Toppersnotes
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CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - IV

PHYSICAL **CHEMISTRY**

SIERRA INNOVATIONS

Index

CHEMICAL - BONDING

1 ques
हर saal आता है

HMOT (Huckel Mol. Orb. Theory)	MOT Mol. Orb. Theory.
→ follow variational principle (LCAO)	→ follow variational principle (LCAO)
→ $\psi = c_1\phi_1 + c_2\phi_2$	→ $\psi = c_1\phi_1 + c_2\phi_2$
→ $P = \int \psi^* \psi \, d\tau$	→ $P = \int \psi_1^* \psi \, d\tau$
$P = c_1^2 + c_2^2 + 2c_1c_2 S_{12}$ $P = 1$	$P = c_1^2 + c_2^2 + 2c_1c_2 S_{12}$ $P = 1$
~~Sij for i and j~~	$Sij \neq 0 \left(\begin{array}{c} i \, \& \, j \text{ are} \\ \text{neighbours} \end{array} \right.$
$Sij = 0 \left(\begin{array}{c} i \, \& \, j \text{ are not} \\ \text{neighbours} \end{array} \right)$	$\boxed{P = c_1^2 + c_2^2 + 2c_1c_2 S_{12} = 1}$
So $\boxed{c_1^2 + c_2^2 = 1 = P}$ $\underset{P_1}{\downarrow} \quad \underset{P_2}{\downarrow}$	$\begin{vmatrix} H_{11}-E & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-E \end{vmatrix} = 0$

$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = 0$

1

HMOT	MOT
$P_1 = c_1^2$	$P_1 = c_1^2 + c_1 c_2 S_{12}$
$P_2 = c_2^2$	$P_2 = c_2^2 + c_1 c_2 S_{12}$

Q. If $\psi_{MO} = 0.8\psi_1 + 0.4\psi_2$ is normalised functn of diatomic mc. Cal overlap Integral ?

Soln

$$\psi_{mo} = \underset{c_1}{\boxed{0.8}}\psi_1 + \underset{c_2}{\boxed{0.4}}\psi_2$$

अगर इनके coefficient के squares का sum 1 आए mtlb $S=0$ है।

given $c_1 = 0.8$

$c_2 = 0.4$

$$P = c_1^2 + c_2^2 + 2c_1c_2 S = 1$$

$$(0.8)^2 + (0.4)^2 + 2 \times 0.8 \times 0.4 \times S = 1$$

$$0.64 + 0.16 + 0.64 \times S = 1$$

$$\underline{S = 0.312}$$

$$S = \frac{1-(c_1^2 + c_2^2)}{2c_1 c_2}$$

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Q. The m.o. of diatomic mc. AB formed by linear combinatn of A & B & the normalised MO functn expressed as

$$\psi_{mo} = 0.8 \phi_A + 0.4 \phi_B$$ Determine the

Probability corresponding to ϕ_A

** (coefficients के sq.का sum 1 नहीं है mtlb

S overlap integral zero नहीं है।
सबसे पहले yhi check krte h.)

$$S = \frac{1 - (c_1^2 + c_2^2)}{2 c_1 c_2}$$

$$S = \frac{1 - [(0.8)^2 + (0.4)^2]}{2 \times 0.8 \times 0.4}$$

$$\boxed{S = 0.312}$$ $$\boxed{P_A = c_1^2 + c_1 c_2 S}$$

$$\frac{P}{A} = (0.8)^2 + (0.8) \times (0.4) \times (0.312)$$ (रसायन c_2
                                                                          नहीं लिया)

$$P_A = 0.739$$

$$\boxed{P_B = 1 - P_A}$$

$$= 1 - 0.739$$

$$P_B = 0.261$$

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(% of time mtlb Probability)

Q. A m.o. of a polar mc. AB has to be formed

$c_A \phi_A + c_B \phi_B$. where ϕ_A & ϕ_B are normalised functn. The e^- in this orb. is found on atom B $\bar{c}$ probability of 90%. Neglecting

