

CH107: 23<sup>rd</sup> sept 2019.

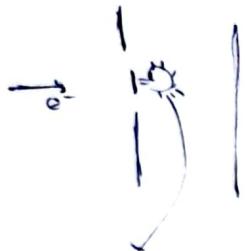
- Atkin's Physics chemistry
- Quantum chemistry: Levine

Reading source:- R. Feynman.

Edward Youman: chemistry at last.

Awesome double slit exp. video

(Dr. quantum) sch. cat.



here; photon will measure'  $e^-$  or 'not measure'  $e^-$ .

\* state of system is completely given by  $\psi(x)$ :  $R \rightarrow$  complex nos.

↳ POSTULATES 1.

$$\psi(x) = N \cdot e^{-2x^2} \text{. normalize!}$$

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

$$\int_{-\infty}^{\infty} N^2 e^{-4x} dx = 1$$

$$2N^2 \cdot \frac{e^{-4x}}{-4} \Big|_0^{\infty} = 1$$

$$\frac{+N^2}{2} = 1$$

$$\boxed{N = \sqrt{2}}$$

$$\psi(x) = e^{i\theta} \cdot \phi(x)$$

(where  $\theta = \text{any real number}$ )

$$\langle \psi(p) | \psi(p') \rangle = \langle \phi(p) | \phi(p') \rangle$$

$\Rightarrow \phi(p) = \phi(p')$

$$\langle \phi(p) | \phi(p') \rangle = \delta(p - p')$$

$$\boxed{D(p)}$$

Acceptable wavefunctions:-

single-valued, continuous, differentiable, finite, square integrable.  
physical sense

operator.

Act of measurement

Postulate-②:

Observables operator: Linear & Hermitian.

Linearity:

$$\hat{O}(c_1\psi_1 + c_2\psi_2) = c_1 \cdot \hat{O}(\psi_1) + c_2 \cdot \hat{O}(\psi_2)$$

Hermitian:

$$\int_{-\infty}^{\infty} \psi_1^* \hat{O}(\psi_2) dx = \int_{-\infty}^{\infty} (\hat{O}(\psi_1))^* \psi_2 dx$$

"to every observable; there exists a linear hermitian operator"  
- A postulate.

\* potential:  $V(x)$ .

$$\hat{V}(\psi(x)) = V(x) \psi(x)$$

\*  $\hat{O}\psi_i(x) = a_i \cdot \psi_i(x)$

(is not a function if  $\psi_i(x)$  is eigenfunction.  
 $a_i$  is a number.)

\* Hermitian operator has real eigen values:

$$\hat{H}\psi = a\psi. \quad \text{what can this be?}$$

by defn:  $\int_{-\infty}^{\infty} \psi_1^* \hat{H} \psi_2 dx = \int_{-\infty}^{\infty} (\hat{H} \cdot \psi_1)^* \psi_2 dx$

(which obey boundary conditions).  
 $\therefore \psi(x) \neq e^{kx}$

$$\therefore \text{let } \psi_1 = \psi_2 = \psi.$$

$$\int_{-\infty}^{\infty} \psi^* a \psi dx = \int_{-\infty}^{\infty} a^* \psi^* \psi dx$$

$$\therefore [a = a^*]$$

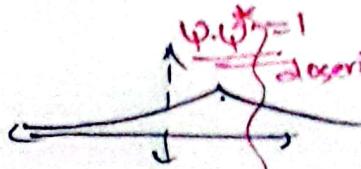
$a$  is real.  $\forall \psi \in \text{eigen functions}$

\* Hermitian operators have a complete set of orthonormal eigen functions  
 $\psi(x) = \sum C_i \psi_i(x)$

Misconception:-

$$\psi(x) = e^{-ikx} \quad \psi(x) = e^{i\theta} \cdot e^{-ikx}$$

$$\psi \cdot \psi^* = e^{i\theta}$$



despite mean particle's position is at  $x=0$ !

see  $\psi \psi^*$ .

Take care!  
don't trust  $\psi$ .

Postulate 3:

"In measurement of observable associated with  $\hat{O}$ ; only values that will be observed are eigenvalues of  $\hat{O}$ .

After measurement, system collapses to that eigenfunction!"

Q)  $\Psi = \sqrt{0.3} \phi_1 + \sqrt{0.7} \phi_2$

if 1st,  $\Psi$  measured, get  $\phi_1$ .

next measurement:  $P(\text{getting } \phi_2) = 0$

→ Properties of Hermitian eigenfunctions:-

\* orthogonal:

$$\hat{O} \Psi(x) = \alpha_i \Psi_i(x)$$

$$\int_{-\infty}^{\infty} dx \Psi_i^* \Psi_j = \delta_{ij} = 1; i=j$$

as usual habit:  
 $= 0; i \neq j$

$$\int \Psi_i^* \Psi_j dx \\ = 0 \text{ (wrong!)}$$

\* completeness:

take an operator  $\hat{O}$ ; & take its all eigenvalues.

there exist,  $c_1, c_2, c_3, \dots$

$$\Psi(x) = \sum c_i \phi_i(x).$$
 Hence, it's sufficient to learn  
"Any function" the operator on its eigen functions

Postulate 4:

Copenhagen interpretation.

$\Psi(x)$  be the wave function of a particle. If the value of some observable with operator  $\hat{O}$  is repeatedly measured; on many such systems.

$$\text{Average} = \frac{\int_{-\infty}^{\infty} \Psi(x)^* \hat{O} \Psi(x) dx}{\int_{-\infty}^{\infty} \Psi(x)^* \Psi(x) dx}$$

$$\text{if } \Psi(x) = \sum c_i \phi_i$$

$$\text{Average} = |c_1|^2 \bar{x}_1 + |c_2|^2 \bar{x}_2 + \dots$$

$$\Psi = c_1 \phi_1 + c_2 \phi_2 + \dots$$

$$\Psi^* = c_1^* \phi_1^* +$$

$$+ c_2^* \phi_2^* + \dots$$

Q)  $\Psi(x) = \sqrt{2} e^{-\frac{|x|}{2}}$

what is average value of  $x$

most probable value of  $x$  { where  $|\Psi(x)|$  is maximum.}

don't use  $\Psi(x)$ ...  
say  $\Psi \cdot \Psi^*$ .  
TC

### Postulate 5:

How system evolves with time.

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \Psi(x,t)$$

this is time dependence of  $\Psi$ .

to get  $\Psi(x,t)$ ; supreme eqn is  $i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \Psi(x,t)$

time  
dependence  
 $\phi(t) = e^{-iEt/\hbar}$

value separately.

Gives  $\Psi(x) = \phi(t) \Psi_0(x)$

solve.

$\Psi(x)$  ka equation.

$$\hat{H} \Psi_0 = E \Psi_0$$

(here; don't against this)

$$\hat{H} \Psi_0 = i\hbar \frac{\partial}{\partial x} \Psi_0$$

Crap ...

Stationary states:

$|\Psi_0(x)\rangle$  doesn't depend on time.

Solutions of Hamiltonian

$$\Psi_1(x), \Psi_2(x), \dots$$

non-stationary states:

$|\Psi(x)\rangle$  depends on time.

$$\Psi(x) = \sum C_i (\Psi_i(t)) \cdot \Psi_i(x)$$

here;  $\Psi_1, \Psi_2, \dots$  are Hamilton eigen.

but not  $\Psi(x)$ .

\* commutators:

if  $[\hat{A}, \hat{B}] \neq 0$ ; then there is no common eigen function of  $\hat{A}$  &  $\hat{B}$ .

\* Hence, as  $[\hat{x}, \hat{p}] = i\hbar$ ; we don't have a common eigen funcn.

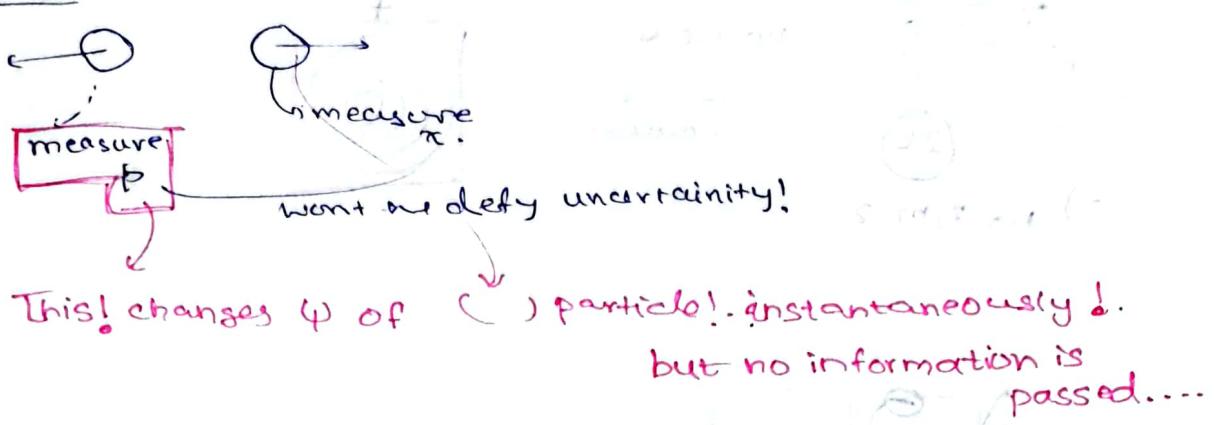
∴ we can't have

$$\hat{x} = 0 \& \hat{p} = 0 \text{ simultaneously}$$

\* we found  $\Psi(x) \& \phi(t)$  separately;

ultimately  $\Psi(x,t) = \Psi(x) \cdot \phi(t)$ .

