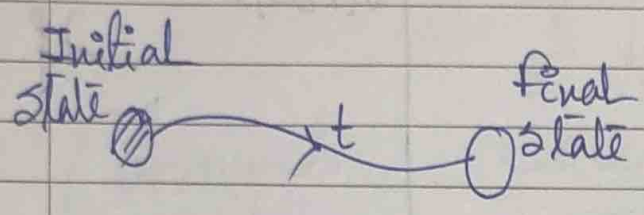


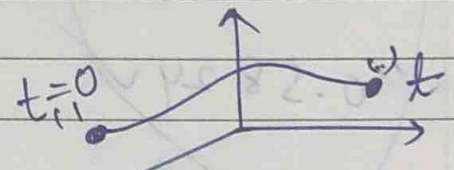
Dynamics



How do I get this state?

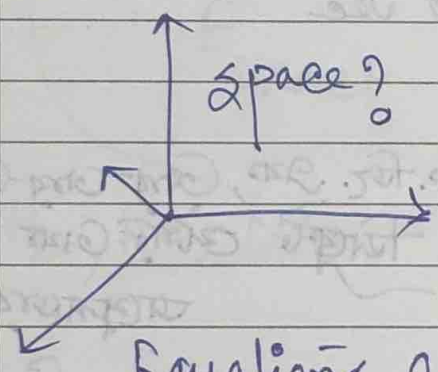
In classical mechanics state is trajectory, point in a space

"phase space"



QM:- space is defined by wavefunction $\Psi(x)$ [one 'd']

$\Psi(x, t=0) \xrightarrow{t} ?$



Hilbert space
(In general vector space)

Equations of motion

CM

Newton's Law

$F = ma$

force

acceleration

most general
 $F = \frac{d}{dt} p$ → momentum

differential eqn

Feynman

$$QM: (q, \dot{q}) \xrightarrow{X} (q_t, \dot{q}_t)$$

position
velocity

It can not happen because of Heisenberg uncertainty principle

can not have a single trajectory

QM state (q) or (\dot{q}) we can not take together.

SE: - (Time dependent)

$$\hat{H}\psi = i\hbar \frac{\partial}{\partial t} \psi(q, t)$$

* Why \dot{q} & q are independent?

$$\hat{p} = -i\hbar \frac{\partial}{\partial q}$$

both together gives momentum

Introduction of Q.M
J. J. Sakurai

\mathcal{L} (Lagrangian) (q, \dot{q}, t)

[J.L Lagrange]

Lorentz

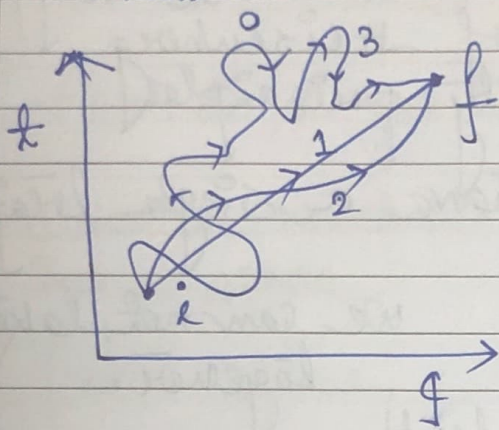
force (where T shows v character
(charge particle in electromagnetic motion))

$\mathcal{H}(p, q) = T + V$
Total energy
(Here use momentum)

* you have well defined velocity, may not have well defined momentum

$$\mathcal{L}(q, \dot{q}, t) = T(\dot{q}) - V(q) \quad \text{[Here use velocity]}$$

→ from this eqn how do we get Equations of Motion?



$$S[q(t)] = \int_{t_i}^{t_f} \mathcal{L}(q, \dot{q}, t) dt$$

Variational principle

classical trajectory is the one that makes S stationary!

