

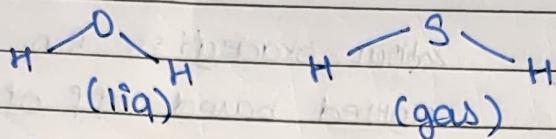
COMPUTING

IN SCIENCES

- Quiz (10 marks)
- Assignments (10 marks)
- Class Quiz/Exercise (10 marks)
- End - Sem 3 (20 marks)

~ Lectures by U. Deva Priyakumar, compiled by Aaryan Shah

* H_2O v/s H_2S :



Q] Why is one a liquid while the other gas?

→ Let us use simple electrostatics to explain this.

In H_2O due to stronger $-I$ the S^+ on the hydrogens & the S^- on the oxygen, have higher magnitude than the Ss of the respective H_2S atoms. Thus, the coulombic F_{EA}, $F = \frac{kq_1q_2}{r^2}$ will be greater in H_2O than H_2S making it liquid.

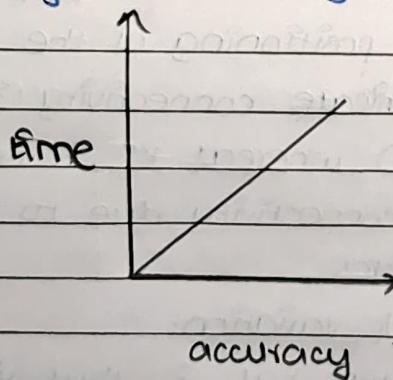
* Reactions classification:

1] molecular reactions: small systems react (quantum mech)

2] biochemical reactions: larger systems react (molecular dynamics)

* Time v/s Accuracy:

- While predicting/running calculations, if you want a higher accuracy it takes more time.



Software Used: Gaussian 16

- .com/.gjf = input file
- .chk = checkpoint
- .log = output file
- when calculations fail a core file is generated , rm it
- login using ssh -X sc4101.[last two digits of your roll no.]@abacus.iit.ac.in
- to start a session - sint7
- load a module: module load G[Tab]1[Tab]
- do gview

---> Calculation Setup:

1. Energy = Single Point
2. Optimization = Maxima/Minima
3. Freq = IR Spectra/ Frequency of vibrational modes
4. Scan = Coordinates

Won't be needing the reset right now.

when we solve for E, we get different values for each molecule, ex: H₂ = E, H₂O = 3E, etc.

- due to this an n-dimensional surface for the potential energy is formed

-geom = connectivity ==> it'll look for the connectivity matrix

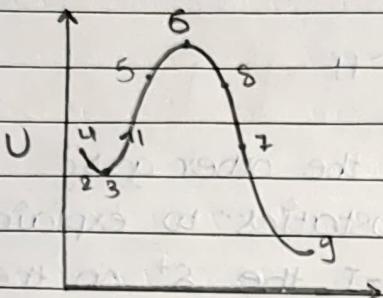
- (check what slurm job script file is (submit.sh??)) & write its detail down from moodle
- vi to view and sbatch to submit .sh files

Difference bw STO-3G and 3-21G

1.STO-3G ---> C₂H₆ = 8 and 2 A,B thus 16 functions

2.3-21G ---> split valence basis set i.e. ex: C = 1s(core orbital) 2s2p (valence orbitals)
3psi 1s - 3 , 2psi 2s,2p - 8 , 1psi 2s,2p - 4 ==> total of 15 functions

* Reaction Progress / coordinate:

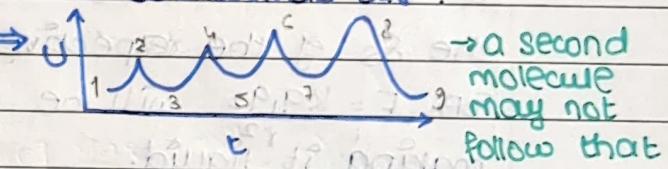


What exactly is Rxn Progress plotted based off of?

→ ① Time?

- @ every instant the molecule has a probability of going in the backwards dir.

