made positive while for the other combining orbital the left lobe is drawn negative.

But there is also another convention where signs of all the lobes of the combining orbitals are shown in the same way. In this method - i) For the spherically sym.  $g$ -orbitals, the (+) combination gives the sigma bonding mol. orbital ( $\sigma$ -BMO) while the (-) combination gives the sigma anti-

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bonding molecular orbital ( $\sigma$ -ABMO).

ii) For the orbitals like p, d, etc. which are not spherically symmetrical, in the  $\sigma$ -type interaction, the (+) combination gives  $\sigma$ -ABMO while the (-) combination gives the  $\sigma$ -BMO, but for the  $\pi$ -type interaction the reverse is true.

## Symmetry Elements in the MOs.



i) Cylindrical Symmetry ( $C_\infty$ ): If the orbital is rotated around the bonding axis, ie molecular axis and it remains unchanged with respect to the sign at any angle of rotation then the orbital is called cylindrically symmetrical. The MOs having  $C_\infty$  are referred to as sigma ( $\sigma$ ) molecular orbitals.

ii) Centre of symmetry or centre of inversion ( $C_i$ ): The centre of sym. indicates that for every point there is an equivalence point (in all respect including the sign) in the just opposite direction at an equal distance measured from the  $C_i$ .

Such orbitals having  $C_i$  are called 'gerade' and is represented as ' $g$ ' and the orbitals lacking  $C_i$  are termed ungerade and is represented by ' $u$ '.

\* Only in the case of homonuclear diatomic mol. providing identical AOs to form MOs the question of  $C_i$ , ie the classification of MOs by ' $g$ ' and ' $u$ ' arises.

iii) Nodal Planes: It indicates the plane along which there is no electron cloud. If there is a nodal plane perpendicular to the internuclear axis and lying between the nuclei, the corresponding orbital is antibonding in nature.

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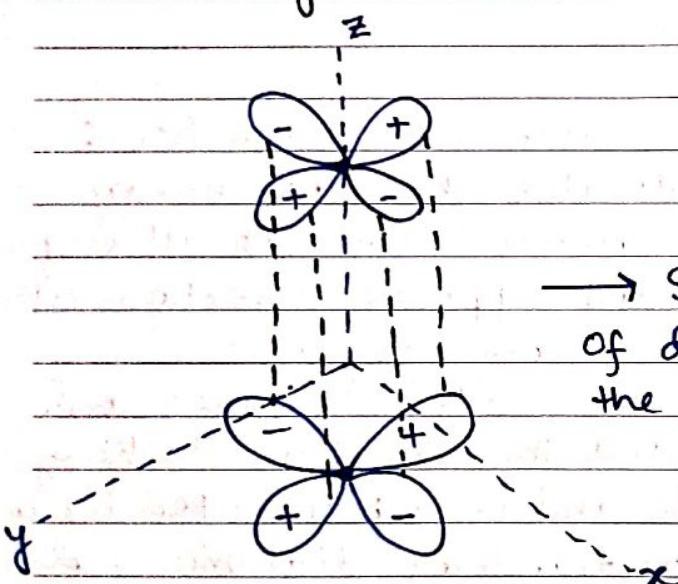
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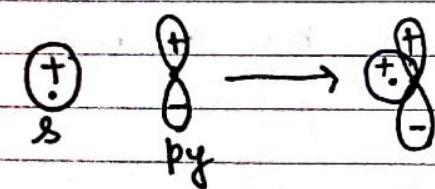


If a nodal plane lies in the internuclear axis the corresponding orbital is  $\pi(\pi)$  in nature. The  $\sigma$ -orbital does not contain the nodal plane containing the internuclear axis.

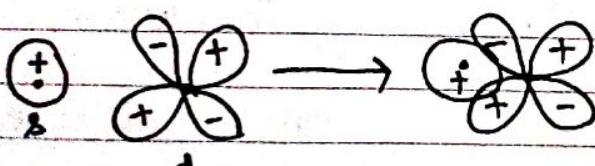
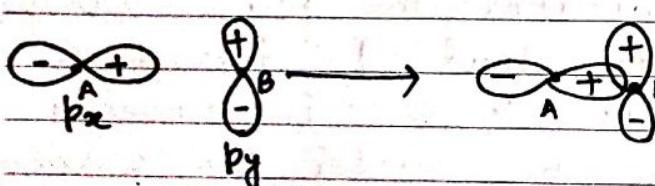
The  $\delta$ -orbital possess two such nodal planes containing the internuclear axis.



