

## Quantum Mechanics.

→ Schrödinger eq<sup>n</sup> :- 1 particle moving in a 1D line

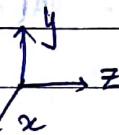
$$\text{1D Schrödinger Eqn: } \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi = E \psi$$

$\frac{\text{KE}}{\text{operator}}$        $\frac{\text{PE}}{\text{operator}}$        $E$  total E of sys.

$$(\hat{H}\psi = E\psi)$$

- Particle moving in Space (3D)

$$\left[ \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x,y,z) \right] \psi = E\psi$$



If we can find  $\psi = f(x)$

→ All details abt sys can be known.

$$* \psi = \left(\frac{2}{L}\right)^{\frac{x}{2}} \sin\left(\frac{n\pi x}{L}\right)$$



$$\psi(x \geq L) = 0$$

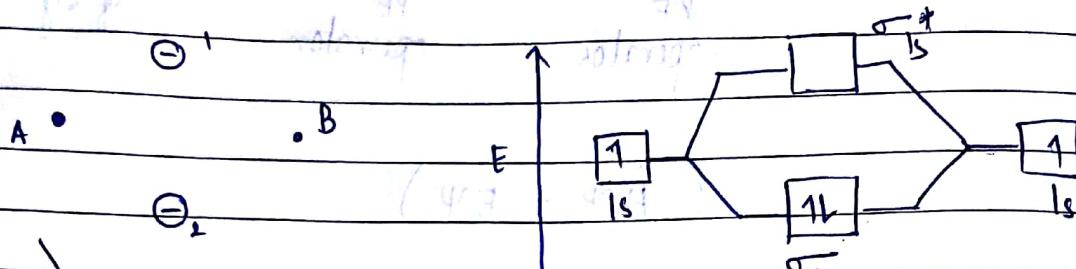
$$\psi(x \leq 0) = 0$$

$$\int_0^L \psi^2 dx = 1 \quad (\text{prob. of finding particle b/w } 0 \rightarrow L \text{ is 1})$$

$$\Rightarrow \int_0^L \psi^* \cdot \psi dx = 1$$

$\langle E \rangle = \int \psi^* \hat{H} \psi \, d\tau$  → replacable fn

$$\int \psi^* \psi \, d\tau \rightarrow \text{generally } = 1.$$

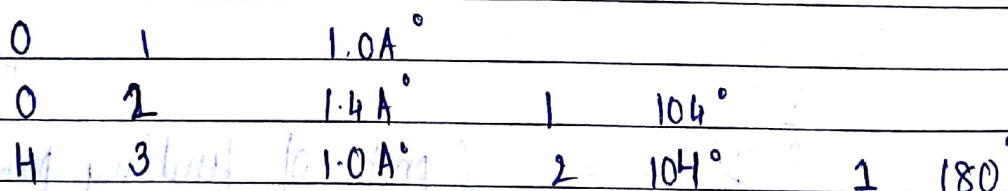
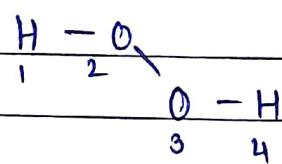
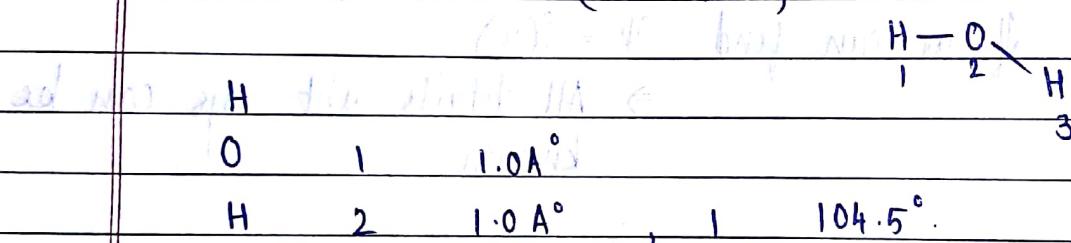


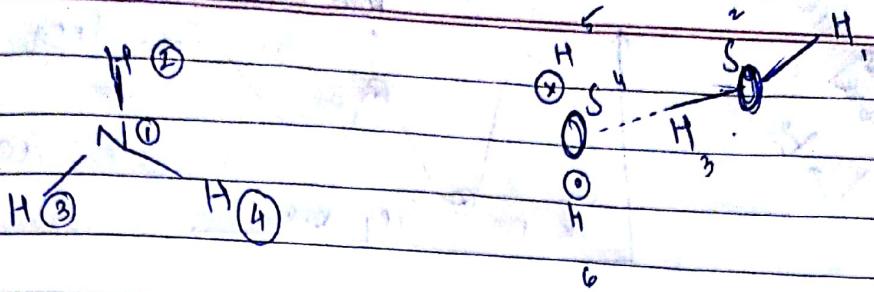
(M.O. = A.O.)

$$\begin{aligned} \Psi_1 &= C_{11} \phi_{1sA} + C_{12} \phi_{1sB} \\ \Psi_2 &= C_{21} \phi_{2sA} - C_{22} \phi_{2sB} \end{aligned} \quad \left. \begin{array}{l} \text{Basis fn.} \\ \vdots \end{array} \right\}$$

M.O. → expressed as LCAO ( $\because$  solvable)

→ Internal coordinates (Z matrix) :





?