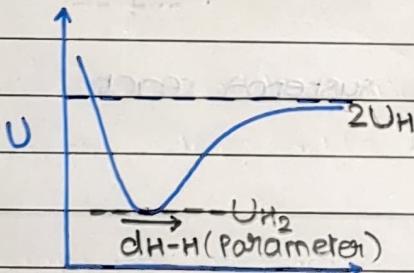
- As 'U' should have an identical graph for each molecule



when plotted against a continuous variable, time no use.

② Geometric Parameters?

- Let us consider this via the example of dissociation of H_2 .



This would cause ambiguity, although accurate for each given rxn, each reaction would have to be plotted wrt diff. parameters

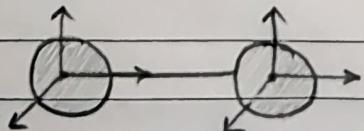
Rxn Progress

The same rxn could use 2 diff.

③ Why Potential Energy?

- It is dependant on relative positioning of the particles and thus, is able to communicate connectivity in terms of relative stability (lower U_f), whereas KE is not able to comment or communicate connectivity due to it being independent of positioning of particles.

④ Analysing Dof to understand U_f variation:



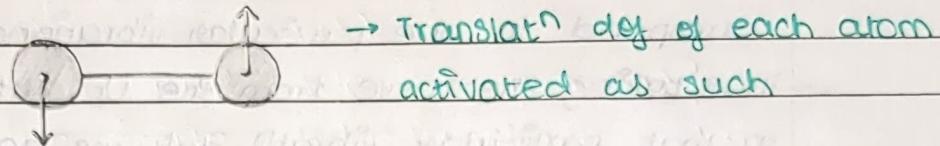
→ Each atom has 3, thus via bond formation i.e. formation of molecule net Dof = 3N

Dof = 3N → Atomicity

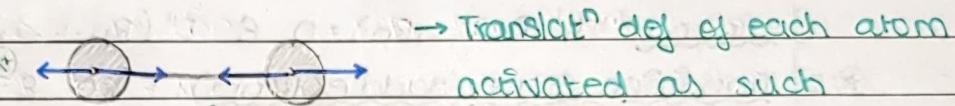
(energy cons)

all might not be active

- ④ How exactly is this $3N$ converted to Translatⁿ, Vibratⁿ, Rotatⁿ?
- A detailed analysis will be studied in a future course but Rotatⁿ can be understood as:



Ily, Vibratⁿ can be understood as:



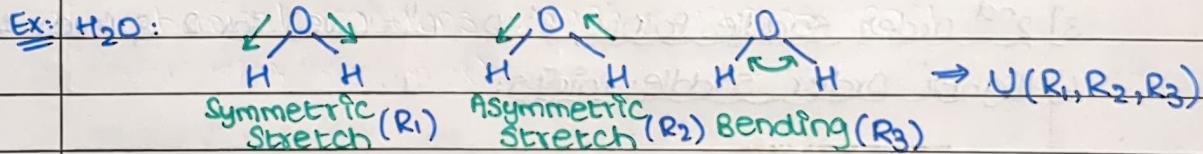
Ex:

	T	R	V	
$O=C=O$	3	2	4	$3N-5$
$H-O-H$	3	3	3	$3N-6$

$\} 3N$

NOTE: → For convenience, ignoring linear molecules & vibratⁿ dof
The U_F surface is a func of $3N-6$ variables.
as for now translatⁿ & rotatⁿ energy have same energy

Ex:



• Simplification of $U(R_1, \dots, R_n)$ to std. Graph:

- Since U has now become a $n+1$ dimensional surface there is a need to simplify it.

• Studying reactions using U :

- Assume a $U(R_1, R_2, R_3)$ for a H_2O molecule.

- Consider the rxn $H_2O \rightarrow H + OH$

↳ To study this, we can locate the posn of H_2O on the graph ($\angle 107^\circ$ & Bond lengths equal) & the coordinate of $H + OH$ at the coordinate of O original

↳ Tracing a minimum energy path along the original U_F surface

↳ get the graph for this reaction, during which the highest energy state would correspond to the TS.