(S=0) overlap Integral, the value of c_A & c_B will be?

$$P_1 = c_1^2 \qquad \qquad P_A = c_A^2 = 0.1$$

OΣ

$$P_2 = c_2^2 \qquad \qquad P_B = c_B^2 = 0.9$$

$$P_B = \frac{90}{100} = 0.9 \qquad \qquad c_A = \underline{0.316}$$

$$\qquad \qquad \qquad c_B = \underline{0.948}$$

$$P_A = \frac{10}{100} = 0.1$$

Q. How many │min. e^-│ are req. for formatn of bond
(MOT के Basik थ्योरी)

ⓐ 1   © zero

eg: ⓑ 2   ⓓ Three
H_2^+ exist करती है|

Q. How many min no. of e^- are req. for formatn of bond acc. to MOT?   Acc. to MOT

ⓐ 1   © zero   Ⓗ₂⁺ exists. (B.O = ½)

ⓑ 2   ⓓ 3

Q. How many min no. of e^- are req. for bond formatn acc. to VBT?

ⓐ 1   © zero   Acc. to VBT

ⓑ 2   ⓓ 3.   Ⓗ₂⁺ does not exist.

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MOT OF H_2^+ :—

→ Acc. to MOT, M.O are formed by LCAO.

→ If Ψ_A and Ψ_B are 2 wave functions of atomic H, then

$$\Psi_{mo} = c_1 \Psi_A + c_2 \Psi_B$$

→ For MOT, i.e for combinatn of A & B, there are 3 conditions satisfied —

① Energy

② → Combining wave functions shud have comparable Energy.

② Overlap :

→ The Atomic Orbitals (A.O'S) representing the e⁻ cloud must undergo overlapping considerably to produce a significant extent of overlap.

③ Overlap ⌉   ⊕ve → BMO
Integral ⌡→ ⊖ve → ABMO
             zero → NonBonding

→ The lobes of combining A.O.'S must have same sym. wrt Bond Axis.
It indicates that lobes of A.O.'S of same sym. can only overlap.

BONDING

Ψ_A
(Symmetric)

Ψ_B
(Sym)

$\xleftarrow{\hspace{1cm}} r_{AB} \xrightarrow{\hspace{1cm}}$

$$\Psi_{mo} = c_1 \Psi_A + c_2 \Psi_B$$
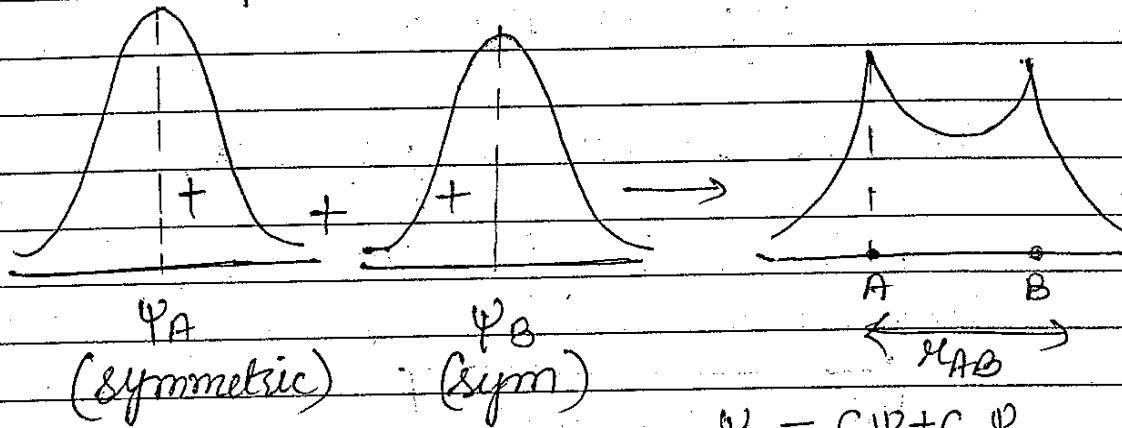
overlap integral $\boxed{S_{AB} > 0}$