N

H 1 1.33

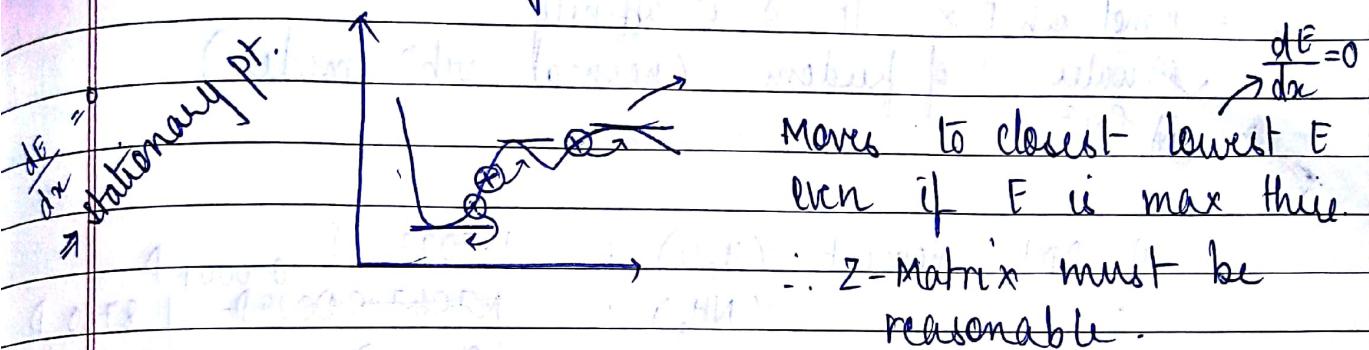
H 2 1.33

H 3 1.33 2 -120°

H 4 0.0

2 -120°

→ Optimisation : Trying to find energy lowest based on change in nuclear coordinates



freq. calc : Calc.  $\frac{d^2E}{dx^2}$  so that reaches  
correct  $\frac{dE}{dx} = 0$  → this is force const.

Calc  $3n$  1<sup>st</sup> order derivatives  
 $n^2$  2<sup>nd</sup> order derivatives  
 $n$   $\frac{\partial E}{\partial x_H}, \frac{\partial^2 E}{\partial x_H^2}, \dots$

→ In theory ; there are  $3N$  degrees of freedom.

for linear

3 trans

2 rot.

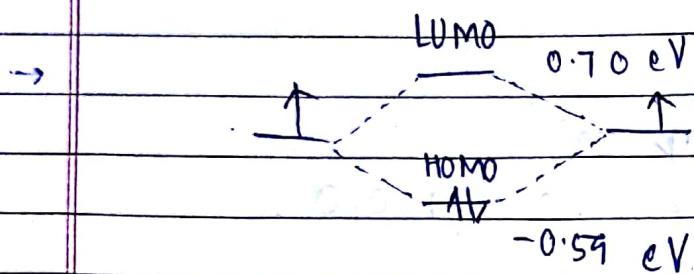
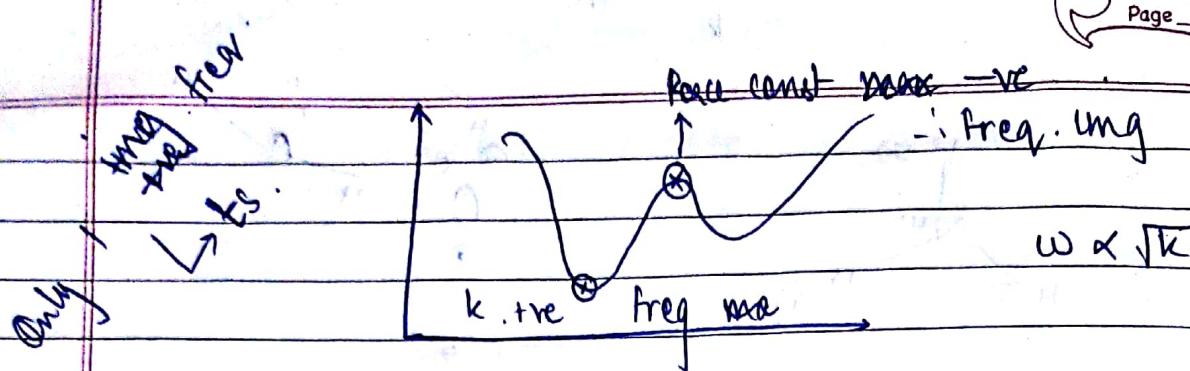
3N-5

3 trans.

3 rotational

{ entire mol.

3N-6



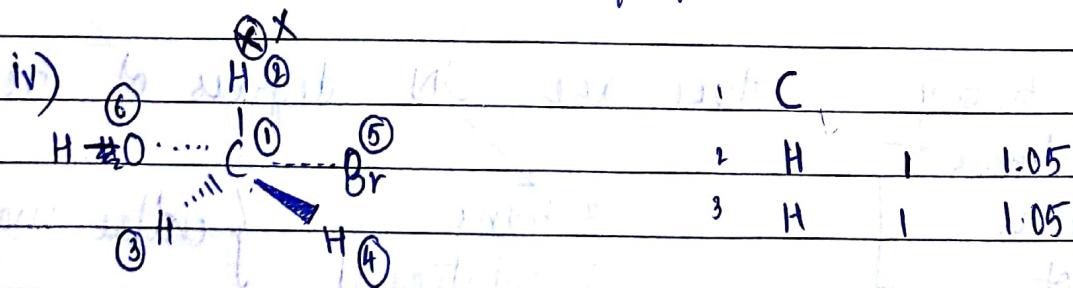
- i) Dipole ?  
 ii) mol. orb E  $\propto$  IE & e- affinity  
 iii) water ° of freedom (normal vibn modes)  
 iv)  $S_N^2$

i) Dipole moment ( $H_2O$ ) : 1.7093 D  
 ( $NH_3$ ) : ~~1.7093 - 0.0020~~ 1.8760  
 (Planar) ( $sp^2$ )

ii) Water (H<sub>2</sub>O) : 1.0267 D.