## EPR experiment:-



## Tarphome:

- 1) Quantisation is a direct result of boundary conditions.
- 2) zero point energy; acknowledge it!

\*  $\Psi_{1(x)}$  is not dimensionless!  
 $\Psi = \sqrt{\frac{2}{L}} \dots$   
units!  
 $|\Psi|^2$  is dimensionless.

$\Psi_{1(x)}$  has  $\frac{1}{x^{1/2}}$

$\Psi(x,y)$  has  $\frac{1}{x}$

## 2D:

### Separation of variables:-

$$\hat{H}_{x,y} \Psi_{1(x,y)} = [\hat{H}_x + \hat{H}_y] \Psi_{1(x,y)} = \phi(x) \chi(y)$$

$$\Psi(x,y) = \phi(x) \chi(y)$$

$$= \hat{H}_x \phi(x) \chi(y) + \hat{H}_y \phi(x) \chi(y)$$

What about other  
other solutions?

only if potential  
is separable.

\* Now  $V = V(x) + V(y)$



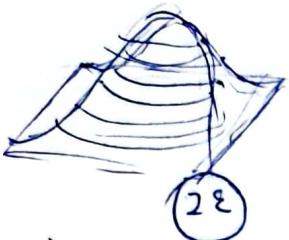
$$\hat{H}_x = \left[ \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right]$$

$$\hat{H}_x \phi(x) = E_x \phi(x).$$

$$\therefore E_x = \frac{n^2 \hbar^2 \pi^2}{2m l^2}; \quad E_y = \frac{m^2 \hbar^2 \pi^2}{2m l^2}. \quad \boxed{E_{\text{tot}} = E_x + E_y.}$$

$$\phi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right); \quad \chi(y) = \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi y}{L}\right).$$

$$\therefore \boxed{(\Psi_{1(x,y)} = \frac{2}{L} \cdot \sin\left(\frac{n\pi x}{L}\right) \cdot \sin\left(\frac{m\pi y}{L}\right))}$$

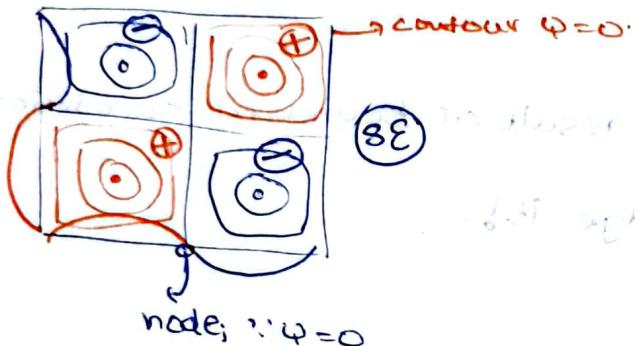


$n=1, m=1$

no node.  
contour



2)  $n=2, m=2$



contour  $\psi=0$

node;  $\therefore \psi=0$

$\epsilon$   $\psi$  changes sign,  $\psi$

Energies:-

$$E = (n^2 + m^2)\epsilon.$$

2ε

$$\frac{5\epsilon}{\sqrt{2}} \quad \frac{5\epsilon}{\sqrt{2}} \quad \frac{5\epsilon}{\sqrt{2}}$$

$\psi_{(1,0)} \quad \psi_{(2,0)} \quad \psi_{(2,1)}$

\* now! due to degeneracy;

$(\psi = C_1 \psi_{1,0} + C_2 \psi_{2,1})$  is an eigenfunction for energy.

\* this degeneracy is consequence of symmetry.

\* can we write  $\psi(x,y) = \phi(r) \cdot \chi(\theta)$  for

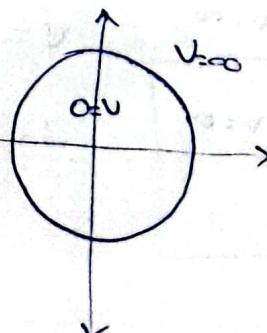
NO!

we need  $H(x,y) = \hat{H}_x + \hat{H}_y$   
to write dec. resp.

But here;

$$V(x) = 0; \sqrt{a^2 - y^2} \neq \lambda$$

$\infty; x > \sqrt{a^2 - y^2}$



$$\therefore V(x,y) \neq V(x) + V(y)$$

∴ Can't write.

→ on ring:

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right).$$

$$x = r \cos \phi; y = r \sin \phi.$$

(using  $r = \text{constant}$ ).

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right) \rightarrow \text{radial!}$$

$$\text{now, } \hat{H}\psi = E_i \psi.$$

$$\frac{-\hbar^2}{2mr^2} \frac{\partial^2 \psi}{\partial \phi^2} = E_i \psi.$$

boundary,  $\psi(0) = \psi(2\pi)$ ,

$$\psi = A e^{+i\sqrt{\frac{E_i 2mr^2}{\hbar^2}} \phi}.$$

$$\sqrt{\frac{2mr^2 E}{\hbar^2}} = \text{integer.}$$

$$E = \frac{n^2 \hbar^2}{2mr^2}$$

$$\text{here } I_z = -i\hbar \frac{\partial}{\partial \phi}$$

$I_z$  is quantized

$$-\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} \right) = \alpha \phi \psi.$$

$$e^{i\sqrt{\frac{2mr^2 \phi}{\hbar^2}}}.$$

$$\hat{H}\psi = E_i \psi.$$

$$-\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} \right) = E_i \psi$$

\* Angular momentum operator

$$I = \vec{r} \times \vec{p}.$$

$$\star \hat{I}_z = (\hat{x}\hat{i} + \hat{y}\hat{j}) \times (\hat{p}_x\hat{i} + \hat{p}_y\hat{j})$$

$$= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

$$= \hat{x} \cdot (-i\hbar \frac{\partial}{\partial y}) - (-i\hbar \frac{\partial}{\partial x}) \hat{y}$$

$$= -i\hbar \left( \hat{x} \frac{\partial}{\partial y} - \hat{y} \frac{\partial}{\partial x} \right)$$

$$\boxed{\hat{I}_z = -i\hbar \frac{\partial}{\partial \phi}} \quad \text{radial!}$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = -\frac{2mr^2 E_i}{\hbar^2} \psi.$$

$$\therefore \psi = e^{\pm i\sqrt{\frac{2mr^2 E}{\hbar^2}} \phi}$$

$$e^{ik\phi}, \quad i$$

$$e^{i2\pi k} = 1.$$

$$2\pi k = 2\pi n.$$

$$k = n.$$

$$x \frac{\partial \psi(r, \theta)}{\partial y} - y \frac{\partial \psi(r, \theta)}{\partial x}$$

$$x \left[ \frac{\partial \psi}{\partial r} \frac{\partial r}{\partial y} + \frac{\partial \psi}{\partial \theta} \frac{\partial \theta}{\partial y} \right]$$

$$r \cdot \sin \theta \cos \theta \frac{\partial \psi}{\partial r}$$

completely logical.

which we learnt in maths...

Proof:

$$x = r \cos \theta \quad \boxed{\frac{\partial x}{\partial r} = \cos \theta} \dots$$

$$y = r \sin \theta \quad \theta = \tan^{-1}(y/x).$$

$$\begin{aligned} \frac{\partial \psi(r, \theta)}{\partial x} &= \frac{\partial \psi}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial \theta} \frac{\partial \theta}{\partial x} \\ &= \frac{\partial \psi}{\partial r} \cancel{\cos \theta} + \frac{\partial \psi}{\partial \theta} \frac{-\sin \theta}{r}. \end{aligned}$$

$$r \sin \theta.$$

$$-OTq$$

orbital is an  $1-e^-$  wave function.)

→ Jumping into 3D - Hydrogen atom:-

$$\hat{H} = \hat{K}E + PE$$

$$\downarrow -\frac{kze^2}{1r^2}$$

$$\text{in xyz: } -\frac{\hbar^2}{2me} \cdot \nabla_e^2 + \left(-\frac{\hbar^2}{2mn}\right) \cdot \nabla_N^2$$

spherical co-ordinate:

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

$$\Omega: [0, \pi] \quad \Phi: [0, 2\pi]$$

$$\nabla^2 V = r^2 \sin\theta \cdot d\theta dr d\phi$$

rem...

→ As we solve  $\hat{H}\psi = E\psi$  & get  $\psi = R(r)\Theta(\theta)\Phi(\phi)$ ;

we have from  $\Theta$ ; (using boundary conditions)

$$\downarrow m = 0, \pm 1, \pm 2, \dots$$

from  $\Theta$ : accepted solutions  
 $l = 0, 1, \dots, l \geq |m|$

from  $R$ : accepted solutions  
 $n = 1, 2, \dots, n > l$   
 $E_n = -\frac{2Q^2 Z^2 \mu e^2}{n^2 \hbar^2}$

$$*\Psi_{(r, \theta, \phi)} = N \cdot e^{-\frac{r}{a_0}}$$

$$n=1$$

$$l, m=0, 0$$

normalise.

$$N = \frac{1}{\sqrt{\pi} \cdot a_0^{3/2}}$$

$$\psi = \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a_0^{3/2}} e^{-r/a_0}$$

average radius =

most probable radius =

1) quantum number - l.

$$\hat{L}_x \checkmark =$$

$$\hat{L}_y \checkmark =$$

$$\hat{L}_z \checkmark$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$= -\hbar^2 \left( \hat{H}_{(r, \theta, \phi)} \right)$$

hamiltonian coincidence! of the system.)