ANTIBONDING

Ψ_A
(Sym)

Ψ_B
(Antisym)

$$\Psi_{mo} = c_1 \Psi_A - c_2 \Psi_B$$
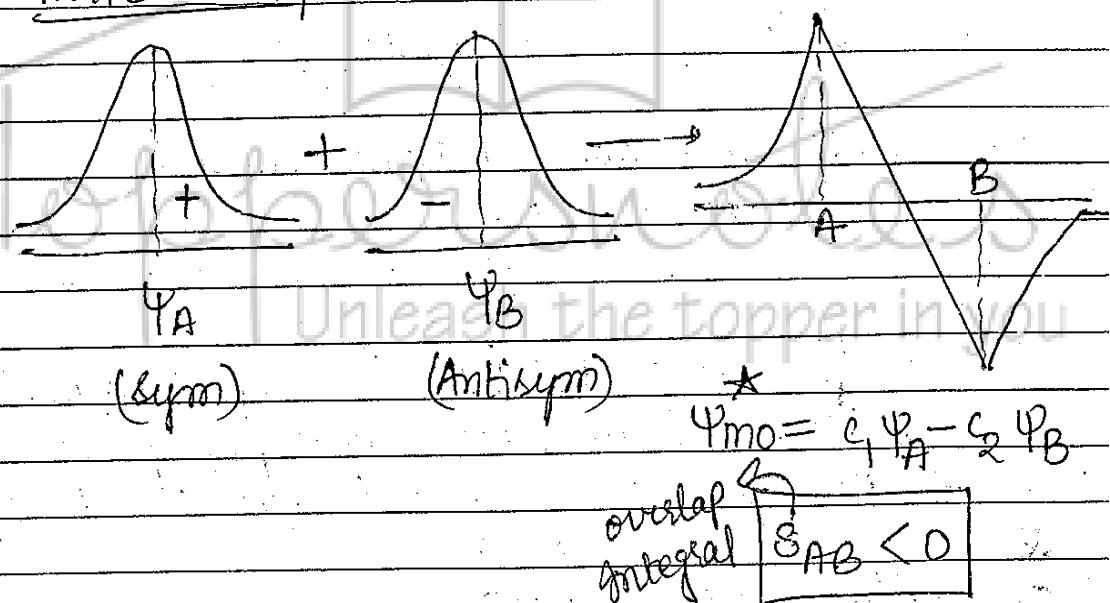
overlap integral $\boxed{S_{AB} < 0}$

Bonding MO	$S_{AB} > 0$	Attract^n, stability $\uparrow$, $E \downarrow$
Anti Bonding MO	$S_{AB} < 0$	Repulsion, Stability $\downarrow$, $E \uparrow$
N.B. MO	$S_{AB} = 0$	

Energy released after formation
of mo = β

Energy released (by) mo formatⁿ = α
before

BMO $\longrightarrow$ $E+ = \dfrac{\alpha + \beta_{AB}}{1 + S_{AB}}$
की Energy

ABMO $\longrightarrow$ $E- = \dfrac{\alpha - \beta_{AB}}{1 - S_{AB}}$
की Energy

$\alpha \longrightarrow$ Atomic Energy of H atom.

$\beta \longrightarrow$ Resonance Integral. (measure of Exchange Energy)

$S_{AB} \longrightarrow$ overlap Integral ; indicating stabilisatⁿ in overlap phenomenon.

Overlapping के लिये same sym चाहिये है।

The secular determinant for H_2^+

BMO	$\alpha_A - E$	$\beta_{AB} - ES_{AB}$
ABMO	$\beta_{AB} - ES_{AB}$	$\alpha_B - E$
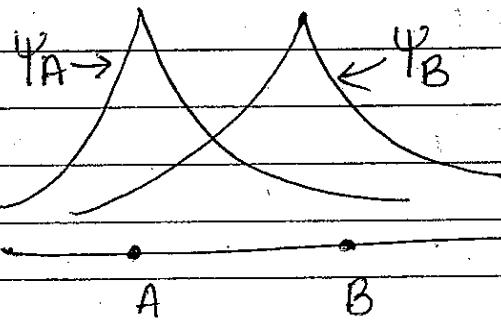
$= 0$

$\Psi_A \rightarrow$ $\leftarrow \Psi_B$

A   B

This figure is of :—
Ψ_A & Ψ_B of Isolated
H_A & H_B atoms.