iii) Water Vibrations : 3b (bending)

Mode 1	: freq	2169.54
Mode 2	: freq	1141.96
Mode 3	: freq	4393.29



# - PE Surface Model.

classmate

Date \_\_\_\_\_

Page \_\_\_\_\_

$$\rightarrow \text{If } 20 \text{ atoms : } 3(N) = 60 \\ \downarrow 20$$

Energy changes 60 - times  
 $E(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_{20}, y_{20}, z_{20})$

$\rightarrow$  HF STO-3G (opt) freq  $\rightarrow$  2nd derivative / force const / freq.

optimisation / minimisation methods : 1st derivative

Pt ① : slope +ve

move -ve  $\leftarrow$

Pt ② : slope -ve

move +ve  $\rightarrow$

Mgn of slope  $\propto$  extent of next step.

$$\left\{ \begin{array}{l} x_{\text{new}} = x_{\text{old}} - \lambda E(x) \\ \text{Steepest Descent.} \end{array} \right.$$

$\rightarrow$  HF  $\rightarrow$  Hartree-Fock method  
 ↳ set of approx. to solve Schrodinger's eqn.

STO-3G  $\rightarrow$  Basis Set

↳ basis fn used to create MO.

no. of MO

= no. of AO

= no. of basis

fn/

1s<sub>A</sub>

1s<sub>B</sub>

1s<sub>C</sub>

$$\sigma = C_1 1s_A + C_2 1s_B$$

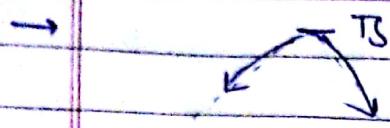
$$\sigma^* = C_3 1s_A - C_4 1s_B$$

basis

fn { H<sub>2</sub>O : (1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>) (1s) (1s) }

$$\begin{aligned} \text{MO} &\leftarrow \theta_m = C_{m1} 1s_A + C_{m2} 1s_B + C_{m3} 1s_C + C_{m4} 2s + C_{m5} 2p_x \\ &+ C_{m6} 2p_y + C_{m7} 2p_z \end{aligned}$$

curved strand-



- i) opt =  $\tilde{t}_k$ , calcfc, no intent.  
ii) IRC (force const.)  $\rightarrow$  mat.

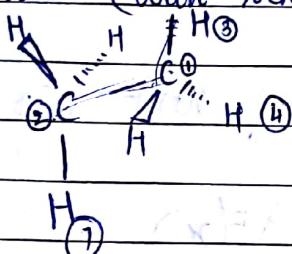
- P

Confirm that TS connects gradients  $\nabla$   $p$  to  $\nabla$   $l$ .

↳ follow one direction either side

(Energy vs reactn coordinate)

→ ① Ethane.com (with %chk)



② Check .chk & .log files

③ Create backup for 'chk' one f → § one b ←

4)  $\text{isrc} \rightarrow \text{g} \leftarrow$

⑤ Plot graph using coordinates

→ Using coordinates XYZ (optimised)

1st      opt = mod redundant -

4 atoms { 1 2 3 4 } S 10.

no.  
steps

20.0

L<sub>u</sub> = r for  
step

- 78 - 30161

-78-30618

$$\Delta E = 600$$

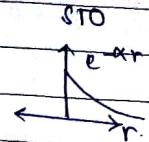
2.8677189  
Klat / und

$$\Delta E = 2.893 \text{ kcal/mol}$$

→ STO - 3G : Basis fn : stores graph eqn of MO  
 eq:  $\infty$ ,  $-\infty$

Basic representation : ( )  $e^{-\alpha r}$

(Slater fn.).



$r$  = distance from centre

Generally used representation

Case I \*

Gaussian fn very (behaviour)  
 diff from Slater

type near nuclei (∴ add G.fn)

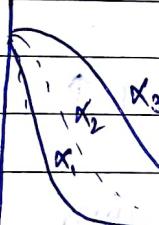
diff values of  $\alpha \rightarrow$  diff graphs.

add all these values of  $e^{-\alpha r^2}$  to get  $e^{-\alpha r}$ .

$$\alpha_1 > \alpha_2 > \alpha_3$$

Gaussian

fn.



$$= c_1 e^{-\alpha_1 r} + c_2 e^{-\alpha_2 r} + c_3 e^{-\alpha_3 r}$$

$e^{-\alpha r^2}$  needed for LCAO to give MO.

AO of form : ( )  $e^{-\alpha r}$

STO - 3G = Slater type orbital - 3 Gaussian fn.

4G | 5G ...

But, this is rigid, AO is fixed in space.

Range of Energy of AO is less : we double  
 zeta / triple zeta

Double zeta basis fn.

(Probability of finding  
e- ↑ on adding e-)

(each AO represented by  
2 func.).

$$\text{before, } \sigma = c_1 1S_A + c_2 1S_B$$

$$\text{Now } \sigma = c_1 1S_A + c_2 1S_{2A} + c_3 1S_{1B} + c_4 1S_{2B}$$

↳ to conquer the issue of changing graph on adding  
e- between H\_A & H\_B.

Energy & son  $c_1, c_2, c_3, c_4, \dots$

But, computational power needed is ↑.

↑ no. of basis fn. is more imp for valence  
in case (II) \* : valence e- E keeps  
changing : shielding

However, in case (I) we need more G  
fn for core orbitals : diff in G & state

: split valence : core valence 6 - 31 G

1 basis 2 Basis fn

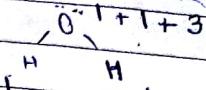
$$\text{fn} = 3G + 1G$$

6 Gaussians

→ STO 3G set on  $H_2O$  mol (Basis sets?)