→ Schematic representation of delta-type interaction b/w the d-atomic orbitals.



Schematic representation of non-bonding type interaction between the AOs.



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Differences between  $\sigma$  and  $\pi$ -bonds and their MOs.



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Property	$\sigma$ -Bonds	$\pi$ -Bonds
i) Mode of overlap	End to end overlap (ie one lobe - one lobe)	Side to side overlap (ie 2 lobes - 2 lobes)
ii) Bond Strength	Stronger due to better overlapping	Weaker due to poorer overlapping
iii) Rotation along the band axis	Due to cylindrical sym. around the band axis, the atoms can be freely rotated around the band axis.	No rotation is possible around the axis.
iv) Delocalisation	$\sigma$ -bonding electrons cannot participate in delocalisation.	$\pi$ -bonding electrons being mobile can participate in a suitable condition (eg conjugated dienes and polyenes)
v) Direction	$\sigma$ -bond determines the direction of the bond.	It has no primary effect in determining the bond direction, but it can shorten the bond length.

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Property $\sigma$ - Bonds $\pi$ - Bonds

vi) Symmetry  
Elements.

Both  $\sigma$  and  $\sigma^*$  contain  
 $C\alpha$ .  
 $\sigma$  only contains  $Ci$ .  
No nodal planes exists  
for both  $\sigma$  and  $\sigma^*$ .  
containing internuclear  
axis.

No  $C\alpha$  axis  
for both  $\pi, \pi^*$   
 $\pi^*$  passes  $Ci$ .  
Both  $\pi$  and  $\pi^*$   
contain the  
nodal plane with  
internuclear axis.

vii) Magnetic  
quantum no.

( $\lambda$ ) of the  
MOs.

$$\lambda = 0$$

$$\lambda = \pm 1$$

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- Delta molecular orbitals.

Two d-orbitals lying in parallel planes can overlap with each other with all four lobes to produce a 'delta' bonding. The produced MO possesses two nodal planes containing the bond axis and the nodal planes are mutually perpendicular.

The  $\sigma$ -MOs can arise from the suitable  $d \pm d$  and  $f \pm f$  combinations.

The magnetic quantum number ( $\lambda$ ) of  $\sigma$ -MO is  $\pm 2$ .

On rotating (by  $360^\circ$ ) the  $\sigma$ -MOs about the inter-nuclear axis the sign of the lobes changes 4 times, while the  $\pi$ -MOs experience the change twice, and the  $\sigma$ -MOs remain unchanged.

\*  $\sigma$ -type interaction can occur in  $d \pm p_{\pi}^*$  - MO interaction. In metal-alkyne and metal-dioxygen (as in dioxygen adduct of Vaska's complex) complexes one  $p^*$  of the  $O_2$  or alkyne makes a  $\pi$ -type int. with the metal d-orbital while the other orthogonal  $\pi^*$ -MO makes a  $\sigma$ -type interaction with the metal d-orbital.

- phi ( $\phi$ ) Bonds -

The overlap, 6 lobes + 6 lobes produces the  $\phi$  bonds, arising from suitable overlap between two f-orbitals.

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### • Mu ( $\mu$ ) Bonds -

The  $\sigma$ -bonds are characterised by the presence of  $C\alpha$  symmetry elements; but the  $\sigma$ -bonds developed by the deviation of elongated  $\pi$ -electron cloud lacks in  $C\alpha$ . Such bonds are formed in different alkene complexes and this type of  $\sigma$ -bonds is described as  $\mu$ -bonds.

- VBT vs. LCAO - MOT.



### Similarities -

- Both the theories explain the covalent bond.
- Both theories demand that to form a covalent linkage the corresponding orbitals must overlap.
- For stabilisation of covalent linkage, both theories demand the concentration of electronic charge between the nuclei.
- Both the theories consider the quantum mechanical exchange phenomenon of the  $e^-$  among the nuclei and the covalent-ionic resonance interaction to explain the stabilisation.
- Both the theories predict the directional properties of the covalent linkage.
- Both the trial  $\Psi_{VB}$  and  $\Psi_{MO}$  can be used in the same way to evaluate the eigen fn. and eigen values.

### Differences -

- In VBT, the individual atoms are gradually brought together from infinity to interact through the overlapping of the AOs. On the other hand, in LCAO-MOT, the MOs are developed through the LCAO from the skeleton of the molecule containing the nuclei at fixed positions. Then the  $e^-$  are placed in polycentric MOs by using Aufbau principle, Hund's rule and Pauli's exclusion pr. as in case of atoms.