For Bonding

Ψ_{mo} (Bonding)

A   B

comparison ठीक से ही
बताया जा सकता है कि
Ψ_{mo} है या Ψ^2_{mo} (deep)

deep है या

$\leftarrow \Psi^2_{mo}$ Bonding

A   B

For AB

Ψ^*_{mo} (AB)

A   B

$\rightarrow \Psi^2_{mo}$ (AB)

A   B
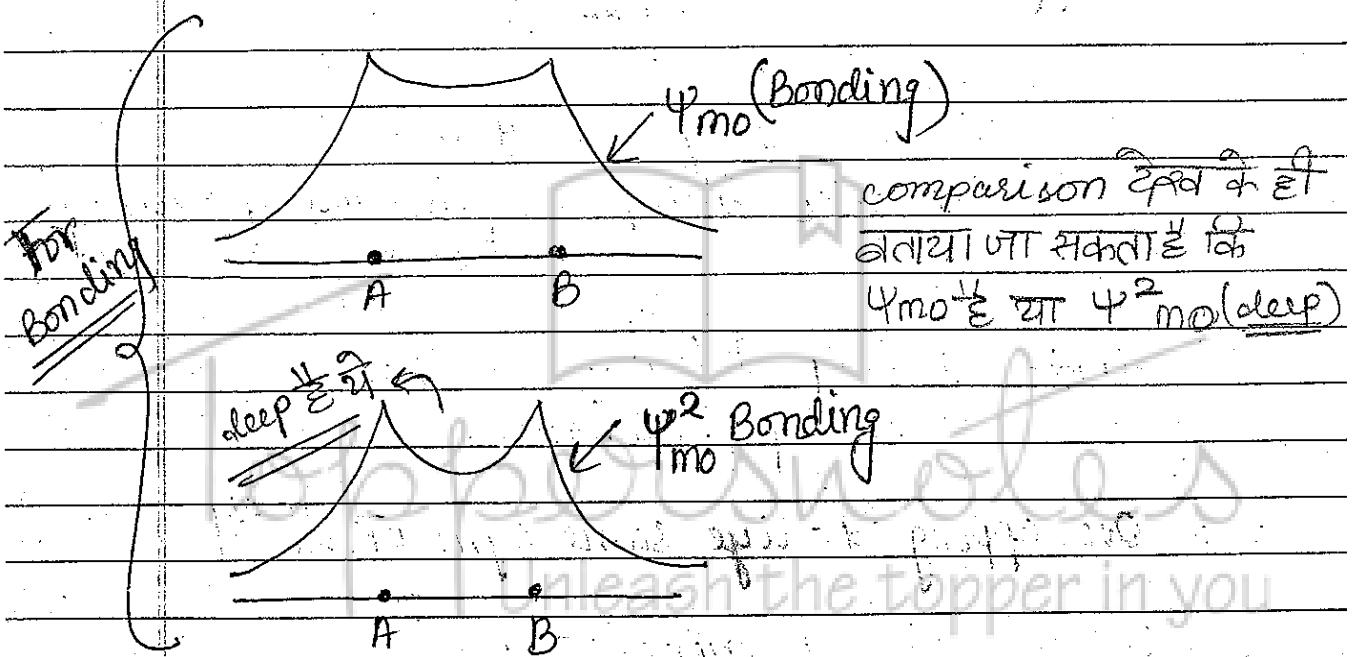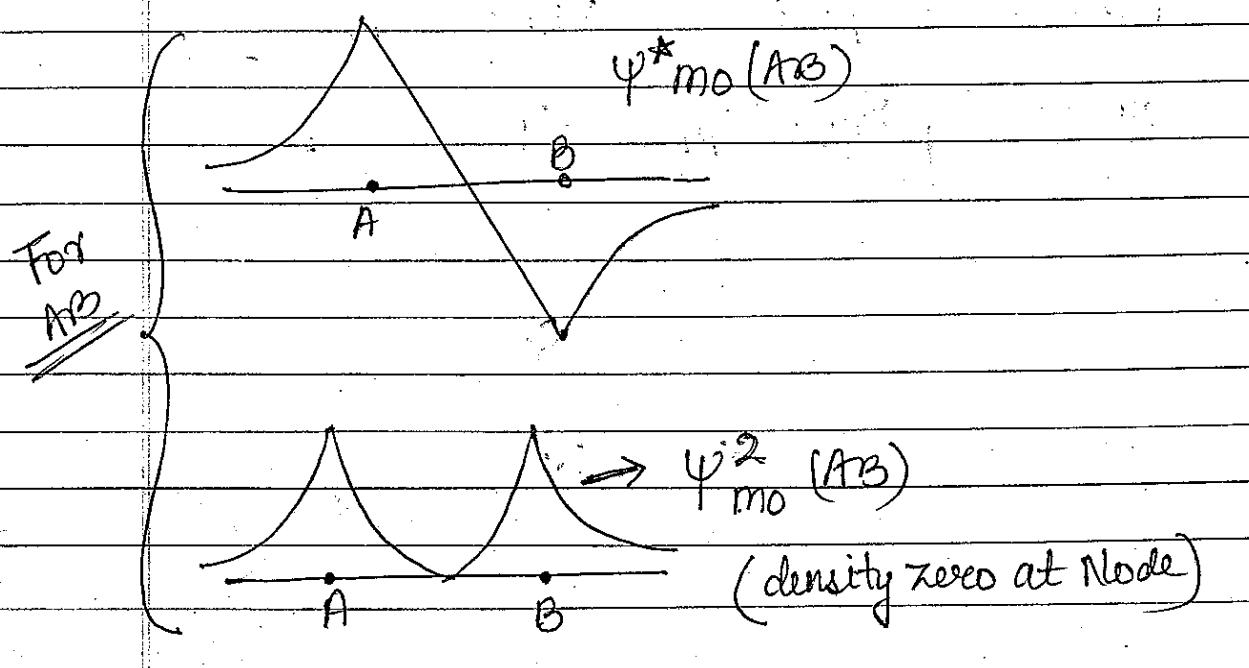
(density zero at Node)