In most generally \mathcal{L} is more used than Hamiltonian because \mathcal{L} gives more realistic view

$$\delta S[q(t)] = \delta \int_{t_i}^{t_f} \mathcal{L}(q, \dot{q}, t) dt$$

$$= \int_{t_i}^{t_f} \delta \mathcal{L}(q, \dot{q}, t) dt$$

$$= \int_{t_i}^{t_f} \left[\frac{\delta \mathcal{L}}{\delta q} \delta q + \frac{\delta \mathcal{L}}{\delta \dot{q}} \delta \dot{q} \right] dt$$

we try to transform it

$$\int_{t_i}^{t_f} \frac{\delta \mathcal{L}}{\delta \dot{q}} \delta \dot{q} dt = \left[\frac{\delta \mathcal{L}}{\delta \dot{q}} \delta q \right]_{t_i}^{t_f} - \int_{t_i}^{t_f} \frac{d}{dt} \left(\frac{\delta \mathcal{L}}{\delta \dot{q}} \right) \delta q dt$$

End points are fixed $\delta q(t) = 0 = \delta q(t_f)$

so first term is zero

so final eqⁿ will be $\Rightarrow - \int_{t_i}^{t_f} \left[\frac{\partial \mathcal{L}}{\partial q} - \frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}} \right) \right] \delta q dt \quad \text{--- (1)}$

$\therefore \int_{t_i}^{t_f} \delta \mathcal{L}(q, \dot{q}, t) \equiv 0$ for any change δq path

so 1 eqⁿ will be zero for all δq

Stationary action principle

$$\frac{\partial \mathcal{L}}{\partial q} - \frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}} \right) = 0$$

$$\downarrow$$

$$F - \frac{d}{dt}(P) = 0$$

$$T(q) = \frac{1}{2} m \dot{q}^2$$

$$\frac{\partial \mathcal{L}}{\partial \dot{q}} = \frac{1}{2} m 2 \dot{q}$$

$$= m \dot{q}$$

$$= p$$

(*) (*) S has the same dimension as $\frac{E}{h}$

$$L(\dot{q}, q) \xrightarrow[\text{Legendre transformation}]{\text{Legendre}} H(P, q)$$

$$H(P, q) = P\dot{q} - L(\dot{q}, q)$$

take differential \rightarrow

$$dH = \dot{q}dP + P d\dot{q} - \frac{\partial L}{\partial \dot{q}} d\dot{q} - \frac{\partial L}{\partial q} dq$$

$P = \text{momentum}$

We can write again \rightarrow

$$dH = \left(\frac{\partial H}{\partial P}\right) dP + \left(\frac{\partial H}{\partial q}\right) dq$$

$$\therefore \left(\frac{\partial H}{\partial P}\right) dP + \left(\frac{\partial H}{\partial q}\right) dq = \dot{q}dP - \frac{\partial L}{\partial \dot{q}} d\dot{q} - \frac{\partial L}{\partial q} dq$$

$$= \left(\frac{\partial H}{\partial P} - \dot{q}\right) dP + \left(\frac{\partial H}{\partial q} + \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q}\right) dq = 0$$

$$\left(\frac{\partial H}{\partial P} - \dot{q}\right) dP = 0 \quad \frac{\partial H}{\partial q} = -\frac{\partial L}{\partial \dot{q}} = -\dot{p} \quad \text{--- (1)}$$

$$\Rightarrow \frac{\partial H}{\partial P} = \dot{q} \quad \text{--- (2)}$$

Conservative system The Eqⁿ solve is a choice of problem

In QM Hamiltonian is preferred because to deal with stationary state ~~conserve~~ with conservation of energy it is better to solve $H\psi = E\psi$