∴  $\psi(r, \theta, \phi)$  is eigen. of  $\hat{L}^2$ .

i.e.

even  $\hat{L}^2$  is fixed!  
(no uncertainty; after knowing E).

Eigen value:  $l(l+1)\hbar^2$

$$\hat{L} = \hbar \cdot \sqrt{l(l+1)}$$

$$2) \hat{L}_z = -i\hbar \frac{d}{d\phi} \psi(r, \theta, \phi)$$

expans same as  $H(\phi)$ .

after full quantum treatment:

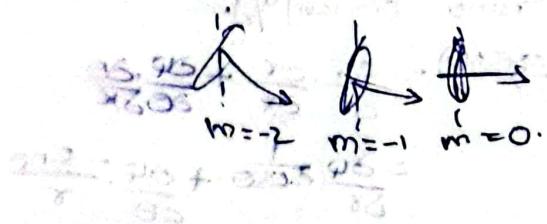
∴  $\psi(r, \theta, \phi)$  is eigenfn.

$\hat{L}_z \rightarrow \text{fixed}$

Eigenvalue

$$\hat{L}_z = \hbar \cdot m!$$

Space quantisation!



PTO.

Nodes: (theorem)

radial:  $n-l-1$

Angular:  $l$ .

$n$ : principle quantum number

- determines energy of electron.

$l$ : orbital angular momentum quantum number

- specifies the magnitude of electron's orbital angular momentum.

$m_l$ : (z-component) of orbital angular momentum.

due to our "definition of  $\theta, \phi$ ".

- specifies the orientation of angular momentum along z-axis.

\*  $\psi_{1,0,0}(r, \theta, \phi) = N \cdot e^{-\frac{r}{a_0}}$

$$\therefore P_{111} = \int r^2 dr d\theta d\phi (N \cdot e^{-\frac{r}{a_0}})^2 \text{ probability element.}$$

$$(\text{overall } \theta, \phi) = \int r^2 dr \cdot (N^2 e^{-2r/a_0})^2 r^2 dr \text{ closing}$$

$$= \int 4\pi r^2 N^2 e^{-4r/a_0} dr$$

$\downarrow$   
in a shell.

$\therefore P(r)$  is max; for  $r = a_0$   
radius of maximum probability

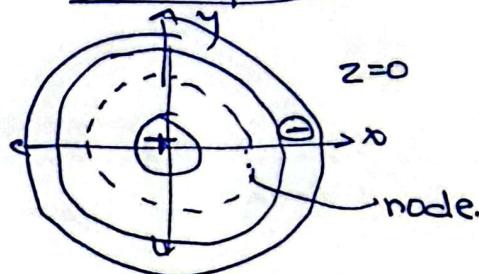
\* Two quantities:

$\psi$ :

+ve & -ve

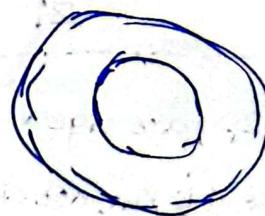


contour plots



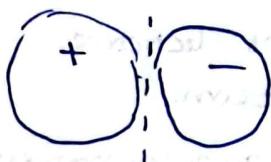
$|\psi|^2$

always non-negative.



for  $2P_z$ :

$\psi_1$ :



$|\psi|^2$ :



contour plot:



Nodes:-

Radial:  $n-l-1$

angular:  $l$ .

Orbital:-

1-electron  
wavefunction.

\* other two solutions are:

$2P_+, 2P_-$

$\downarrow$  linear combination

$$N \cdot \sin\theta \cdot e^{i\phi} \quad N \sin\theta e^{-i\phi}$$

$$2P_x = \frac{2P_+ + 2P_-}{2}$$

$$2P_y = \frac{2P_+ - 2P_-}{2i}$$

$2P_x, 2P_y$  are eigen functions

of  $\hat{H}_z$  But, not of  $\hat{L}_z$ ;

But; Yes eigenfun of  $\hat{l}^2$ .

$2P_x$  is eigen fun. of  $\hat{L}_x$ .

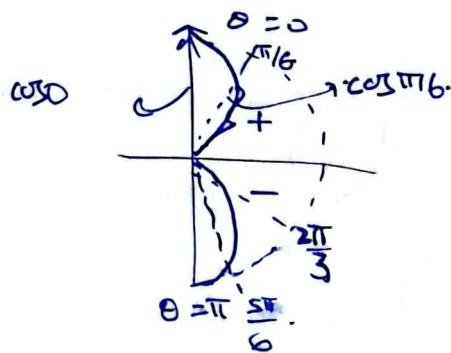
$2P_z \quad 2P_x \quad 2P_y$

$m=0 \quad m=? \quad m=?$

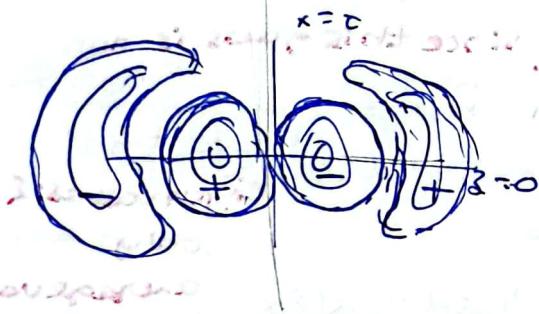
## Polar plot:-

$\phi(\theta) \text{ vs } \theta:$

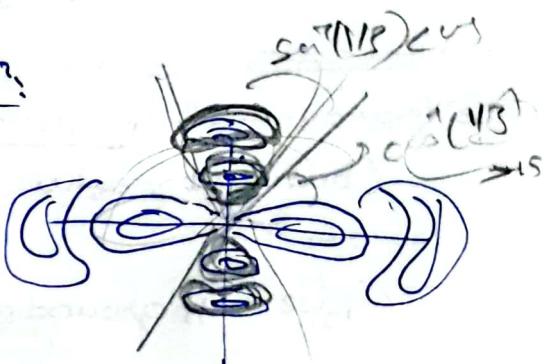
$$\text{if } \phi(\theta) = \cos\theta$$



\*  $3d^2$ : contour with  $y=0$



$2d^3$ :



pass through COM, cartesian frame.

→ writing Hamiltonians:-

1) Hydrogen:

$$\begin{array}{l} \text{Ground} \\ \text{polar:} \end{array} \hat{H} = -\frac{\hbar^2}{2m_N} \nabla_N^2 + \frac{-\hbar^2}{2me} \nabla_e^2 - \frac{kze^2}{|\mathbf{r}_{Ne}|}$$

com transform:

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_{\text{COM}}^2 + \frac{-\hbar^2}{2u} \nabla_e^2 - \frac{kze^2}{|\mathbf{r}_{Ne}|}$$

Ground cartesian  $\xrightarrow{\quad}$  relative COM  
Polar frame.

2) Helium

$$\begin{array}{l} \text{com:} \\ \text{pair:} \end{array} \hat{H} = -\frac{\hbar^2}{2m} \nabla_N^2 + \frac{-\hbar^2}{2u} \nabla_1^2 + \frac{-\hbar^2}{2u} \nabla_2^2 - \frac{kze^2}{|\mathbf{r}_{N1}|} - \frac{kze^2}{|\mathbf{r}_{N2}|} + \frac{kze^2}{|\mathbf{r}_{12}|}$$

roughly.

cartesian:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

..... (same as above) but here  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ .

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

transform into polar

$$\text{strictly: } (\text{above } \hat{H}) + \frac{-\hbar^2}{2mn} \frac{\partial^2}{\partial r_1 \partial r_2}$$

ignore! ab; S, small term

## \* Hamiltonian for n-e:-

$$\begin{aligned}\hat{H}_{el} &= \frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2 + \dots + \nabla_n^2) \\ \text{electronic} \\ \text{hamiltonian} &\quad - Qze^2 \cdot \left( \sum_{i=1}^n \frac{1}{r_{Ni}} \right) \\ &\quad + Qe^2 \left( \sum_{i=1}^n \sum_{j=i+1}^n \frac{1}{r_{ij}} \right) \\ &= \sum \hat{H}_i + Qe^2 \left( \sum_{i=1}^n \sum_{j>i} \frac{1}{r_{ij}} \right)\end{aligned}$$

\*; Here the  $\hat{H}_{el}$  is not separable.

∴ the solution  $\Psi(r_1, r_2) = \Psi(r_1) \cdot \Psi(r_2)$ .

### → Orbital approximation:-

we "approximate"  $\Psi(r_1, r_2)$  as  $\Psi(r_1) \cdot \Psi(r_2)$ . Since this guess is not an eigenfunction;  
(but don't neglect  $\frac{Qe^2}{|r_{12}|}$  term in  $\hat{H}$ ).