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$\rightarrow$ <u>BONDING</u> :—

$\Psi_{mo} = c_1 \Psi_A + c_2 \Psi_B$
(Bonding)

$c_1 = c_2$ ∵ (same height है dono की)

$$\boxed{c_1 = c_2 = \frac{1}{\sqrt{2(1+S_{AB})}}}$$ $\longrightarrow$ Bonding का Normalisat^n Constant

$$\boxed{\Psi_{mo} = \frac{1}{\sqrt{2(1+S_{AB})}} (\Psi_A + \Psi_B)}$$

$\Longrightarrow$ Anti Bonding :—

$\Psi^*_{mo} = c_1 \Psi_A - c_2 \Psi_B$

$$\boxed{c_1 = c_2 = c^* = \frac{1}{\sqrt{2(1-S_{AB})}}}$$

$$\boxed{\Psi^*_{mo} = \frac{1}{\sqrt{2(1-S_{AB})}} (\Psi_A - \Psi_B)}$$

$\alpha_A = \alpha_B = \alpha$

$$\boxed{\alpha = E_H + J + \frac{1}{R}}$$

where; $J \rightarrow$ Coulomb Integral; represent the electrostatic attraction.

Attract^n की P.E. = $\ominus$ve hotih.

repulsion की P.E = $\oplus$ve

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$R \longrightarrow$ Inter nuclear dist.