$$\frac{\partial \mathcal{L}}{\partial \dot{q}}(q, \dot{q}) = p$$

only T no V.
free particle $\mathcal{L} = \frac{1}{2} m \dot{q}^2$

$$\frac{\partial \mathcal{L}}{\partial \dot{q}} = m \dot{q} = p$$

$$= \dot{q} = \frac{p}{m}$$

$$\text{Hamiltonian } \mathcal{H} = p \dot{q} - \mathcal{L}$$

$$= p \frac{p}{m} - \frac{1}{2} m \left(\frac{p}{m} \right)^2$$

$$= \frac{p^2}{m} - \frac{1}{2} \frac{p^2}{m}$$

$$= \frac{1}{2} \frac{p^2}{m}$$

for free particle

$$\dot{q} = \frac{\partial \mathcal{H}}{\partial p} = \frac{1}{m} p \quad (\text{from eqn 2})$$

$$\dot{p} = -\frac{\partial \mathcal{H}}{\partial q} = 0$$

Momentum is conserved

(from eqn 3)

(q, p)

$f(q, p)$

$g(q, p)$

$$\left(\frac{\partial f}{\partial q} \right) \left(\frac{\partial g}{\partial p} \right) - \left(\frac{\partial f}{\partial p} \right) \left(\frac{\partial g}{\partial q} \right)$$

$\equiv \{f, g\}$ poisson Bracket

$$\begin{aligned} & \hat{f}, \hat{g} \\ & = \hat{f} \hat{g} - \hat{g} \hat{f} \\ & = [\hat{f}, \hat{g}] \end{aligned}$$

$$[q, p] = i\hbar$$

don't commute

$$f = q, g = p \quad \{q, p\} = 1$$

equal happens only in fundamental level but these are always a connection

$$\frac{1}{i\hbar} [\hat{q}, \hat{p}] \sim \{q, p\}$$

QM CM

QM = Heisenberg Representation

$$\frac{d}{dt} \hat{F} = \frac{i}{\hbar} [\hat{H}, \hat{F}] + \frac{\partial}{\partial t} \hat{F}$$

states are fixed, operators are changing

classical dynamics

$$\frac{d}{dt} f = \{f, H\} + \frac{\partial}{\partial t} f$$

$$\Rightarrow \frac{1}{i\hbar} [\hat{F}, \hat{G}] \neq \{f, g\} + o(\hbar)$$

$$= \{f, g\} + o(\hbar)$$

SHO,

$$H(p, q) = \frac{1}{2m} p^2 + \frac{1}{2} m \omega^2 q^2$$

$$\dot{q} = p/m \quad \ddot{q} = \frac{1}{m} \dot{p} = -\frac{1}{m} m \omega^2 q = -\omega^2 q$$

$$\dot{p} = -m \omega^2 q$$

$$m=1, \omega=1$$

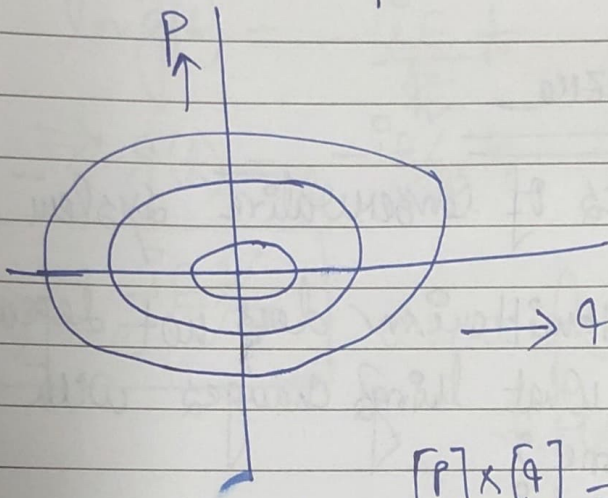
$$\dot{q} = p, \quad \dot{p} = -q$$

can see beautiful symmetry b/w q & p

$$\frac{1}{2} p^r + \frac{1}{2} m \omega^2 q^2 = E$$

$$= \frac{p^r}{(\sqrt{2mE})^2} + \frac{q^r}{(\sqrt{2E/m\omega^2})^2} = 1$$

equation of ellipse



dimension $[p] \times [q] = \hbar$

change variables

$$q = \sqrt{\frac{2I}{m\omega}} \sin \theta \quad p = \sqrt{2m\omega I} \cos \theta$$