↳ Ily, for $H_2O \rightarrow O + 2H$ we go to O, O, O

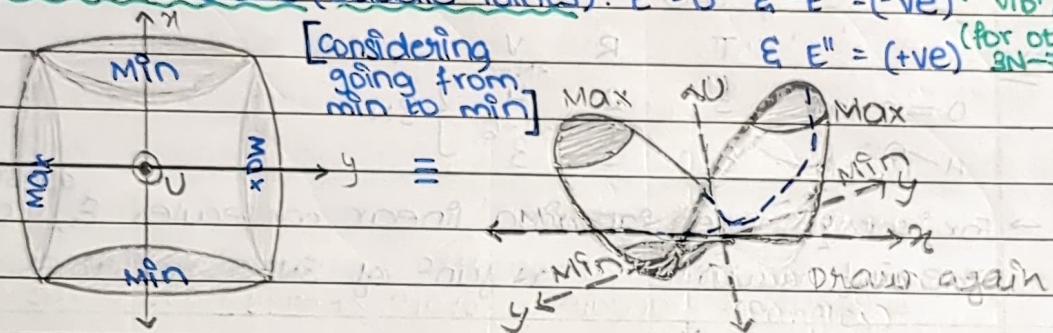
- As there are multiple dimensions a molecule can move in, each dimension would correspond to a different 'destination' & thus the required 'destination' would only correspond to one particular vibrational dof.
- Thus, taking the curve from the UF surface corresponding to that particular vibratⁿ dof, we get a 2-D graph.

Important Points on a UF surface/Rxn coordinate graph:

1) Minima: $E'(R_1, \dots, R_n) = 0$ & $E''(R_1, \dots, R_n) = (+ve)$

2) Transition State (saddle points): $E' = 0$ & $E'' = (-ve)$ (for req. vibⁿ dof)
 $E'' = (+ve)$ (for other 3N-7 dof)

Ex:



3) 2nd Order Saddle Points: $E' = 0$, $E'' = (-ve)$ for 2 & (+ve) for 3N-8

4) Higher Order Saddle Points:

* Quantum Mechanics

- Due to constant motion of quantum particles, they display wave like nature, represented by a wave function (Ψ):

1) $\Psi(r, t) = \Psi(r) \cdot \Psi(t)$ (Ψ func of posⁿ & time) ($r \rightarrow$ sometimes)

2) Purpose of $\Psi(r)$: \rightarrow Any physically observable property of system

$$\langle A \rangle = \int \Psi(r)^* \hat{A} \Psi(r) d\tau$$

$$\int \Psi(r)^* \Psi(r) d\tau$$

} try to equate
D^r to 1 by
concentric
absorbing

$\rightarrow \Psi(r)^*$: complex conjugate of $\Psi(r)$

$\rightarrow \hat{A}$: operator

$\rightarrow d\tau$: volume element

Ex: for cub^{old} box a, b, c : $\int_a^b \int_b^c \int_c^d \Psi(r)^* \hat{A} \Psi(r) dz dy dx$

3) Schrödinger's Equation: (Time Independant)

$$\rightarrow [\hat{H}\Psi = E\Psi]$$

\hookrightarrow Hamiltonian

Ex: Consider an e^- trapped inside a sealed capillary tube:

→ Particle in a 1-D box



$$\begin{aligned} \Rightarrow U(x) &= 0 \\ &= \infty \\ \Rightarrow \Psi(x) &= 0 \end{aligned}$$

\hookrightarrow find

$$U(x) = \infty$$

$$\Rightarrow \Psi(x) = 0$$

■ Hamiltonian operator:

$$- \hat{H} = \hat{T} + \hat{U} \rightarrow \text{PE operator}$$

\hookrightarrow KE operator

$$\hookrightarrow \text{for 1 particle} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\rightarrow \hat{U} = 0 \text{ for } x \text{ b/w } 0 \text{ to } L$$

$$\text{HW} \rightarrow \text{To solve: } -\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi$$

$$\Rightarrow \frac{d^2\Psi}{dx^2} = -\frac{2mE}{\hbar^2} \cdot \Psi \quad \because (\text{Similar to SHM})$$

$$\frac{d^2\Psi}{dx^2} = \frac{d}{dx} \left(\frac{d\Psi}{dx} \right) = \frac{d^2V}{dx^2} \Rightarrow V = \frac{d\Psi}{dx} \rightarrow \frac{dV}{dx} = \frac{dV}{d\Psi} \frac{d\Psi}{dx} = V \frac{dV}{d\Psi}$$