$E_H \longrightarrow$ Energy of $1S$ -orb. of isolated H atom

$\beta_{AB} \longrightarrow$ Resonance Integral.

$$\beta_{AB} = E_H S_{AB} + K + \frac{S_{AB}}{R}$$

$K \longrightarrow$ Exchange Integral.

HYDROGEN Molecule MOT:
(2 electron – 2 Centre system)

$$\Psi_{mo} = \left(\Psi_A^{(1)} + \Psi_B^{(1)} \right) \left(\Psi_A^{(2)} + \Psi_B^{(2)} \right)$$

* पहले add होते hai fir

$\Psi_{mo} = *$ (multiply होते है MOT में)

$$\Psi_{mo} = \Psi_A^{(1)} \Psi_A^{(2)} + \Psi_B^{(1)} \Psi_A^{(2)} + \Psi_A^{(1)} \Psi_B^{(2)}$$

$$+ \Psi_B^{(1)} \Psi_B^{(2)}$$

covalent term
(50%)

Ionic term

(25% ; 25% each)
ionic term

$\rightarrow$ $2e^-$ – 3centred system (eg : H_3^+)

$$\psi_{mo} = \left(\psi_A(1) + \psi_B(1) + \psi_C(1)\right)\left(\psi_A(2) + \psi_B(2) + \psi_C(2)\right)$$

$\ast\ast$ (पहले add hote hai फिर multiply hote)
$\underset{\text{MOT में}}{}$

Imp # VBT v/s MOT :-
(aega aega)

MOT	VBT
$\rightarrow$ min 1 e^- in a system is needed. i,e 1e⁻ 2centred system possible.	$\rightarrow$ min 2e^- are req. in a system (i,e 1e⁻ 2c system NOT possible.
$\rightarrow$ For $2e^-$ 2centred	
$\psi_{mo} = \underset{\text{Ionic term}}{\underbrace{\psi_A(1)\,\psi_A(2)}} + \underset{\text{covalent}}{\underbrace{\psi_A(1)\,\psi_B(2)}}$	Pure covalent term $\psi_{VB} = \psi_A(1)\,\psi_B(2) +$
$\underset{\substack{\text{covalent}\\\text{term}}}{+\psi_A(2)\,\psi_B(1)} + \underset{\text{Ionic term}}{\underbrace{\psi_B(1)\,\psi_B(2)}}$	$\psi_A(2)\,\psi_B(1)$
(पहले add then multiply) MOT में	(VBT में पहले multiply then add hote h)
(0Σ)	
$\psi_{mo} = \left(\psi_A(1) + \psi_B(1)\right)\left(\psi_A(2) + \psi_B(2)\right)$	
$\rightarrow$ MO has 50% Ionic & 50% covalent term.	$\rightarrow$ VBT is pure covalent term.

→ MO's are polycentric involves more than one nucleus

→ Acc to MOT, H_2 mc. dissociate as

$$H_2 \longrightarrow \begin{cases} H^{\bullet} + H^{\bullet} \text{ (covalent)} \\ H^+ + H^{\bullet-} \text{ (ionic)} \end{cases}$$

→ VBT are Monocentric

→ VBT of H_2 mc.
2 types of wave func^ns possible
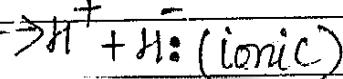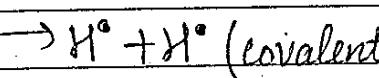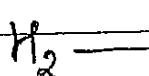
$$\Psi_{Sym} = N\left(\Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)\right)$$

$$\Psi_{Antisym} = N\left[\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1)\right]$$

$N \rightarrow$ Normalisation const.

$$\boxed{N = \frac{1}{\sqrt{2\left(1 \pm S_{AB}^2\right)}}}$$

for Sym. $\Psi_{(S)}$

$$N = \frac{1}{\sqrt{2\left(1 + S_{AB}^2\right)}}$$

$$\Psi_S = N\left[\Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)\right]$$

for Antisym Ψ_{AS}

$$N = \frac{1}{\sqrt{2\left(1 - S_{AB}^2\right)}}$$

$$\Psi_{AS} = N\left[\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1)\right]$$