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- ii) In LCAO-MOT the combining atoms lose their individual identities, while in VBT the combining atoms retain their individual identities to a large extent.
- iii) In LCAO-MOT, the odd e<sup>-</sup> bonds are explainable while there cannot find any explanation in VBT.
- iv) In VBT, O<sub>2</sub> is considered to be diamagnetic but it is not supported by the exp fact. The LCAO-MOT can explain the paramagnetic behaviour of O<sub>2</sub>.
- v) VBT appears easier to explain the polyatomic molecules in terms of the localised covalent bonds while in MOT, the molecular orbitals are delocalised. But MOT has been found more promising to explain the molecular properties.

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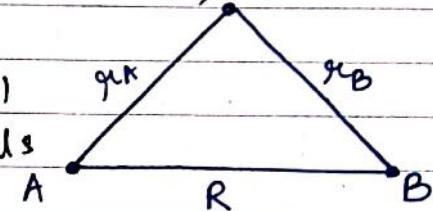
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The LCAO-MO treatment of Diatomic Hydrogen Molecule Ion ( $H_2^+$ ) .

One Electron - Two centre (1e - 2c) System.

The system contains two protons (ie two nuclei) electron and one electron.

In the ground state the atoms will utilise the lowest atomic orbitals (ie 1s) to form the MOs.



In the molecule, the MOs can be obtained by a linear combination of the individual atomic orbital wave functions  $\Psi_A$  or  $\Psi_B$  as :  $\Psi_{MO} = c_1 \Psi_A + c_2 \Psi_B$

The corresponding Schrödinger wave equation is given by -  $\hat{H} \Psi_{MO} = E \Psi_{MO}$

$$\text{where, } \hat{H} = \frac{-\hbar^2}{8\pi^2 m} \nabla^2 - e^2/r_A - e^2/r_B + e^2/R$$

$$\therefore E = \frac{\int \Psi_{MO} \hat{H} \Psi_{MO} d\tau}{\int \Psi_{MO}^2 d\tau}$$

$$= \frac{\int (c_1 \Psi_A + c_2 \Psi_B) \hat{H} (c_1 \Psi_A + c_2 \Psi_B) d\tau}{\int (c_1 \Psi_A + c_2 \Psi_B)^2 d\tau}$$

$$= \frac{c_1^2 \alpha_A + c_2^2 \alpha_B + 2c_1 c_2 \rho_{AB}}{c_1^2 + c_2^2 + 2c_1 c_2 S_{AB}}$$

$$[\because \int \Psi_A^2 d\tau = \int \Psi_B^2 d\tau = 1 \text{ (from the normalisation cond. of AO's)}]$$

where,  $\alpha_A = \int \Psi_A \hat{H} \Psi_A d\tau$  ;  $\alpha_B = \int \Psi_B \hat{H} \Psi_B d\tau$  ;  $\rho_{AB} = \int \Psi_A \hat{H} \Psi_B d\tau$  ;  $S_{AB} = \int \Psi_A \Psi_B d\tau$

$$\rho_{AB} = \int \Psi_A \hat{H} \Psi_B d\tau ; S_{AB} = \int \Psi_A \Psi_B d\tau$$

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$\alpha_A$  and  $\alpha_B$  are called Coulomb Integrals.

These are very close to the energies of the  $e^-$  in the isolated resp. atoms ie  $\alpha_A \approx E_A$  and  $\alpha_B \approx E_B$ . Thus here, Coulomb integral actually gives the measure of energy released when an  $e^-$  separated from the nucleus by an infinity occupies the 1s orbital of a H-atom.

Thus  $\alpha$  is negative and from the definition the ionisation potential is given by  $-\alpha$ .

$P_{AB}$  is referred to as Resonance Integral.

It gives the measure of exchange energy of an  $e^-$ .

$P_{AB}$  is a negative quantity indicating stabilisation through the exchange phenomenon.

$S_{AB}$  is called Overlap Integral representing the extent of overlap b/w the AOs, and is important in characterising the diff. types of MOs ie BMO, ABMO, NBMO. It actually gives the measure of  $e^-$  density between the nuclei.

This  $e^-$  density is measured wrt the isolated atoms.

The conditions are:  $S_{AB} > 0$ , BMO

$S_{AB} = 0$ , NBMO

$S_{AB} < 0$ , ABMO.