$$\rightarrow V \frac{dV}{d\Psi} = -\alpha^2 \Psi \Rightarrow \frac{V^2}{2} = -\alpha^2 \frac{\Psi^2}{2} + C_1 \quad (\text{Now } V = \frac{d\Psi}{dx})$$

$$\rightarrow \frac{d\Psi}{\sqrt{C_1 - \alpha^2 \Psi^2}} = dx \rightarrow \frac{1}{\alpha} \sin^{-1} \left(\frac{\Psi \alpha}{\sqrt{C_1}} \right) = x + C_2$$

$$\Rightarrow \Psi = \frac{\sqrt{C_1}}{\alpha} \sin(\alpha x + \alpha C_2)$$

$$\therefore \Psi = A \sin Kx + B \cos Kx \quad \equiv \Psi = A \sin(Kx + \phi)$$

Now, $A \neq 0$ but $B = 0$ as $\Psi(x) = 0$ for $x < 0$

$$\therefore \Psi = A \sin Kx$$

② # Ψ^2 denotes the probability of finding the particle. ($\Psi^2 = \Psi \Psi^*$)

$$\rightarrow \int \Psi^* \Psi dx = 1 \quad \because (\text{sum of probabilities}) \rightarrow \text{Normalisation}$$

$$\rightarrow A^2 \int_0^L \sin^2 Kx \cdot dx = 1 \quad \boxed{\text{Solving}} \quad \text{gives } A \text{ on solving}$$

$$\therefore \Psi = \frac{1}{L} \sin \left(\frac{n\pi x}{L} \right), n=1, 2, \dots$$

\hookrightarrow Quantum Number

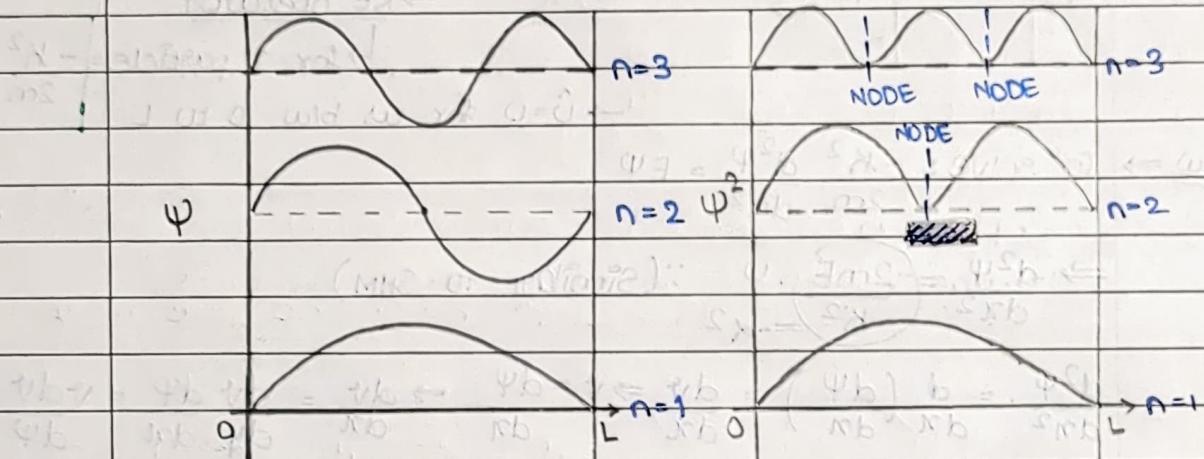
$$\rightarrow E = \int_0^L \Psi(x)^* \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \Psi(x) dx / L$$

$$\therefore E = \frac{n^2 h^2}{8mL^2} \quad \text{Check}$$

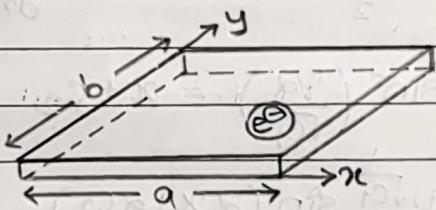
→ Checking for quantum no.s:

$$- E = \frac{h^2}{8mL^2} (n=1), 4E (n=2), 9E (n=3), \dots$$

Plotting Ψ : → Plotting Ψ^2 :