~~Basis~~

11 111 + 1 A.O.  $\Rightarrow$  7 basis fn  
(each basis fn of 3G)



→ No. of Basis fn using 6 - 31 G. for  $H_2O$ :

$$\frac{4 \times 2 + 3}{6 \times 2 + 1} = \cancel{\cancel{\cancel{\cancel{\cancel{\cancel{13}}}}}} \quad \text{Basis fn}$$

$$G = 6 \times 4 + 6 = 30 \quad G$$

→ To account for polarisation is atoms eg:  $-O-H$ .

we do for add polarisation fn: 6 - 31 G\*

if s exists  $\rightarrow$  add p d.

s, p  
s, p, d

One \* : polarisation  $\nexists$  except H.

\*\* : polarisation  $\nexists$  all!

Incase of  $H_2O$  (G\*): ~~13 + 5 = 18~~ Basis fn.

$$13 + 6 = 19$$

$\hookrightarrow$  cartesian rep of d  
= 6 ways

B - 8\*

→ Cartesian representation of  $G_A^n$ :

$$n(x^a + y^b + z^c) e^{-\frac{r^2}{2}}$$

$$a+b+c = 0 \Rightarrow S$$

$$2 \Rightarrow P$$

$$3 \Rightarrow D$$

$$3 \Rightarrow F$$

(10 ways)

6 ways  $\Rightarrow$  G basis fn for each of 1 G fn.

→ If  $G - 81 + G$  or  $+ + G$   
 $\overline{\text{to add extra diffused fn.}}$   
 for every valence orbital

→ { opt freq.  $\Rightarrow$  vibrational freq.  $\approx E$ , Vibratn modes  
 # HF { opt = (ts, calcfe, noeigentst) freq. TS : E  
 STO-3G opt = modredundant conformers.

# RCTC & CTCirc = (rcirc, forward)  
 reverse

#

Rcirc

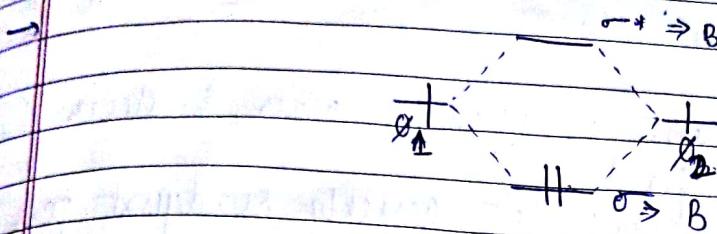
maxpoints = n

#irc1 hf / STO-3G

#irc1 hf / STO-3G

→ Increase accuracy  $\uparrow$  no. of basis fn.

→ Pople basis set:



$$\begin{aligned}\psi_1 &= c_1 \alpha_1 + c_{12} \alpha_2 \\ \psi_2 &= c_{B1} \alpha_1 + c_{B2} \alpha_2\end{aligned}$$

} HF lets you calc  
c<sub>1</sub>, c<sub>2</sub> ...  
} You can calculate.

$$\rightarrow \Psi_{HF} = N \begin{vmatrix} \psi_A(1) & \psi_B(1) \\ \psi_A(2) & \psi_B(2) \end{vmatrix}$$

Expectation value :  $E = \int \Psi_{HF}^* H \Psi_{HF} dx$ .

→ Assumption of HF eq<sup>n</sup>:

H atom eq<sup>n</sup>: Fix nuclei  $\Rightarrow$  only e<sup>-</sup> moving

$$\left[ \frac{\hbar^2}{2m_e} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) + V(x, y, z) \right] \Psi = E \Psi$$

$\nabla$

$\underbrace{-\frac{k e^2}{r}}$

$$\frac{V = Z_A Z_B e^2}{k r} \quad \text{H mol eq<sup>n</sup>: } \begin{array}{c} A \cdot - \\ \cdot - B \end{array} \quad ( \rightarrow \text{Nothing is fixed})$$

$$\left[ \frac{\hbar^2}{2m_e} \left( \nabla_1^2 + \nabla_2^2 \right) + k \left( \nabla_A^2 + \nabla_B^2 \right) + V_{AB} + V_{A+1} + V_{B1} + V_{12} + V_{B2} + V_{A2} \right] \Psi$$

→ mass is diff (consider it)

Can't calc  $\therefore$  nothing is fixed

$\therefore$  use Born-Oppenheimer:

Because nuclei is much heavier & slower

consider it fixed

(if nuclei moves,  $e^-$  quickly readjust possible)

In conformational analysis:

nuclei position changes

can't directly use Schrödinger only for coord.

we use Schrödinger eq<sup>n</sup> with nuclei fixed

$\therefore$  opt needed

→ changes nuclear coord.

→ get lowest energy

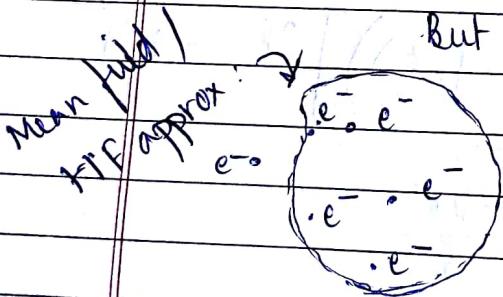
If nuclei is fixed:

~~$V_{12}$  is fixed~~

$V_{12}$  depends only  $x_1, y_1, z_1$

$V_{23}$  depends only  $x_2, y_2, z_2$

But  ~~$V_{12}$~~  still depends on 2 atoms.