The magnitude of  $S_{AB}$  gives the measure of bond strength of the covalent bond formed b/w A and B. With the  $\uparrow$  of positive value of  $S_{AB}$  the bond st.  $\uparrow$  see.

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For the above mentioned 1e-2c system by following the Variation Principle to find out the conditions to minimise the energy we get -

$$\alpha_A = \alpha_B = \alpha \text{ (say)} \quad \text{and} \quad c_1 = \pm c_2$$

Eigen functions and eigen values are as follows :-

$$\Psi_{MO(+)} = c_+ (\psi_A + \psi_B), \quad E_+ = \frac{\alpha + \beta_{AB}}{1 + S_{AB}}$$

$$\Psi_{MO(-)} = c_- (\psi_A - \psi_B), \quad E_- = \frac{\alpha - \beta_{AB}}{1 - S_{AB}}.$$

$\Psi_{MO(+)}$  stabilises the system and is called BMO( $\Psi_{MO}$ ),  $\Psi_{MO(-)}$  destabilises the system and is called ABMO( $\Psi_{MO}^*$ ).

By imposing the cond. of normalisation,

$$c_+ = c \quad \text{and} \quad c_- = c^*$$

$$c_{\pm} = \frac{1}{\sqrt{2(1 \pm S_{AB})}}$$

If overlap integral is very small then  $c = c^* = \frac{1}{\sqrt{2}}$

$$\text{Then, } \Psi_{MO} = \frac{1}{\sqrt{2}} (\psi_A + \psi_B), \quad E = \alpha + \beta_{AB}$$

$$\Psi_{MO}^* = \frac{1}{\sqrt{2}} (\psi_A - \psi_B), \quad E^* = \alpha - \beta_{AB}.$$

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- Existence of  $\text{He}_2$  (effect of  $S_{AB}$  on the energies of MO)

$S_{AB}$  can never be zero in forming a real covalent linkage it has only been neglected compared to other terms (in mathematical calculations only).

In  $\text{He}_2$  molecule without neglecting  $S_{AB}$  it is found that the destabilization induced by the ABMO ( $\psi^*_{MO}$ ) is greater than the stabilisation produced by the corresponding BMO ( $\psi_{MO}$ ). Here also entropically the system of  $2\text{He}$  is favoured over the  $\text{He}_2$  system.