VALENCE BOND TREATMENT
OF H_2—MOLECULE :—

$\Psi_A = N(\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1))$

$+ve$

0

$-ve$

$\Psi^0 = \Psi_A(1)\Psi_B(2)$

coulomb E. (J)

Exchange Energy (K)

$\boxed{E_{H_2} - 2E_H}$

I

II

$\Psi_{covalent} = N[\Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)] = \Psi_S$

covalent-ionic reso. Energy

III

$\Psi_{H_2} = (1-\lambda)\Psi_{cov} + \Psi_{ionic}$

(Valence Bond Treatment of H_2 molecule)

Internuclear dist.

$\hat{A} = \dfrac{L^2}{2I}$
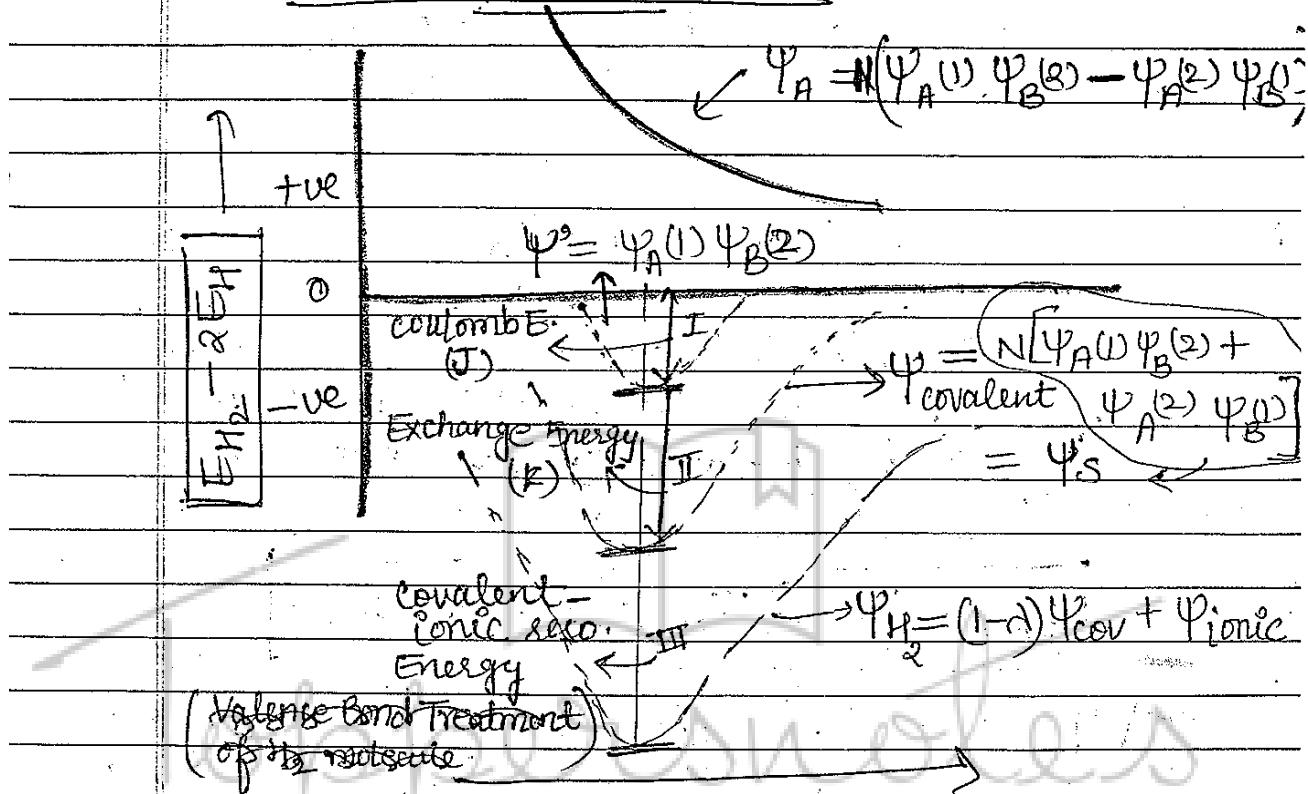
$E_{sym} = \int \Psi_S \hat{H} \Psi_S \, dz$