Here each  $e^-$  is described  
in Sch. eq<sup>n</sup> & eq<sup>n</sup> for 1  $e^-$

$\rightarrow$  HF said take all  $e^-$  as one

$\Rightarrow$  one  $e^-$  &  $e^-$

one  $e^-$  eq<sup>n</sup>

avg field

Issue : ① All  $e^-$  EF generalised (avg)

② ↓ other possibilities ignored

$$\Psi_{HF} = N \left| \begin{array}{cc} \Psi_A & \Psi_B \\ \Psi_{A1} & \Psi_{B1} \\ \Psi_{A2} & \Psi_{B2} \end{array} \right| \rightarrow \text{Static determinant.}$$

But there's no  $e^- \Psi_B$ .

$$\Rightarrow \Psi_{HP} = N \left| \begin{array}{cc} \Psi_A \alpha(1) & \Psi_A \beta(1) \\ \Psi_A \alpha(2) & \Psi_A \beta(2) \end{array} \right| + \dots$$

$\alpha, \beta \rightarrow f_n$

$\alpha$  = spin ( $L=2$ )

where  $\int \alpha \cdot \alpha = 1$

$\Rightarrow \beta$  - spin ( $\uparrow$ )

$\int \beta \cdot \beta = 1 \quad \nexists \int \alpha \cdot \beta = 0$

$$N \left( \begin{array}{c} (\Psi_A \alpha(1) - \Psi_B \beta(2)) \\ - (\Psi_A \alpha(2) - \Psi_B \beta(1)) \end{array} \right)$$

Possibilities  $\alpha$  :

$$+ + \quad \text{or} \quad + -$$

single excitation

double excitation

$$\therefore \Psi = a_0 \Psi_{HF} + \sum a_1 \Psi^{\text{single}} + \sum a_2 \Psi^{\text{double}} + \dots$$

OR use

CCSD

CID

MP<sub>x</sub> ( $x = 2, 3 \dots$ )

CC

CCSD

CCSDCT

Soluble.

(couple cluster)

MCCSF  $\rightarrow$  CASSCF

CASPT2

but time  
taken  $\gg$

HF

Congress will 1:

Chk if ~~if~~ ~~you~~ move from last found & go backwards.

→ Density fn. theory & (DFT) :

$\psi(r)$  → fn. of position of n particles

- Here, no  $\psi(r)$

- Energy of system can be expressed as e density  $E(e)$

↳ Can be expressed as 3 variables  
(∴ lesser variable) (calc. are faster) (more accurate)

- Issue : There's no known fn<sup>al</sup>. form to find  $e \notin E$

$e \rightarrow$  fn depends on  $x, y, z$

$E \rightarrow$  functional  $\propto$  on  $e$

eg: B<sub>3</sub> function  
LVP functional } BLYP

→  $\Delta F = (E_p - E_r) \times$  kcal/mol.] 1 molecule E received → convert to per mole ∵ R-R forces not considered

↳ Can also calc S, G, H.

→ Generally reactions take place in solvent,  
but we have ignored the  $\Delta H_{sol}$  till now  
because  $\Delta H_{sol}$  of reactant  $\approx \Delta H_{sol}$  of prod  
Majority cases (approx. : Even though 2 react  $\not\approx$  1 prod), so  
gets cancelled

(Gaussian)

→ PCM : Let's use model solvents explicitly (as a continuum).

Commonly use solvents :  $H_2O$

DCM

n-hexane

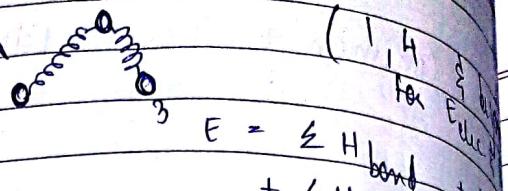
acetonitrile

DMSO

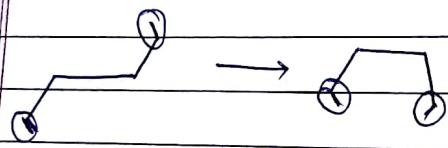
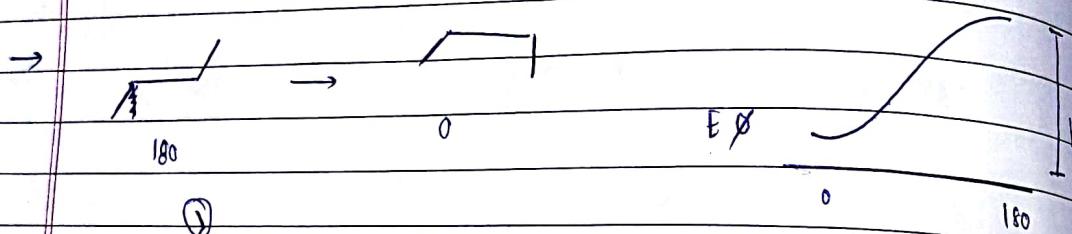
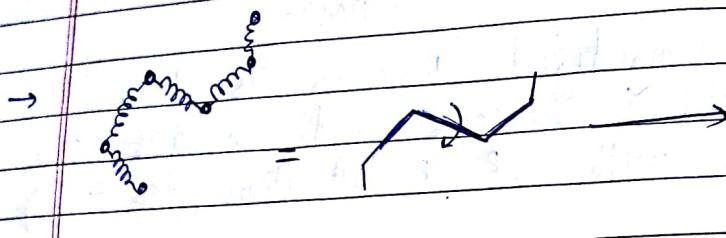
(Till now we considered R-R. E is taken as negligible & considered in gas-state isolated with R-R attraction (rep  $\approx 0$ )

## Molecular Mechanics

→ Representation of  $\text{H}_2\text{O}$ :



$$E = \epsilon_{\text{elec}} + \epsilon_{\text{H bond}} + \epsilon_{\text{dihedral}} + \epsilon_{\text{LJ}}$$

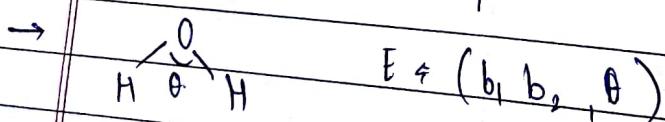


Graph is like this.