$$H(I, \theta) = \frac{1}{2} m p^r + \frac{1}{2} m \omega^2 q^r$$

$$= \frac{1}{2m} (2m\omega I) \cos^2 \theta + \frac{1}{2} m \omega \left(\frac{2I}{m\omega} \right) \sin^2 \theta$$

$$= \omega I \cos^2 \theta + I \omega \sin^2 \theta$$

$$H(I, \theta) = I \omega$$

$$\dot{I} = -\frac{\partial H}{\partial \theta} = 0$$

$$\dot{\theta} = \frac{\partial H}{\partial I} = \omega$$

I is conserved
Canonical transformation

$$\rightarrow E_{nr} = \frac{\hbar \omega}{2} \left(nr + \frac{1}{2} \right) ; nr = 0, 1, 2$$

$$\downarrow \hat{H}(I, 0) = I \omega \quad \text{compare}$$

$$\boxed{I = \frac{\hbar}{\omega} \left(nr + \frac{1}{2} \right)}$$

Proof. Amirban HAZMA

Dynamics of Conservative system

If Hamiltonian does not depend on time. then what things changes with evolution of time?

Atom, molecules \rightarrow that does not depend on time. chemists show interest.

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

$$\psi(x,t) = f(x)g(t)$$

separation of variable (position & time)

$$i\hbar f(x) \frac{\partial g(t)}{\partial t} = g(t) \hat{H} f(x)$$

$$i\hbar \frac{\partial g(t)}{g(t) \partial t} = \frac{\hat{H} f(x)}{f(x)}$$

$$f(x) = g(t)$$

it holds true when it gives some constant value.

$$\text{L.H.S, } E = \frac{\partial g(x)}{g(x)} = -\frac{iE}{\hbar} t \quad \text{--- (1)}$$

$$\text{R.H.S, } E = \hat{H}f(x) = Ef(x) \quad \text{--- (2)}$$

Integrating (1)

$$\ln g(x) = -\frac{iE}{\hbar} t$$

$$\Rightarrow g(x) = e^{-iE/\hbar t}$$

$$\boxed{g(x) = e^{-iEt/\hbar}} \quad \text{where } f(x) \text{ is eigen for}$$

$$\hat{H}f(x) = Ef(x)$$

$$\boxed{\Psi(x, t) = \sum_n C_n f_n(x) e^{-iE_n t/\hbar}}$$

where $\hat{H}f_n(x) = E_n f_n(x)$

* Any initial state can be written as a linear combination of some eigen for.

$$\Psi_{\text{initial}}(x, t=0) = \sum_n C_n f_n(x)$$

$$\langle f_n | \Psi_{\text{initial}} \rangle = C_n$$

$$\boxed{\Psi(x, t) = \sum_n C_n f_n(x) e^{-iE_n t/\hbar}}$$

Solving the eigen value problem is hardest thing/time consuming thing.

if we don't want to solve eigenvalue eqn

$$i\hbar \delta\psi = H\psi \delta t \Rightarrow \psi(x, t=0+\delta t)$$

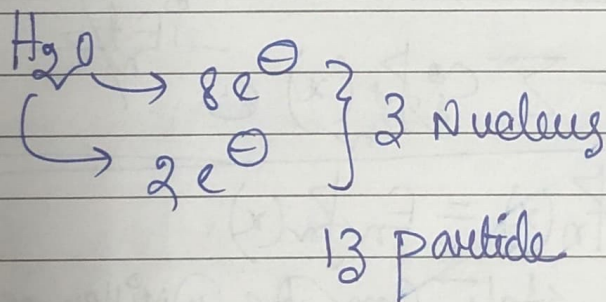
there is another way to solve but here time lengthy step