$E_{antisym} = \int \Psi_a \hat{H} \Psi_a \, dz$

$Q \rightarrow$ Coulomb Integral

$A \rightarrow$ Exchange Integral.

$\boxed{\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}^0}$

$\boxed{E_{S_{ym}} = 2E_H + \dfrac{Q+A}{1+S^2_{AB}}}$

$\boxed{E_a = 2E_H + \dfrac{Q-A}{1-S^2_{AB}}}$

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Treatment of H_2 mc as VBT :—

$$E_{Binding} = E_{Sym} - 2E_H = \frac{Q+A}{1+S^2_{AB}}$$

Ans → Acc. to VBT, ψ contain purely covalent character but it is NOT correct bcz heterodiatomic molecules like HCl exist ionic character so we have to modify VBT wave function (ψ_{VBT}) by introducing Ionic part as

$$\psi_{VBT} = (1-\lambda)\,\psi_{covalent} + \lambda\,\psi_{ionic}$$

λ ψ → mixing coefficient (measuring the extent of mixing) i.e. $\frac{\text{of ionic wave functn}}{\text{the covalent wave function}}$. i.e λ determines the % of Ionic character.

→ The acceptable ψ_{VBT} is expressed as :—

$$\psi_{VBT} = \psi_{covalent} + \lambda\,\psi_{ionic}$$

Normalisatn Const $(N) = \dfrac{1}{\sqrt{1+\lambda^2}}$

→ So Normalised VBT functn :—

$$\psi_{VBT} = \frac{1}{\sqrt{1+\lambda^2}}\left(\psi_{cov} + \lambda\,\psi_{ionic}\right)$$

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$$\Psi_{VBT} = \boxed{\frac{1}{\sqrt{1+d^2}}} \Psi_{cov.} + \boxed{\frac{d}{\sqrt{1+d^2}}} \Psi_{ionic}$$
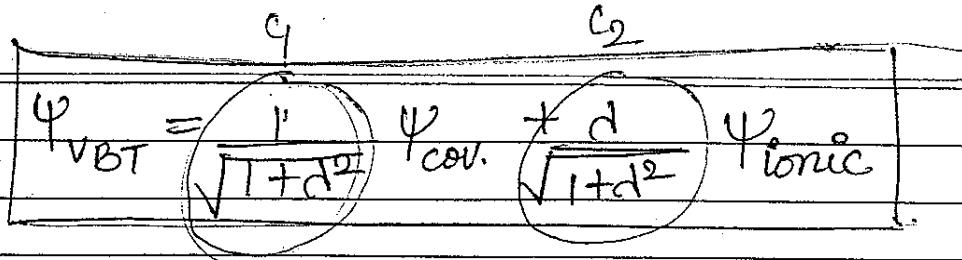
→ The % Ionic character $\left(\frac{P}{2}\right)$

$$\% \frac{P}{2} = C_2^2 \times 100 \%$$

$$\% P_2 = \frac{d^2}{1+d^2} \times 100 \% \longrightarrow \% \text{ Ionic character}$$

$$\% \text{ Covalent character} = \frac{1}{1+d^2} \times 100 \%$$

Q. The wave functn of diatomic mc. has form :—

$$\Psi = 0.89 \, \Psi_{cov} + 0.45 \, \Psi_{ionic}$$

The % Ionic character will be?

Normalised $\frac{\Psi}{E}$

$(0.89)^2 + (0.45)^2 = 1$

$$\% I.C. = C_2^2 \times 100 \%$$
$$= (0.45)^2 \times 100 \%$$
$$= 20.25 \%.$$