∴ we say; ground state of He is

$$\Psi(1, 2) = \Psi_{1S}(1) \cdot \Psi_{1S}(2).$$

We don't find eigenvalues;  $\Sigma$   
only average values.

### \* average electronic energy:

$$\begin{aligned}< \Psi_{1S} | \hat{H} | \Psi_{1S} > &= \int < 1S(1) 1S(2) | \hat{H} | 1S(1) 1S(2) > \\ &\quad + < 1S(1) | \hat{H}_2 | 1S(1) > \\ &\quad + < 1S(2) | \frac{Qe^2}{|r_{12}|} | 1S(2) > \\ &= 2(-13.6) \sum_{Z=2}^{\infty} \frac{1}{n^2} + < \frac{Qe^2}{|r_{12}|} > \\ &= -108.8 \text{ eV} + < \frac{Qe^2}{|r_{12}|} >\end{aligned}$$

this cannot be ignored.

$$^1 \text{He K}_{\alpha} \text{ energy} = -78 \text{ eV}.$$

in a computer;  $< \left( \frac{Qe^2}{|r_{12}|} \right) > = +34 \text{ eV}$ .  
can't ignore  $\frac{1}{r_{12}}$  term!

## Shielding:-

$$\hat{H}_{\text{ex}} = \sum_{i=1}^{\infty} \left( \frac{\pi^2}{2m} \cdot J_{\text{eff},i}^2 - \frac{k_{\text{eff}} e^2}{|\mathbf{r}_{\text{FN}}|} \right)$$

by applying to Helium,

$$E = -2 \times 13.6 \frac{Z_{\text{eff}}^2}{n^2}$$

$$\text{we have. } Z_{\text{eff}} = 0.7 + 1 = \underline{1.69}$$

∴ 0.3 shielding  $\Rightarrow$  Slater rule.

## Spin:-

- quantum mech. property; no classical analogue.
- Intrinsic; like charge & mass.

\*  $e^-$  can be a small ball; rotating about itself;

if so; its radius is bigger than atom.

SPIN ANG-momentum  $S = \hbar \sqrt{s(s+1)}$ .

$s = \text{sum of all } \frac{1}{2} \text{ spins.}$

$m_s$  from  $-s$  to  $s$

by  $-s, -s+1, \dots, s-1, s$ .  $\frac{(2s+1)}{\text{values.}}$

$$\underline{S_z = m_s \hbar}$$

∴ for  $e^-$ ;  $s = 1/2$ ;  $m_s = -1/2, 1/2$ .

$$S_z = \frac{-\hbar}{2}, \frac{\hbar}{2}.$$

↓  
Spin up ( $\alpha$ )  
Spin down ( $\beta$ )

\*  $\alpha, \beta$  are orthogonal.

$\alpha, \beta$  are independent of space

coordinates.

$$\int \alpha^* \alpha d\sigma = 1.$$

some variable.

(not enough)

→ revisiting all wavefunctions:-

1) Hydrogen atom:-

$$\Psi = \psi_{1s} \cdot \alpha.$$

or

$$\psi_{1s} (\alpha + b\beta)$$

now orbitals → spin orbitals.

- Spin orbitals are orthogonal & normalised;  
quantum numbers are

$n, l, m, m_s$ .

(or)  $m_l$ .  $m_s$  not  $S$ .

$m_l$ .  $s = \pm \frac{1}{2}$

$m = \pm \frac{1}{2}$  (i.g.)

$m_s \rightarrow$  magnetic spin Q. num

$S \rightarrow$  spin Q. number.

↳ intrinsic to particle system.

Spin quantum number:-

This describes the spin

(intrinsic

angular

momentum)

of the electron within that orbital.

gives the projection of

spin ang-

momentum

along specified axis.

$$\left( S_z = m_s \cdot \hbar \right)$$

6<sup>th</sup> postulate of Q.Mech.:-

(can be proved, but not here.)

The "complete wavefunction" of a system of Identical fermions (electrons)  
must be anti-symmetric wrt interchange of any two coordinates.  
(both spatial & spin).

$$\text{i.e. } \left( \Psi_{(2,1)} = -\Psi_{(1,2)} \right)$$

\*. If  $\Psi = \alpha(l_1) \cdot \alpha(l_2)$

then  $\Psi_{(1,2)} = \Psi_{(2,1)}$  } Acceptable

$\Psi = \alpha(l_1)\beta(l_2)$  } unacceptable

$\therefore \Psi = \frac{\alpha(l_1)\beta(l_2) - \alpha(l_2)\beta(l_1)}{\sqrt{2}}$  } acceptable.

$$\Psi = \Psi_{\text{spatial}} \cdot \Psi_{\text{spin}}$$

both must be symmetric or antisymmetric.

∴ Basis is

"Fermions are indistinguishable!"  
[Because too].

∴ for He<sub>2</sub>:

Ground state:  $\underline{1S^2}$ .

$$\therefore \Psi = \underbrace{\Psi_{1S(1)} \cdot \Psi_{1S(2)}}_{\text{symm.}} \cdot \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(2)\alpha(2)) \quad \text{antisymm...}$$

$$\Psi = \begin{vmatrix} 1S(1) \alpha(1) & 1S(2) \alpha(2) \\ 1S(1) \beta(1) & 1S(2) \beta(2) \end{vmatrix}$$

General Slater determinant:-

$$\Psi_{\text{Ground State}}^{(1, 2, \dots, N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(1) S_1(1) & \Psi_2(1) S_2(1) & \dots & \dots \\ \Psi_1(2) S_1(2) & \Psi_2(2) S_2(2) & \dots & \dots \\ \Psi_1(3) S_1(3) & \Psi_2(3) S_2(3) & \dots & \dots \\ \vdots & \vdots & \ddots & \ddots \end{vmatrix}$$

$N!$  terms in the expanded det.

- Any multielectron wave function = Slater determinant or

{ Linear combination of }  
Slater determinants.

\*

→ Lithium G.S.:  $1S^2 2S^1$

$$\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2S(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2S(3)\alpha(3) \end{vmatrix}$$

→ Helium excited states:

$1S^1 2S^1$

lets try:  $\frac{1}{\sqrt{2}} \begin{vmatrix} 1S(1)\alpha(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 2S(2)\alpha(2) \end{vmatrix}$  (or)  $\frac{1}{\sqrt{2}} \begin{vmatrix} 1S(1)\alpha(1) & 2S(1)\beta(1) \\ 1S(2)\alpha(2) & 2S(2)\beta(2) \end{vmatrix}$

$\frac{1}{\sqrt{2}}$  good  $\frac{1}{\sqrt{2}}$  not good!

$\Psi \neq \Psi_{\text{spatial}} \cdot \Psi_{\text{spin}}$

$$\frac{1}{\sqrt{2}} \left\{ \Psi_{\text{Spatial}} \text{ is } \underbrace{1s(1)2s(2)-2s(1).1s(2)}_{\Psi_{\text{Spin}} \text{ is } \underbrace{\alpha(1)\beta(2)+\alpha(2)\beta(1)}} \right.$$

$$\Psi = \underbrace{(1s(1)2s(2)-1s(2)2s(1))}_{(\alpha(1)\beta(2)+\alpha(2)\beta(1))}$$

~~can be written as a sum of Slater determinants.~~

$$\Psi = \alpha 1s(1)2s(2)\alpha(1)\beta(2) - 1s(2)2s(1)\alpha(2)\beta(1)$$

$$\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix}$$

$$+ 1s(1)2s(2)\alpha(2)\beta(1) - 1s(2)2s(1)\alpha(1)\beta(2)$$

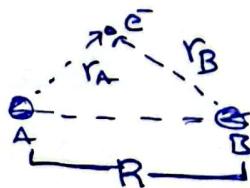
these both are  
Slater determinants.

$$\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}$$

But, their expansion can't be written as  $\Psi_{\text{Space}} \times \Psi_{\text{Spin}}$  (separately)

### → Chemical bonding:-

$\hat{H}$ :  $H_2^+$  in cartesian



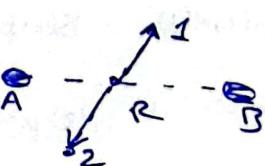
$$\hat{H} = -\frac{\hbar^2}{2m_N} (\nabla_A^2 + \nabla_B^2)$$

$$+ \frac{-\hbar^2}{2m_e} (\nabla_e^2)$$

$$- \frac{kZ_e^2}{r_A} - \frac{kZ_e^2}{r_B}$$

$$+ \frac{kZ_e^2 e^2}{R}$$

$\hat{H}$ :  $H_2$  in cartesian



$$\hat{H} = -\frac{\hbar^2}{2m_N} (\nabla_A^2 + \nabla_B^2)$$

$$- \frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2)$$

$$- \frac{ke^2}{r_{1A}} - \frac{ke^2}{r_{2A}} - \frac{ke^2}{r_{1B}} - \frac{ke^2}{r_{2B}}$$

$$+ \frac{ke^2}{r_{12}} + \frac{ke^2}{r_{AB}}$$

## Born - Oppenheimer Approximation

"Nucleus are stationary wrt movement of electron!"