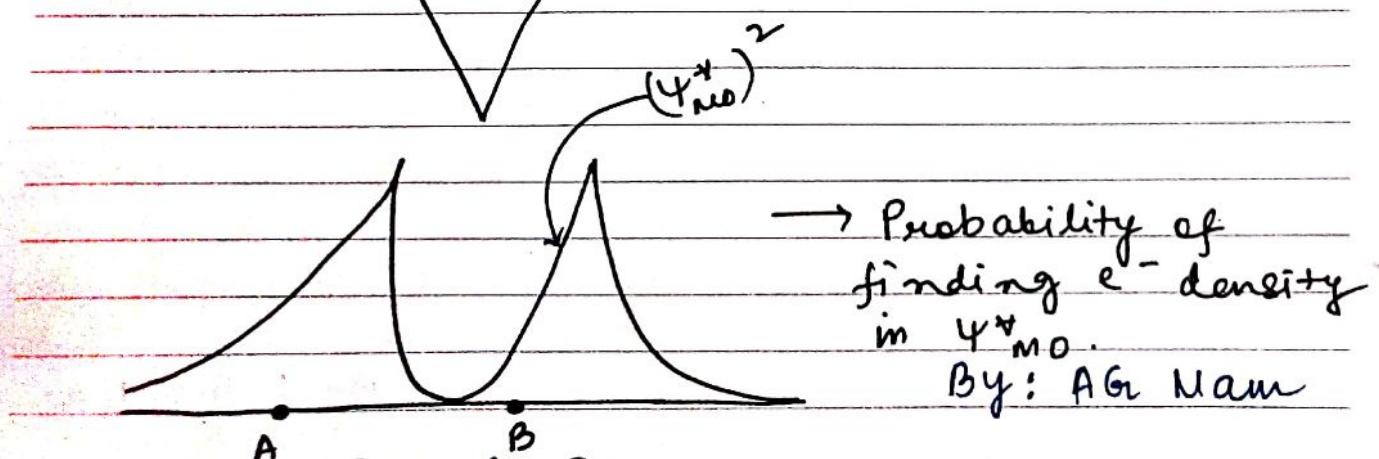
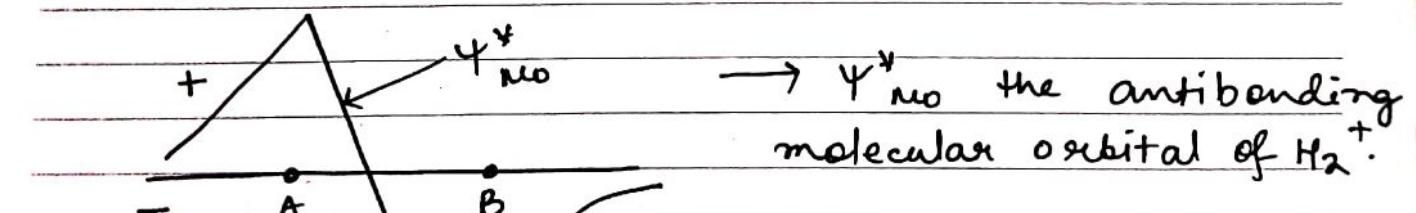
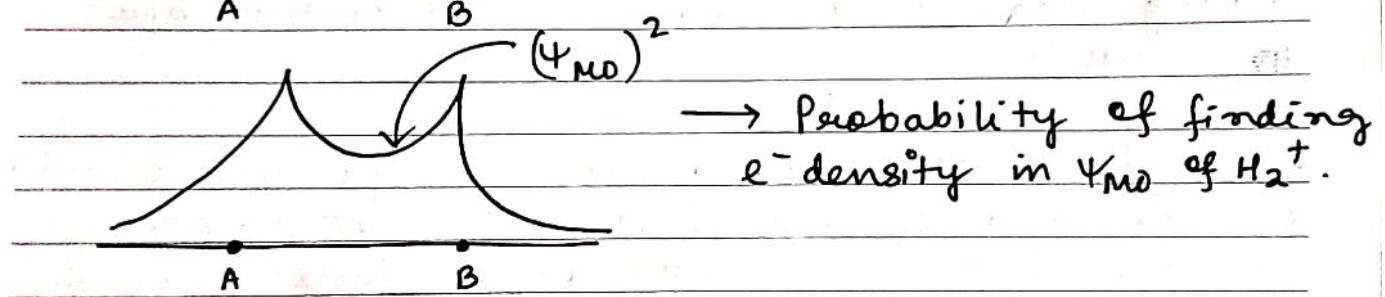
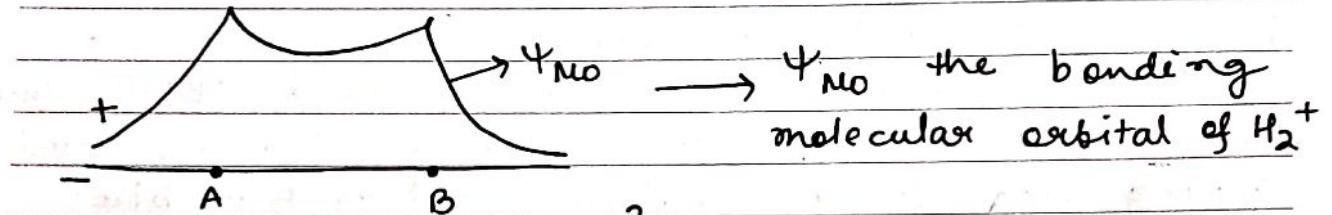
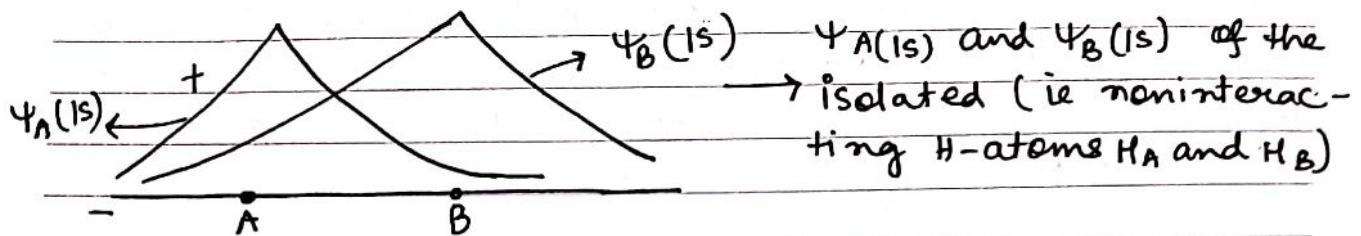
If in  $\text{He}_2$  the stabilization get balanced by an equal amount of destabil. giving rise to no net Stabilisation or destabilisation w.r.t the starting He-atoms then, we would get  $\text{He}_2$  along with the isolated He atoms.