H changes based on  
or attr.  $\delta \text{O} \approx \delta \text{O}$

→  $\epsilon_{\text{LJ}}$  (Lennard-Jones) : deals with steric factors

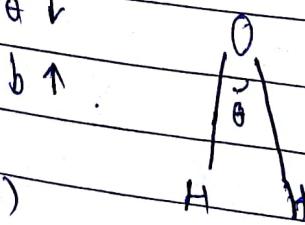
$\epsilon_{\text{elec}}$  : Due to partial charges on atoms.



$$E \propto (b_1 b_2 / \theta)$$

$\begin{bmatrix} \text{H} \approx \text{H} & \text{not considered} \\ \therefore 1, 3 \end{bmatrix}$

Coupling! e.g.: if  $\theta \downarrow$



∴ can define

$$\epsilon(b, \theta)$$

one coupl'd L.

$V(b, \theta, \alpha, r_{ij})$  disp from eq<sub>b</sub><sup>m</sup>

$$V_E = \sum k_b (b - b_0)^2 \quad \text{Harmonic fn. (for B-L)}$$

↓ eq<sub>b</sub><sup>m</sup> dist

$$+ \sum k_\theta (\theta - \theta_0)^2 \quad (\text{for B-A})$$

↓ eq<sub>b</sub><sup>m</sup> Bond L<sup>u</sup>

$$+ \sum k_\alpha [1 + \cos(n\alpha - \delta)] \quad (\text{for dihedral})$$

multiplicity ← ↓ ↘ phase L<sup>u</sup> L<sup>u</sup>  
absolute dihedral L<sup>u</sup>

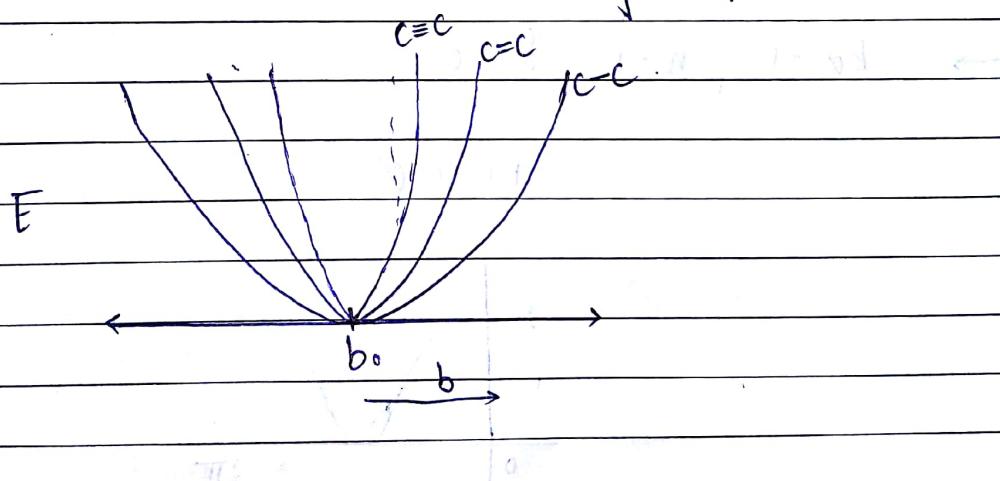
$$(V = \sum k_b (b - b_0)^2 + \sum k_\theta (\theta - \theta_0)^2 + \sum k_\alpha (1 + \cos(n\alpha - \delta)))$$

- If bond is very easy to break;  $k_b \downarrow$

$k_b \propto$  rigidity

↳ (like spring const.)

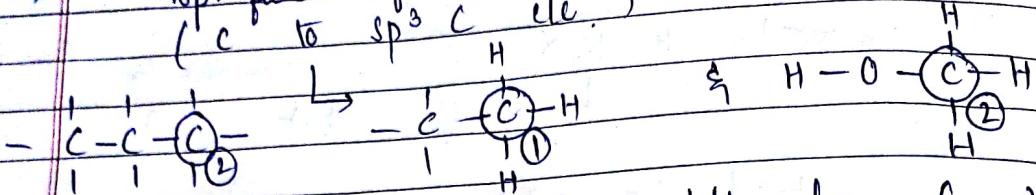
↳ defines strength of the bond.



We need to know  $k_b$ ,  $b_0$  for easy calc.

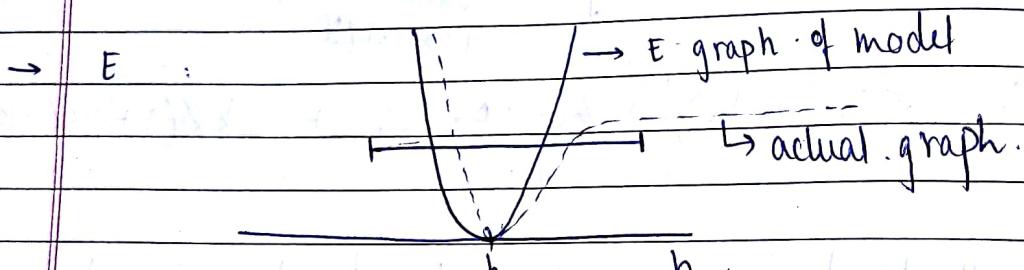
So the above  $V$  with known values of ( $k_b$ ,  $b_0$  ..) is called force field

→ Top. file defines the atom type, connectivity  
(C to  $sp^3$  C etc.)



$C_1$  is very diff from  $C_2 \& C_3$  also  
(connected to O).

But  $C_1 \& C_3$  are alkanes.