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2mn} (\nabla_A^2 + \nabla_B^2)}_{\text{can be ignored (1)}} - \frac{\hbar^2}{2me} (\nabla_e^2)$$

$$\left. \begin{aligned} & -\frac{k e^2}{r_A}, \quad -\frac{k e^2}{r_B}, \quad \frac{k e^2}{R} \\ & \end{aligned} \right\} \rightarrow \text{constant (2)}$$



→ this includes the R information too.

$$\hat{H} = \hat{H}_N + \hat{H}_e^R$$

↑ neglect.

$$\left. \begin{aligned} & -\frac{\hbar^2}{2mn} (\nabla_A^2 + \nabla_B^2) \\ & -\frac{\hbar^2}{2me} \nabla_e^2 + \frac{k e^2}{R} - k e^2 \left( \frac{1}{r_A} + \frac{1}{r_B} \right) \end{aligned} \right\} \text{constant.}$$

\*\*  $\hat{H}_e^R \Psi_e(r_A, r_B, R) = E(R) \cdot \Psi_e(r_A, r_B, R)$

-  $\hat{H}\Psi = E\Psi$   $\rightarrow$  the energy is a function of R.

$$E^R \Psi_e = E_e^R \Psi_e$$

$(\Psi_N \Psi_e \cdot \chi(R))$  (means?)  $\rightarrow$  conclusion from B.O. Approximation.

$E \approx \langle \Psi_e | \hat{H} | \Psi \rangle$  ( $\because$  we can't find eigen values; depending on approximate  $\Psi$ .

→ Finding  $\Psi_e$  &  $E(R)$  :-

Guessing the wavefunction.

so, we gotta work with average values).

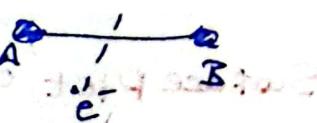
model-1: UBT. Straight forward. NO concept of MO's

$$\Psi_{el} = 1S_A(1) \cdot 1S_B(2) - 1S_B(1) \cdot 1S_A(2) \text{ for H}_2.$$

Bluntly writing  $\Psi_{el}(1,2,R)$

\*\* some limitations:-

- only for covalent bonds
- no ions or radicals.



VB & MO Are competing theories & have their regions of validity.

## Model - 2:- Molecular orbital theory.

- M.O. is an 1-electron-wave-function, just like A.O.  
Polycentric.

M.O. generated by LCAO of A.O. of different atoms.

Why we do?...

- decent approxn.

Symmetry charge distibution is not much different; from superposition principle of charges.

Z axis is  
internuclear axis.

The swing!  
Arindam Choudhury  
9969437094

$$\psi_{AB} = \psi_A + \psi_B$$

$$*\Psi_{BMO} = C_1 1S_A + C_2 1S_B$$

by symmetry,  $C_1 = \pm C_2$

Dont forget

write

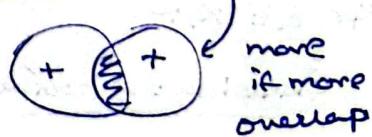
$\frac{1}{\sqrt{2}}$  ! NOT orthogonal.

$$= C_1 (1S_A + 1S_B)$$

$$(\Psi_{BMO})^2 = C_1^2 (1S_A^2 + 1S_B^2 + 2 |1S_A| |1S_B|)$$

normalize.

$$z = C_1^2 (1 + 1 + 2 S_{AB})$$

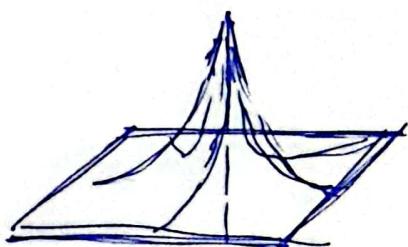


more if more overlap

$$\Psi_{ABMO} = \frac{1}{\sqrt{2(1-S)}} (1S_A - 1S_B)$$

AO, BO (positive minus)

Surface Plot of  $\Psi_{CIS}$



$\text{H}_2^+$

after Born-Oppenheimer approximation.

$$\text{H} = \frac{1}{\hbar^2} \left( -\nabla_{\text{el}}^2 - \frac{1}{r_{\text{eA}}} \right) + \frac{1}{r_{\text{AB}}} - \frac{1}{r_{\text{eB}}}$$

system.

This "CAN" be solved exactly to get a claffada solution.

We will try to approximate out the  $\Psi$  by VBT  
2) MOT.

for  $\text{H}_2^+$ ; VBT



$$\Psi = \underbrace{\psi_{1s}(1) \psi_{1s}(2)}_{A} - \underbrace{\psi_{1s}(1) \psi_{1s}(2)}_{B}$$

MOT: we try out this new concept of MOs by LCAO. But, finally; this is only

$$\Psi_{\text{MO}} = C_1 \psi_{1sA} + C_2 \psi_{1sB}$$

[Now; don't think of  $\epsilon$ ,  
approximat]

$$(C_1 = C_2 \dots)$$

think about orbitals only].

$$\Psi_{\text{MO}} = \underbrace{C_1^2 \psi_{1sA}}_{\int=1} + \underbrace{C_2^2 \psi_{1sB}^2}_{C_2^2} + \underbrace{2C_1 C_2 \psi_{1sA} \psi_{1sB}}_{2C_1 C_2 / S \text{ overlap integral.}}$$

$$\therefore \Psi_{\text{b}+} = \frac{1}{\sqrt{2+2S}} (\psi_{1sA} + \psi_{1sB})$$

$$\Psi_{\text{a}-} = \frac{1}{\sqrt{2-2S}} (\psi_{1sA} - \psi_{1sB})$$

\* Gran be true, -ve, 0.

\* essential when the two have overlap regions.  
as it is product of  $\Psi_1, \Psi_2$ .

overlap integral

$S \rightarrow 0$

means, no MO.  
Why!

\* Now;  $E_+ = \langle \Psi_+ | \text{H} | \Psi_+ \rangle$  (as  $\Psi_+$  is not exact eigenfunction of H)

(PTO)

$$E_{\text{BMO}} = \underline{H_{ii} + H_{ij}}$$

$$E_{\text{AMO}} = \frac{H_{ii} - H_{ij}}{1-S}$$

$$H_{ii} = \langle \Psi_i | \text{H} | \Psi_i \rangle$$

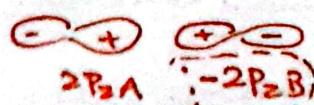
$H_{ij} = \langle \Psi_i | \text{H} | \Psi_j \rangle$  Antibonding

$\Psi_i = \begin{cases} 2p_z A & = \\ 2p_z B & = \end{cases}$

defined in z-direction...

$2p_z A - 2p_z B$  Bonding.

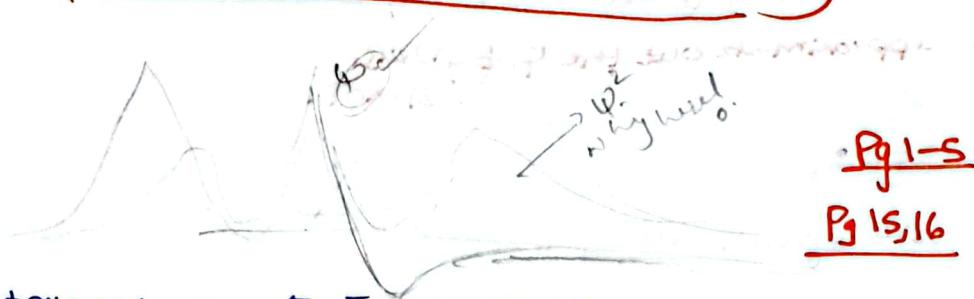
Take care!



\*  $1S + 1S \rightarrow$  bonding; we will draw.

$2S + 2S \rightarrow$  bonding; how to draw?? ...

draw  $\Psi_{1S}$  vs  $r$  for both and see!



Pg 1-S

Pg 1S, 16

### Interpretation of Energy Stabilisation of MOs:

$$* E_+ = \langle \Psi_+ | H | \Psi_+ \rangle \text{ of } H_2^+ \text{ system. equal!}$$

calculating average value:

$$= \frac{1}{2(1+S)} \left[ \langle \Psi_{1SA} | H | \Psi_{1SA} \rangle + \langle \Psi_{1SB} | H | \Psi_{1SB} \rangle + \langle \Psi_{1CB} | H | \Psi_{1CB} \rangle \right]$$

H<sub>ii</sub>

H<sub>ij</sub>

$$\therefore E_+ = \frac{H_{ii} + H_{ij}}{1+S} \quad \& \quad E_- = \frac{H_{ii} - H_{ij}}{1-S}$$

Now, let's see how the stabilisation of  $E_+$  wrt  $E_{1S}$  occurs:-

$$H \approx \left( -\nabla^2 \frac{1}{r_{1A}} \right) - \frac{1}{r_{1B}} + \frac{1}{r_{AB}} = \left( H_{1S} - \frac{1}{r_{B1}} + \frac{1}{r_{AB}} \right)$$

$$\therefore \text{now } \langle H_{1S} | H_{1S} \rangle_{\text{pi}} = E_{\text{Hydrogen}} + \frac{1}{R_{AB}} - \left[ \langle \Psi_{1SA} | \frac{1}{r_{B1}} | \Psi_{1SA} \rangle \right] = \frac{e^2}{r_{B1}} = J(R_{AB})$$

H<sub>ij</sub>:

$$\langle \Psi_{1SA} | H | \Psi_{1CB} \rangle$$

Coloumb integral.