By: Agnaw

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- Graphical representation of the MO.



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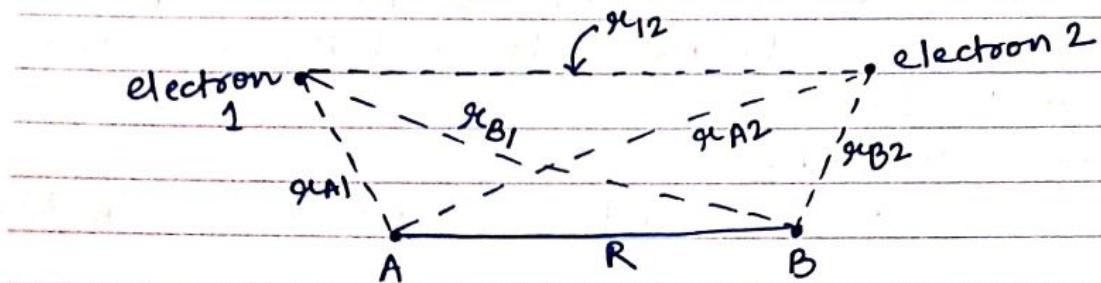
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- The antisym. combination in  $\Psi_{MO}$  shows its zero value in the midway b/w the nuclei. The symmetric combination in  $\Psi_{MO}$  shows a high value in the range b/w the nuclei.
- BMO leads to an accumulation of  $e^-$  density between the nuclei to minimize the nucleus-nucleus repulsion. On the other hand ABMO remove the  $e^-$  density from the region b/w the nuclei giving rise to a repulsive interaction b/w the nuclei.
- Bonding MO arising from the positive overlap of  $\Psi_A$  and  $\Psi_B$  brings a higher  $e^-$  density b/w the nuclei than the sum of  $e^-$  density of the two isolated H-atoms.

By : A E Man

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The LCAO-MO Treatment of Diatomic  $H_2$  molecule  
 — A Two Electron-Two Centre ( $2e - 2c$ ) System.



Schematic representation of the hydrogen molecule ( $H_2$ ) skeleton where A and B are the nuclei of two H-atoms and 1, 2 are electrons present.

The Hamiltonian Operator for the title system is given by -

$$\hat{H} = -\frac{\hbar^2}{8\pi^2 m} \left( \nabla_1^2 + \nabla_2^2 \right) + \frac{e^2}{R} + \frac{e^2}{r_{A1}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}}$$

$$- \frac{e^2}{r_{B2}}$$

It is a two electron system, hence the total orbital wave fn. is the product of the wave fn. for each electron.

Electron 1 will occupy the molecular orbital given by :  $\Psi_1 = c_1 \Psi_A(1) + c_2 \Psi_B(1)$

Electron 2 will occupy the molecular orbital given by :  $\Psi_2 = c_1 \Psi_A(2) + c_2 \Psi_B(2)$

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Thus  $\Psi_1$  and  $\Psi_2$  are the linear combination of the two atomic H-orbitals (i.e. 1s) and the net MO is given by :-

$$\Psi_{MO} = \Psi_1 \times \Psi_2 \\ = [c_1 \Psi_A(1) + c_2 \Psi_B(1)] [c_1 \Psi_A(2) + c_2 \Psi_B(2)]$$

By using the cond. to normalise the  $\Psi_{MO}$  we get,

$$\int \Psi_{MO}^2 d\tau = 1.$$

It produces the normalising constant  $1/[2(1+S_{AB})]$  (under the condition,  $c_1 = c_2$ ) for the BMO. Thus, we get the wavefn. of the BMO as follows -

$$\Psi_{MO} = \frac{1}{2(1+S_{AB})} [\Psi_A(1)\Psi_A(2) + \Psi_B(1)\Psi_B(2) + \Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)].$$

The first two terms represent the ionic forms i.e.  $H_A^- H_B^+$  and  $H_A^+ H_B^-$  resp.

The other two terms represent the contribution of the covalent canonical forms originated from the electron exchange phenomenon.

The energy of the system can be evaluated by using the variation principle from the following Schrö.

$$\text{equ. } E \Psi_{MO} = \hat{H} \Psi_{MO}.$$

$$\text{or, } E = \frac{\int \Psi_{MO} \hat{H} \Psi_{MO} d\tau}{\int \Psi_{MO}^2 d\tau}.$$

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