propagates over time $= \psi(x, t=0) + \delta\psi$

numerical solution takes time

$$\langle \psi(x=0) | \psi(x) \rangle$$

$$\int dx \int dx' \underbrace{\langle \psi(0) | x \rangle}_{\psi^*(x)} \underbrace{\langle x | e^{-iHt/\hbar} | x' \rangle}_{\text{propagator}} \underbrace{\langle x' | \psi(0) \rangle}_{\psi(x)}$$



degrees of freedom $\rightarrow x, y, z$

$$3 \times 3 = 29$$

practical solution requires basis function $\{b_1(x), b_2(x), \dots, b_N(x)\}$

$$\psi(x) = \sum c_i b_i(x)$$

Linear operator special property

$$\hat{A}[a f(x) + b g(x)] = \hat{A} a f(x) + \hat{A} b g(x)$$

//_

$\hat{A}\psi(x)$
 \uparrow
 N basis functions $\rightarrow (N \times N)$

Now consider

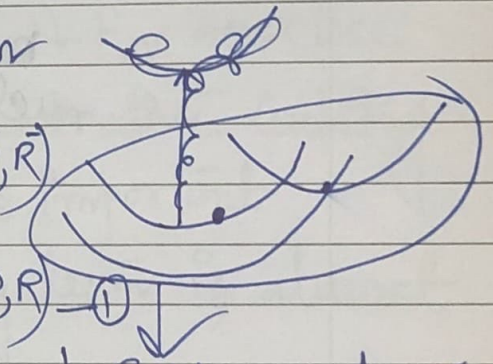
~~$\psi(x, y)$~~ 2d $\psi(x, y) \rightarrow N^2$ basis functions
 $\left\{ \begin{array}{l} b_1(x)b_1(y) \quad b_2(x)b_2(y) \dots \\ b_1(x)b_2(y) \quad b_2(x)b_1(y) \dots \end{array} \right\}$

Exponential scaling

Born-Oppenheimer approximation :-

Consider a molecular Hamiltonian described by the

$$\hat{H} = \hat{T}_N + \hat{T}_e + V(\vec{r}, \vec{R})$$



Want to solve, $\hat{H}\psi(\vec{r}, \vec{R}) = E\psi(\vec{r}, \vec{R})$ (1)

At fixed nuclear geometry

Electronic problem eqn is

$$\hat{T}_e + V(\vec{r}, \vec{R})$$

variable parameter

$$\hat{H}_e \Phi_n(\vec{r}; \vec{R}) = \epsilon_n(\vec{R}) \Phi_n(\vec{r}; \vec{R})$$

Real system problem
 Non-adiabatic case.

Let us write $\psi(\vec{r}, \vec{R})$ in the following ansatz

$$\Psi(\vec{r}, \vec{R}) = \sum_n X_n(\vec{R}) \phi_n(\vec{r}; \vec{R})$$

unknown
(have to solve)

From eq (1)

$$(\hat{H} - E) \Psi(\vec{r}, \vec{R}) = 0$$

$$\Rightarrow (\hat{H} - E) \sum_n X_n(\vec{R}) \phi_n(\vec{r}; \vec{R}) = 0$$

$$\Rightarrow (T_N + V_e - E) \sum_n X_n(\vec{R}) \phi_n(\vec{r}; \vec{R}) = 0$$

Work out

$$\sum_{R=1}^M \nabla_{\vec{R}}^r [T_N + V_n(\vec{R}) - E] X_n(\vec{R}) = \sum_{m} \Lambda_{nm} X_m(\vec{R})$$

number of molecule bond

$$\Lambda_{nm} = \sum_{\vec{e}=1}^M \langle \phi_n | \frac{\partial}{\partial R_i} \phi_m \rangle \frac{\partial}{\partial R_i}$$