(non bonded energy)

viewed as interaction b/w H - - - H<sup>+</sup>

(ionic one or VBT).

$$= \langle \Psi_{1S} | \left[ H_{1S} + \frac{1}{R_{AB}} - \frac{1}{r_{B1}} \right] | \Psi_{1S} \rangle$$

$$= E_{1S} \cdot S + \frac{1}{R_{AB}} \cdot S - \langle \Psi_{1S} | \frac{1}{r_{B1}} | \Psi_{1S} \rangle$$

$$= K(R_{AB}) \quad \text{exchange integral}$$

Resonance Integral.

purely quantum mechanical origin.

No classical analogue.

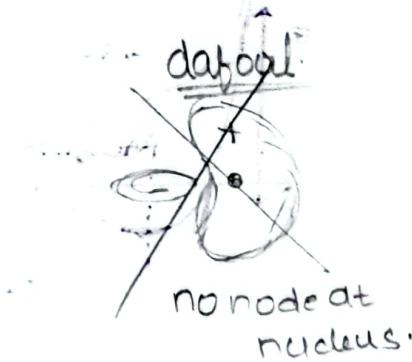
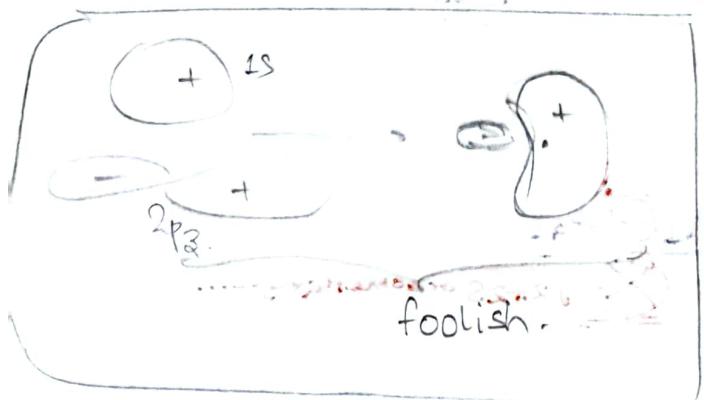
(cont. next page)

$\rightarrow$  Hybridization: (purely based on experimental)

not theoretical

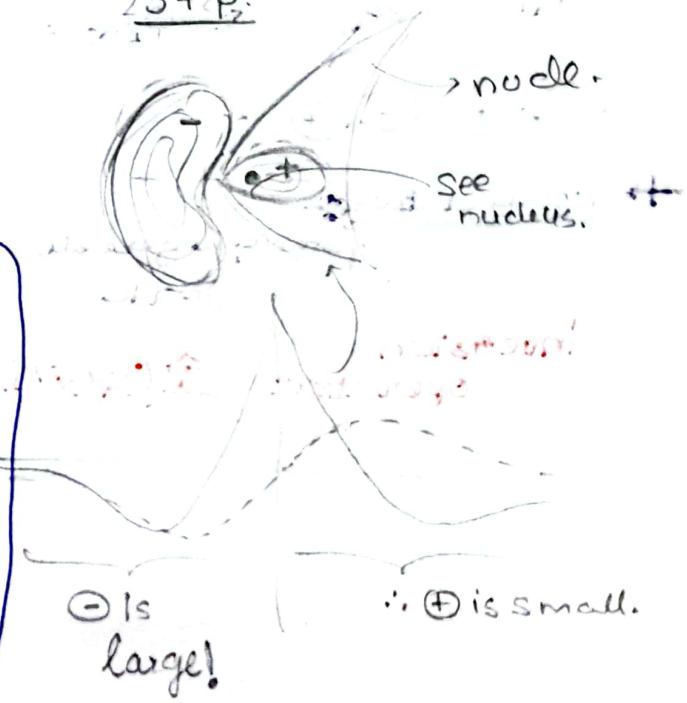
$2S + 2P_3$  is correct!

$1S + 2P_2$  is sensible.



Bad drawing.

$2S + 2P_2$



$$\Psi_{\text{BOND}} = \frac{1}{\sqrt{2}} (\Psi_{1s} + \Psi_{1s})$$

utter wrong! ...

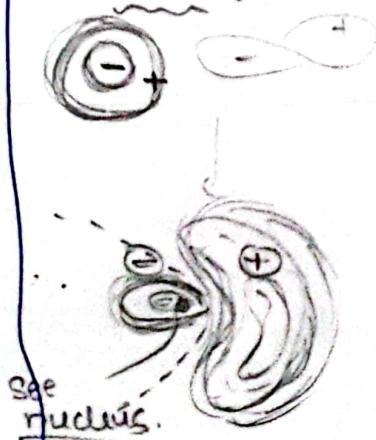
$$= C_1 (\Psi_{1s} + \Psi_{1s})$$

$$C_1^2 + C_1^2 + 2C_1 \cdot S = 1$$

$$C_1 = \sqrt{\frac{1-S}{2(1+S)}}$$

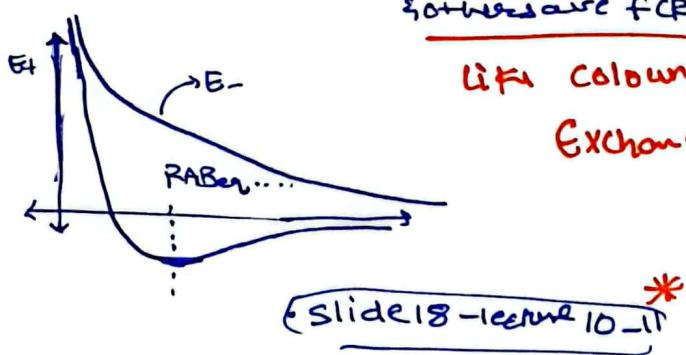
- \*  $S_{ab}$  vs  $R_{ab}$  can be asked for bonding or antibonding combination.

$-2S + 2P_2$



Now; this  $E_{+}$  is a function of  $R_{AB}$ . as  $b = g(R_{AB})$

so others are  $f(R_{AB})$  too..



Likewise Coulomb integral ( $\delta(R_{AB})$ )

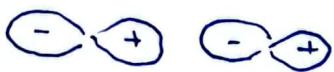
Exchange integral ( $K(R_{AB})$ )

Funny trap:-

$2P_{3/2}$

$2P_{1/2}$

$$\therefore \Psi_{BMO} = \frac{2P_{3/2} - 2P_{1/2}}{\sqrt{2+2S}}$$



~~2P<sub>3/2</sub>~~  $\sqrt{2+2S}$  or something.....

+ nomenclature-

gerade; ungerade.

gerade

inversion

$$\text{operator: } \hat{I}(\Psi(\vec{r})) = \Psi(-\vec{r}) = \begin{cases} + & \Psi(\vec{r}) \\ - & \Psi(-\vec{r}) \end{cases}$$

+ → gerade

- → ungerade.

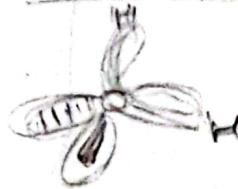
Non equivalent hybrid orbitals :-

resource :-

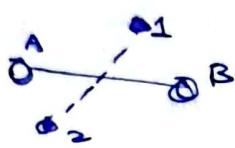
Physical chemistry

Engel & Reid.

H<sub>2</sub>O molecule



## Treatment of H<sub>2</sub> molecule by MOT:-



after Born-Oppenheimer approximation,

$$H = \left(-\nabla_1^2 - \frac{1}{r_{1A}}\right) + \left(-\nabla_2^2 - \frac{1}{r_{2B}}\right) - \frac{1}{r_{12}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{r_{AB}}$$

$$H = H_{1s_A} + H_{1s_B} - \frac{1}{r_{12}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{r_{AB}}$$

cannot be solved exactly,

approx  $\psi$ ; guessed by MOT. 😊

$2e^-$  in  $\Psi_{\text{BMO}}$  ✓

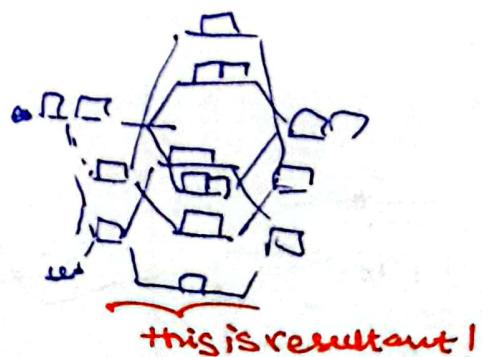
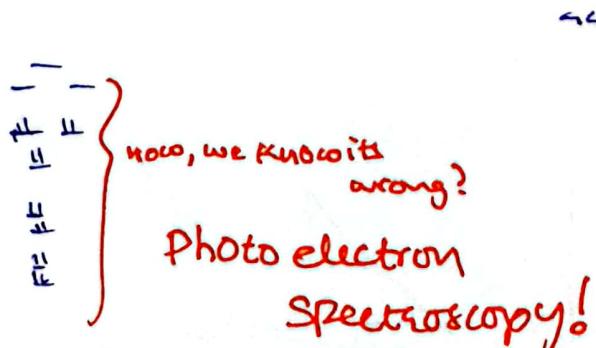
$$\Psi_{\text{BMO}} = \frac{1}{\sqrt{2(1+s)}} (\Psi_{1s_A} + \Psi_{1s_B})$$

{ also; spin part:  $\{\alpha(1)\cdot\beta(2) - \alpha(2)\beta(1)\}/\sqrt{2}$

$$\therefore * \Psi_{\text{el}} = \frac{1}{\sqrt{2(1+s)}} (\Psi_{1s_A}(1) + \Psi_{1s_B}(1)) (\Psi_{1s_A}(2) + \Psi_{1s_B}(2)) \cdot \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

Note: matching energies of AOs is a must; for LCAO.