Ex:



$$\text{Thus, } \hat{H} = \hat{T} + \hat{U} \rightarrow 0$$

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

$$\rightarrow \text{In principle: } -\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = E_x \Psi(x) \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Separation of variables}$$

$$E_x = -\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = E_x \Psi(x)$$

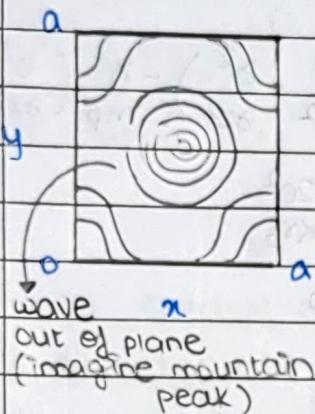
$$\Rightarrow \Psi(x,y) = \sqrt{\frac{2}{a}} \cdot \sqrt{\frac{2}{b}} \sin\left(\frac{n\pi x}{a}\right) \cdot \sin\left(\frac{n\pi y}{b}\right)$$

$$\text{consider: } a=b \Rightarrow E = \frac{(n_x^2 + n_y^2) \hbar^2}{8ma^2}$$

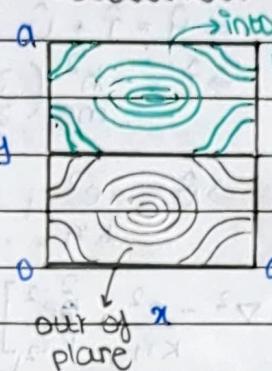
$$\Rightarrow \begin{array}{c} (2,3) & (3,2) \\ (2,2) & 8E \\ (1,2) & (2,1) \\ (1,1) & 5E \\ \hline & 2E \end{array}$$

Plotting Ψ : (in terms of $x \& y$)

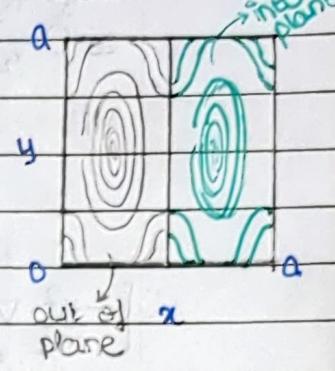
$$\textcircled{1} (x,y) = (1,1)$$



$$\textcircled{2} (x,y) = (1,2)$$



$$\textcircled{3} (x,y) = (2,2)$$



* Hydrogen Atom:

$$\hat{T} = -\frac{\hbar^2}{2me} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + (-\frac{\hbar^2}{2mp}) \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

$$\text{AO } (x,y,z)$$

↳ nucleus

$$\hat{U} = -\frac{e^2}{kr}$$

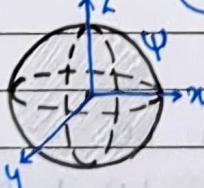
$$\hat{H}\Psi = E\Psi \rightarrow (\hat{T} + \hat{U})\Psi = E\Psi$$

$$\text{hydrogen: } \left[-\frac{\hbar^2}{2me} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{1}{mp} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right] + \frac{(-e^2)}{kr} \Psi = E\Psi$$

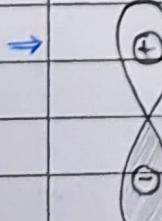
- We can reduce the system from 2 particles to one particle of reduced mass & use CoM knowledge.
- or consider a spherical coordinate system & kill yourself trying to integrate it.

Plotting Ψ :

- If we plot Ψ wrt x, y, z for atoms we get orbitals
- ⇒ for hydrogen:



i.e. $\Psi(r, \theta, \phi)$

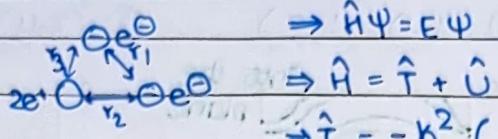


Represents change in phase of the respective particles.