Issue with this model is that for at  $b \rightarrow \infty$

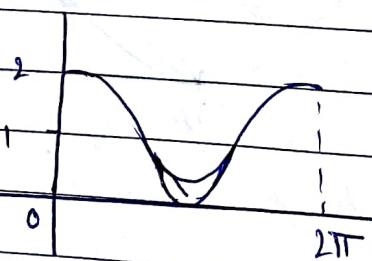
$$\Rightarrow V \rightarrow \infty$$

Only valid below the line.

$$[k_b(b - b_0)^2]$$

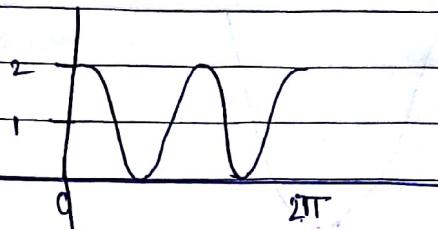
$$\rightarrow k_b = 1, n = 1, \delta = 0$$

$$1 + \cos \phi$$



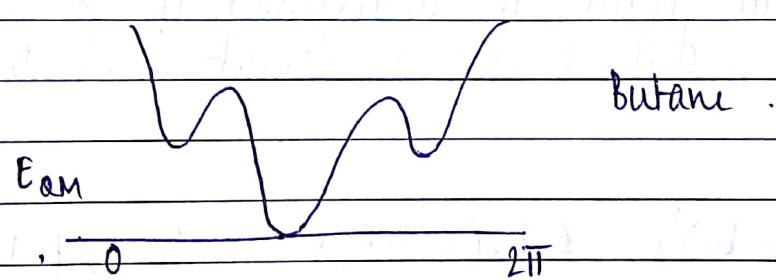
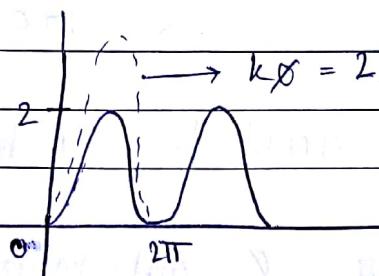
$$k\phi = 1, n = 2, \delta = 0$$

$$1 + \cos 2\phi$$

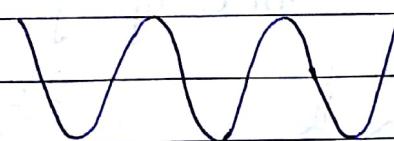


- $n$  changes no. of max & min.
  - $k\phi$  - amplitude
  - $\delta$  conventionally is 0 or 180.
- } 3 parameters

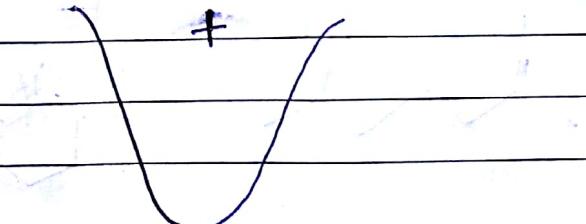
$$k\phi = 1, n = 2, \delta = 180$$

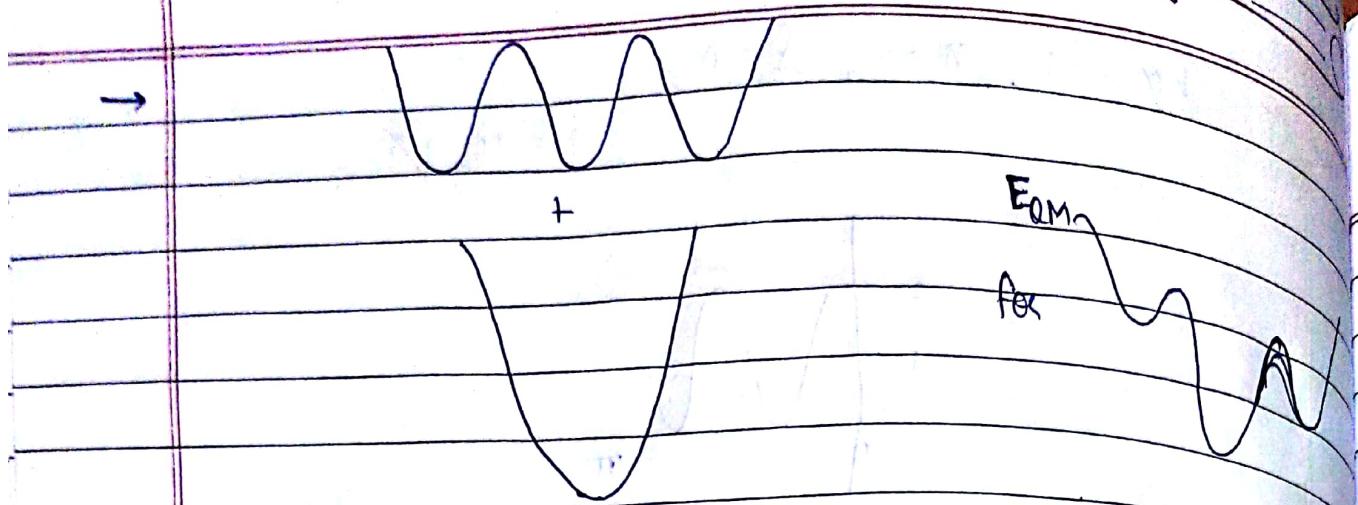


So plot using comb'n of  $2(\cos)$ . fn



+





Thus asymm. & stabilizing interactions (distant H-bond classic factors)