### \* Energy levels for N<sub>2</sub>:



S, P;  $\Delta E$  being less; undergoing mixing.

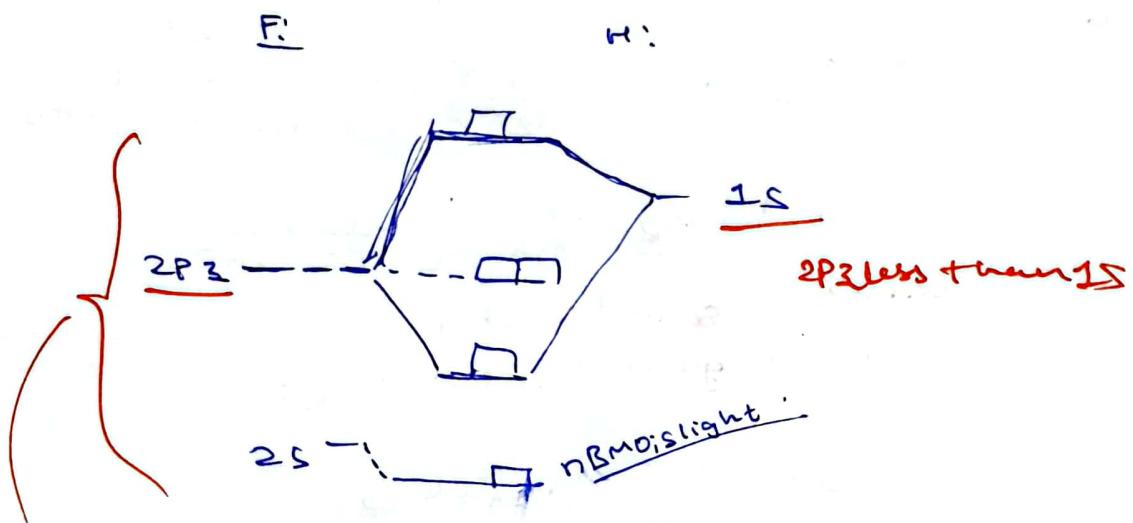
these orbitals will now form MO.

in O<sub>2</sub>, F<sub>2</sub> → energy difference is good.

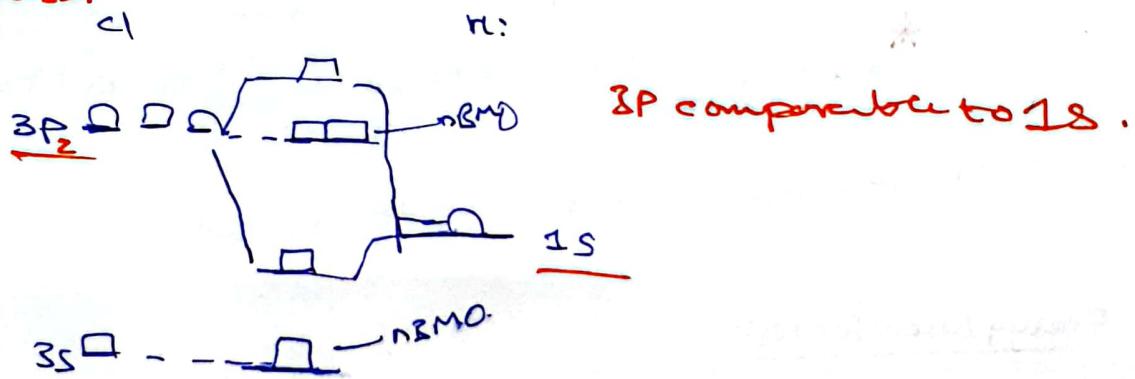
PTO:

## Heteronuclear molecules:-

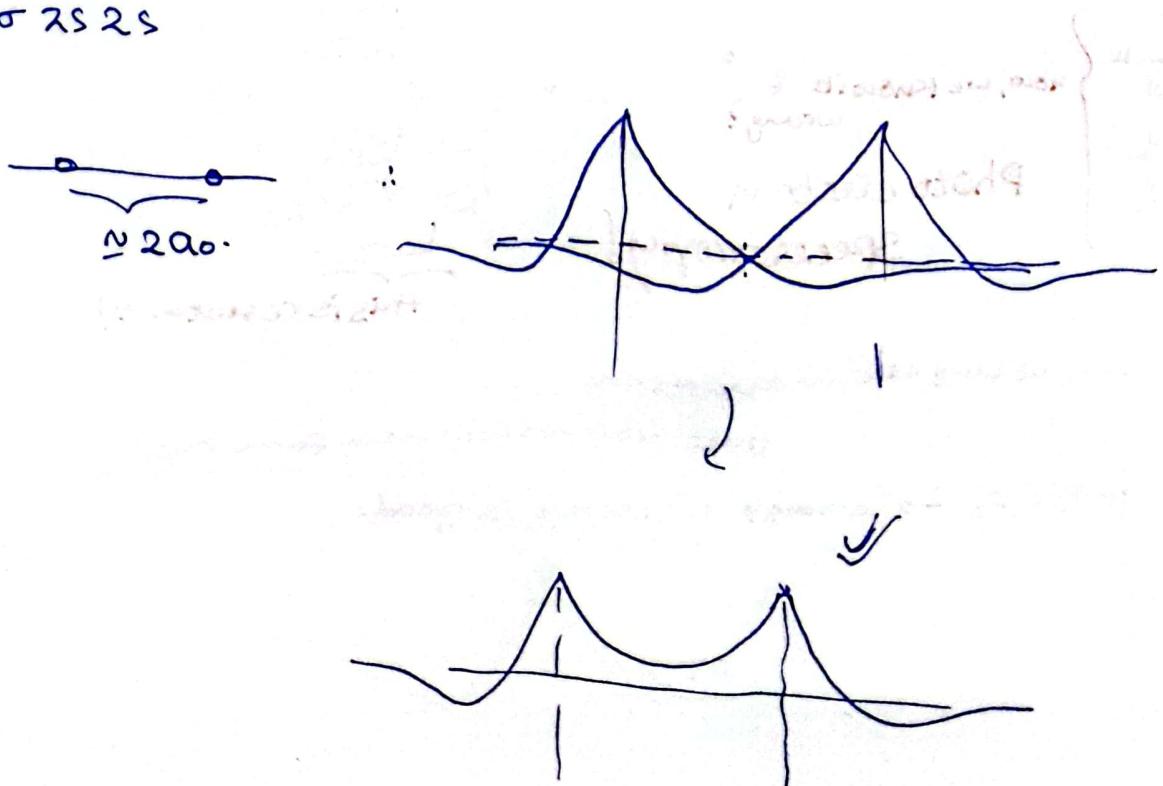
HF.



can assert  $\text{HCl}$ :  
its correctness  
only by expt or  
 $\alpha\text{-m. calcns.}$



\*  $\sigma 2s 2s$



→ Hybrid A.O.; Linear combination of A.O. of same atom -

$$\angle \text{ for } \text{BF}_3; \Psi_{\text{MO}} = \frac{1}{\sqrt{2}} (\Psi_{1sA} + \Psi_{1sB})$$

but here:

$$\Psi_{\text{H.A.O.}} = \frac{1}{\sqrt{2}} \Psi_{1sA} + \frac{1}{\sqrt{2}} \Psi_{2pA} \text{ is valid;}$$

as they are of same atom;  
L are orthonormal.

All hybrid orbitals are orthonormal to each other.

$$\Psi_{h_1} = C_1 1s + C_2 2p_3$$

$$\Psi_{h_2} = \sqrt{1-C_1^2} 1s + \sqrt{1-C_2^2} 2p_2$$

mind these

$$C_1^2 + C_2^2 = 1$$

$$\text{also } C_1 = \sqrt{1-C_2^2}$$

$$\therefore \frac{1}{\sqrt{1-C_2^2}}$$

$$\therefore \Psi_{h_1} = \frac{1s}{\sqrt{2}} + \frac{2p}{\sqrt{2}}$$

these H.O.; form

$$\Psi_{h_2} = \frac{1s}{\sqrt{2}} - \frac{2p}{\sqrt{2}}$$

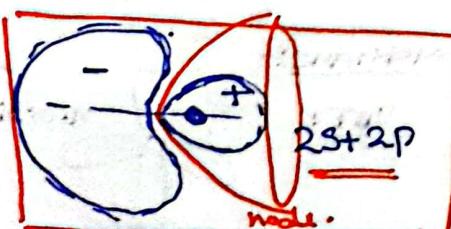
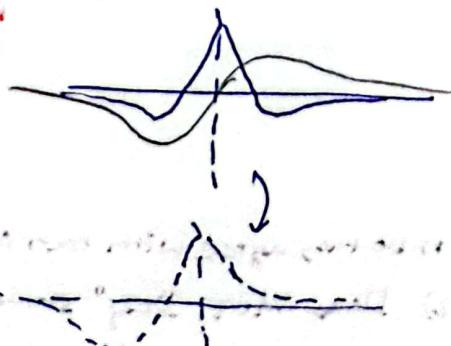
} see direction.