Multiplicity: Total no. of possible e^- configurations

* Helium Atom:

- $\hat{H}\Psi = E\Psi$



$$\Rightarrow \hat{T} = -\frac{k^2}{me} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{k^2}{mp} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$$-\frac{k^2}{mp} \stackrel{\text{imp}}{\cancel{m_e}} - k^2 \Rightarrow \hat{U} = -\frac{e^2}{Kr_1} + \frac{2e^2}{Kr_2} + \frac{2e^2}{Kr_3}$$

$$\therefore \left[-\frac{k^2}{me} \nabla^2 - \frac{k^2}{mp} \nabla^2 - \frac{e^2}{Kr_1} + \frac{2e^2}{Kr_2} + \frac{2e^2}{Kr_3} \right] \Psi = E\Psi$$

→ slightly incorrect

inverted signs

(distance not fixed)

→ Assume nucleus fixed:

Helium: $\left[-\frac{\hbar^2}{2me} (\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{Kr_2} - \frac{2e^2}{Kr_3} + \frac{e^2}{Kr_1} \right] \Psi = H\Psi$

Q) Why is \uparrow NOT solvable?

→ Not solvable as r_1, r_2, r_3 depend on each other making \hat{U} ambiguous and impossible to solve without making certain assumptions regarding the inter-particle interactions and the effect it has on other related phenomena.

* Internal Coordinate System:

- It takes a lot of effort to translate our bond angle θ , bond length knowledge to coordinate system on cartesian coordinates. Thus, we use an internal coordinate system.

Ex: H_2

or H_2O

⇒ 1) H

1) H

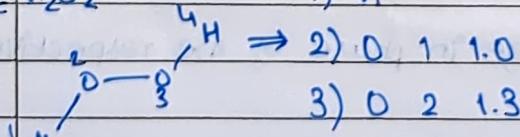
2) H 1 0.9

2) O 1 1.0

3) H 2 1.0 1 107°

Ex: H_2O_2

1) H

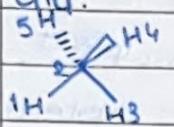


3) O 2 1.3 1 107°

4) H 3 1.0 2 107° 1 180°

HW Q] Write internal coordinate systems for CH_4 , $\text{CH}_3\text{-OH}$, $\text{CH}_3\text{-CH}_3$, C_6H_6 in the .cam file & try running calculations.

→ CH_4 :



1) H

2) C 1 1.x

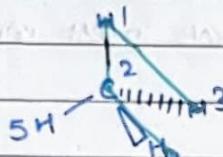
3) H 2 1.x 1 109.5°

4) H 2 1.x 1 109.5° 3 120°

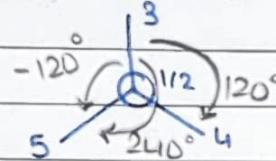
5) H 2 1.0x 1 109.5° 3 120°

choose middle
look through
intern

→ for dihedral:



∴ 3124 → look through 1, 2



* Hydrogen Molecule:

$$\begin{aligned} \text{(-1)} &\Rightarrow \hat{H} = -\frac{\hbar^2}{2M} \left[\frac{1}{m} (\nabla_A^2 + \nabla_B^2) + \frac{1}{m} (\nabla_1^2 + \nabla_2^2) \right] + \\ A + B & \quad \frac{e^2}{K_{AB}} + \frac{e^2}{K_{A1}} - \frac{e^2}{K_{A2}} - \frac{e^2}{K_{B1}} - \frac{e^2}{K_{B2}} \end{aligned}$$

$$\text{Then, } \text{H}\Psi = E\Psi$$

NOTE: Here, we can't assume nuclei to be stationary & use a reduced mass system due to the presence of multiple nuclei, as their movement is independent of each other.

Thus, we make certain approximations to make it solvable

* Born-Oppenheimer Approximation:

- As movement of electrons is much faster than the movement of nuclei, we can assume them to be stationary
- Considering \hat{H} of H_2 again:

$$\Rightarrow -\frac{\hbar^2}{2M} \nabla_A^2 - \frac{\hbar^2}{2M} \nabla_B^2 - \frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + \frac{e^2}{K_{AB}} + \underbrace{\frac{e^2}{K_{A1}} - \frac{e^2}{K_{A2}} - \frac{e^2}{K_{B1}} - \frac{e^2}{K_{B2}}}_{\downarrow \text{constant}} \quad \text{only dependant on position of } e^-$$

- It's still not entirely solvable due to the e^-e^- repulsion & its $\hat{V} = \frac{e^2}{K_{AB}}$, preventing separation of variables as well.