$$\therefore V = V + \sum_{i,j>1} q_i q_j / \text{ATT} E_{rij}$$

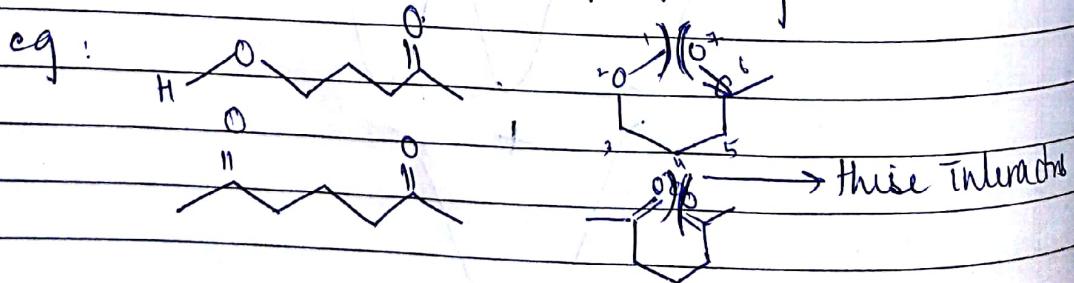
$i, j$  should be 1, 4 beyond. ( $1, 2 \notin 1, 3$  not calculated)

(We can use  $\propto$  diff values to degenerate asymm. but it's easier to understand if  $\propto$  values are sym diff & values doesn't disturb sym.)

$$V = k_b(b - b_0)^2 + \sum k_0(\theta - \theta_0)^2 + \sum k_x [1 + \cos(n\pi - \delta)]$$

(1,2 interactions) (1,3) (1,4)

+  $\frac{-q_i q_j}{\text{ATT} E_{rij}}$  } takes of interactions beyond 1,4.

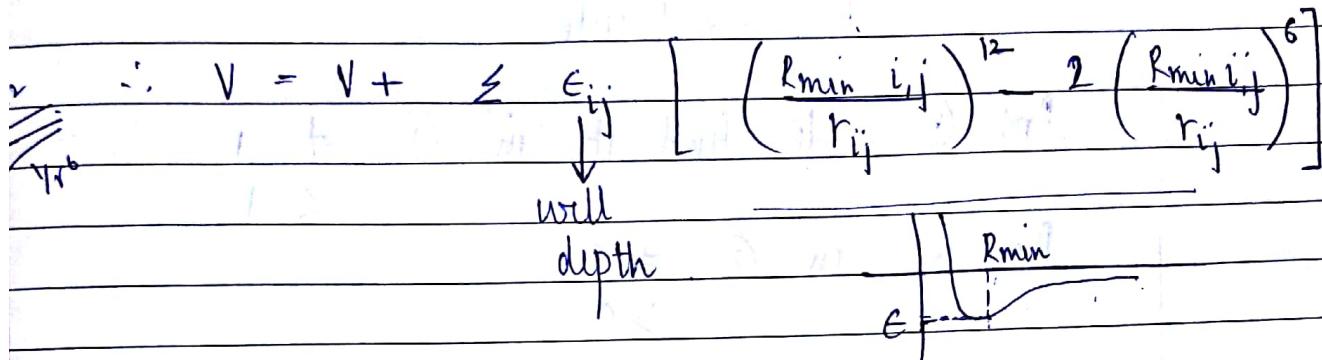


$\text{Na}^+$  $\text{U}^-$ 

$$E = -\frac{1}{kr_{\text{Na-U}}}$$

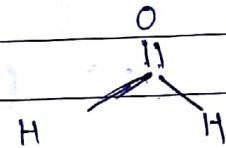
0

Repulsion b/w nuclei  
nuclei not considered



There's no polarization  $\therefore$  charges fixed  
in Top. files

\* Improper  $\angle$  not considered  
(vibrations)



$$\begin{array}{l} \text{Ley - Bradley} \longrightarrow k_w (v - v_0)^2 \\ \text{Improper } \angle \longrightarrow k_w (\omega - \omega_0)^2 \end{array}$$

Molecular dynamics simulation :

- MD tries to

i) Structure

mimic what

Given the initial posn only,  
MD steps :

happens in reality

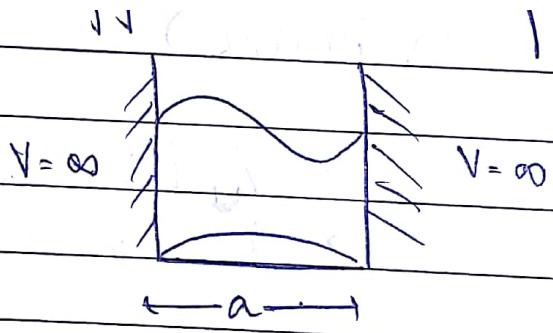
1) Initialize mtn. by using random  
velocities for every particle  
 $\hookrightarrow$  follow Maxwell - Boltzman  
situation

- Only a particular

conformer of mol.  
can undergo a  
particular process  
(eg: butane;

ii) Calc the next expected posn  
(CONTD.)

degree of F for  
a conformer)



$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi.$$

$$\psi = N \sin\left(\frac{n\pi x}{a}\right).$$

$$\langle E \rangle = \frac{\int \psi^* H \psi dx}{\int \psi^* \psi dx} = \frac{n^2 \hbar^2}{a^2}$$

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 = E\psi$$

→ order  
- time step in fs. (sol every small mln k count)

→ If time step is fs:

$$\begin{array}{c} 1 \text{ fs} \rightarrow 0 & 0 & 0 \\ & 0 & 0 \\ & 0 & 0 \end{array} \quad | \quad \begin{array}{c} 1 \text{ fs} - 0 & 0 \\ 0 & 0 \end{array}$$

2 fs →

(0.5 fs)

fs = 10^-12 s + 10^-11 s = 10^-11 s

so fs = 10^-11 s

classmate

Date \_\_\_\_\_  
Page \_\_\_\_\_