M.O.S together with Hydrogen

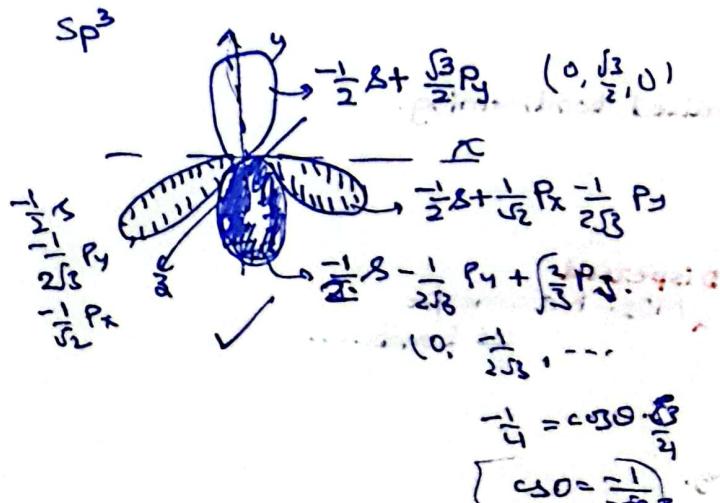
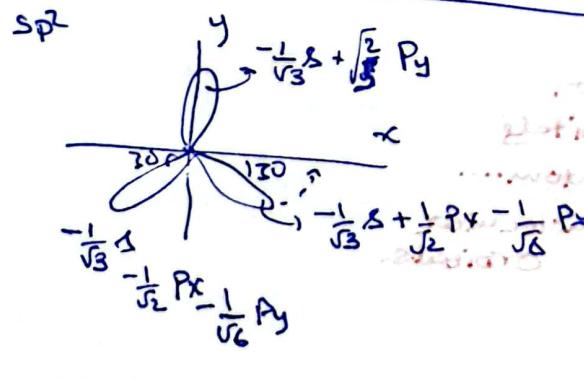


Hybrid orbital's P from 2s, 2p

2s+2p: T8V



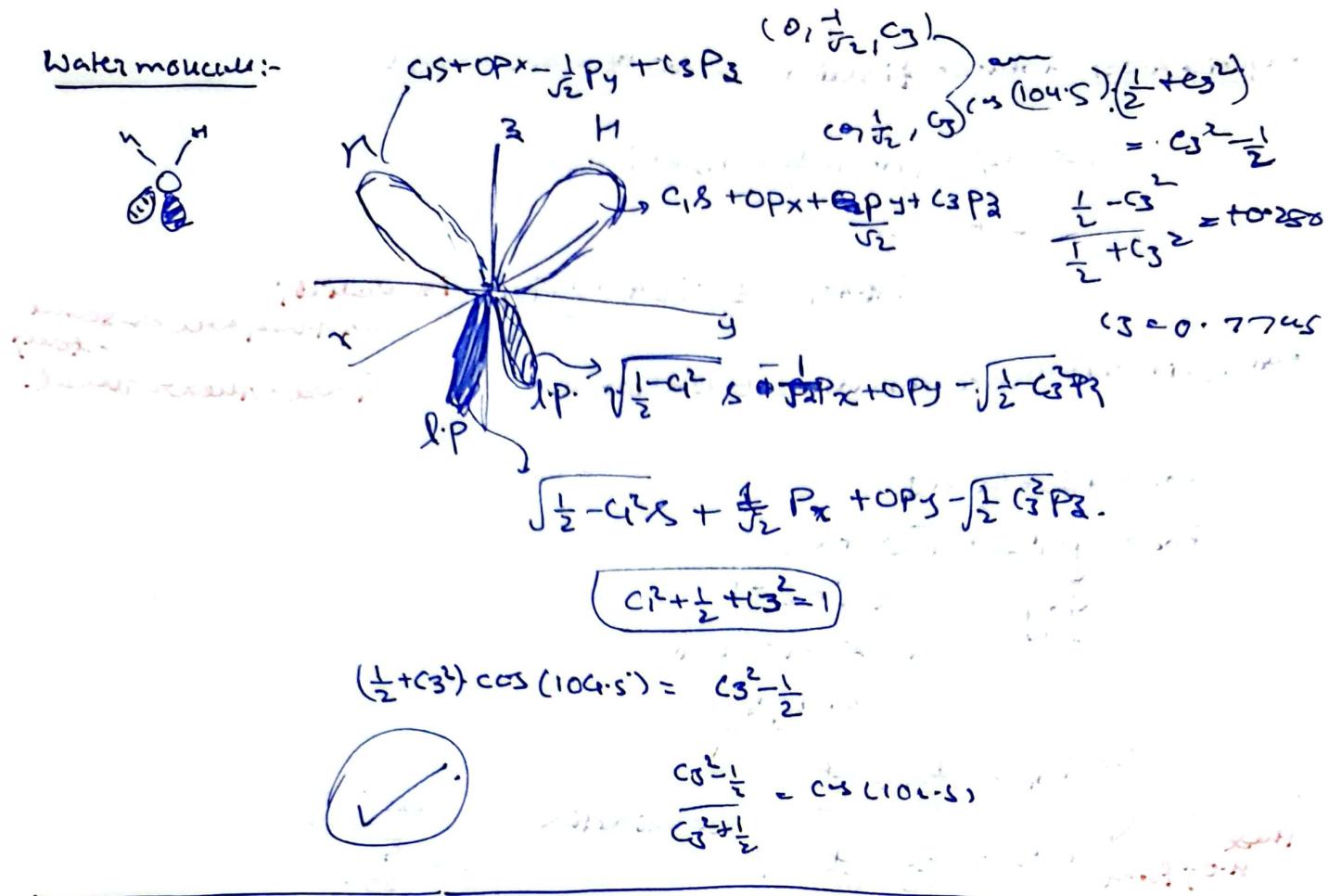
Wedge needed  
at center for  
drawing convenience.



Hybridization of p-orbitals in  $\text{BF}_3$

PTO

### Water molecule:-



### Hybridization vs MOT:-

VBT

MO's are formed by linear combination of atomic orbitals of each atom....

can't use molecular orbitals.

1) Do they agree with each other?

2) Does MOT "say" something "extra"?

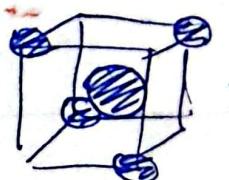
### Methane:-

VBT:



4. orbitals... localized bond forming.

MOT:  
and bonding  
picture  
similar



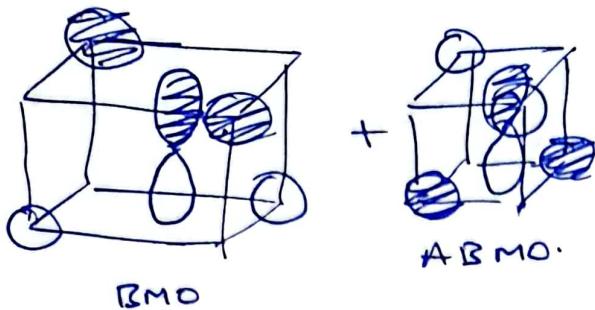
Dispersed.  
MOs: No concept of bonds....

Bond...

anti bonding.

see: only 1 A.O. from each atom.

no hybrid orbitals.

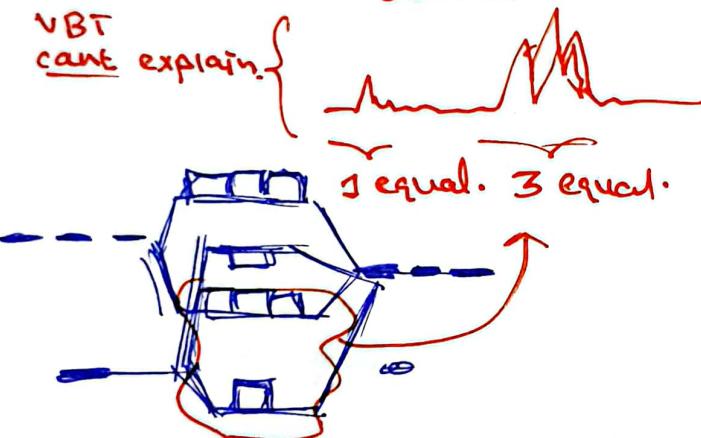


∴ 3 pairs of 1 kind ( $C_p + H_s + H_s + H_s$ )

1 pair of 1 kind ( $C_s + H_s + H_s + H_s$ ) .

∴ Not all the BMOs are of same energy!

### photoSpectroscopy electron



"It doesn't matter how beautiful your experiment is!  
How smart you are!  
If it doesn't agree with experiment;  
it's wrong!"

But! Bond lengths are equal! ...

∴ each MO contributes to a single bond! ....

But MOs themselves are not bonds.