↓
Derivative Coupling

↓
2nd derivative Coupling

$\sqrt{H_0}$

$$\begin{bmatrix} T_N + V_1(\vec{R}) - \hat{\Lambda}_{11} & & & \\ & -\hat{\Lambda}_{12} & & \\ & & T_N + V_2 - \hat{\Lambda}_{22} & \\ & -\hat{\Lambda}_{21} & & \end{bmatrix} \begin{bmatrix} X_1(\vec{R}) \\ X_2(\vec{R}) \\ \vdots \\ \vdots \end{bmatrix} =$$

M x M M x 1

RHS

$$E \begin{bmatrix} \chi_1(R) \\ \chi_2(R) \end{bmatrix}$$

Set $\hat{A}_{ij} = 0$
 → Nonadiabatic coupling operators

Solve $[\hat{T}_N + V_1(R)] \chi_1(R) = E \chi_1(R)$

$$[\hat{T}_N + V_2(R)] \chi_2(R) = E \chi_2(R)$$

* 1st derivative coupling term $\propto \frac{1}{E_n - E_m} \frac{d}{dR} \langle \phi_i | \frac{\partial \phi_j}{\partial R} \rangle$

So two P.E.s are close enough

When E_n & E_m are close then derivative coupling term is important.

* 2nd derivative coupling term is almost negligible

Adv. Chem Phys
 57, 559 (1984)

Koppel, Domcke
 Domcke, Cederbaum

Prof. Mahapatra

Time dependent SE

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

We can not tell position & velocity simultaneously in QM due to uncertainty.

$$\begin{aligned} \psi(x,t) &= \phi(x) f(t) \\ &= \phi(x) e^{-iEt/\hbar} \end{aligned}$$

$$|\psi(x,t)\rangle = \psi(x) f(t) \quad \text{--- (1)}$$

$$i\hbar \frac{\partial |\psi(x,t)\rangle}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 |\psi(x,t)\rangle}{\partial x^2} + V(x) |\psi(x,t)\rangle$$

Put here (1) condition $i\hbar \frac{\partial}{\partial t}$ --- (2)

finally we get,

$$\frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)$$

This is possible when it is equated with some constant value which is E (here)

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) = E$$

at time $t=0$, $V=0$

$$\psi(x,t) = e^{-iEt/\hbar} \psi(x, t=0)$$

$t = \text{parameter}$

$$\hat{H} = -\frac{1}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{1}{2} \sum_e \nabla_e^2 - \sum_{\alpha} \sum_e \frac{Z_{\alpha}}{r_{\alpha e}} + \sum_e \sum_{i,j} \frac{1}{r_{ij}} + \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}}$$

$$m_N = m_e = 1836$$

→ molecule, molekül do not parturbed in electronic wave function

$$E_{elec} \sim \langle T_e \rangle \sim \frac{\hbar^2 k_{elec}^2}{m} \sim \frac{\hbar^2}{m d^2}$$

k = kinetic

d = molecule diameter

$$E_{vib} \sim \hbar \sqrt{\frac{k}{\mu}}; k = \frac{\partial^2 E_{elec}}{\partial R^2} \sim \frac{E_{elec}}{d^2}$$

$$E_{vib} = \frac{\hbar^2}{m d^2} \times d^2 = \frac{\hbar^2}{m d^2} \sim \hbar \sqrt{\frac{1}{M m d^4}} \approx \sqrt{\frac{m}{M}} \frac{\hbar^2}{m d^2}$$

$$= \sqrt{\frac{m}{M}} E_{elec}$$

$$E_{rot} \sim \langle T_{rot} \rangle \sim \frac{\hbar^2}{I} = \frac{\hbar^2}{M d^2} = \frac{m}{M} E_{elec}$$

$$T_e + V_{eN} + V_{ee} + V_{NN} = \hat{H}$$

for electronic SE

$$\hat{H}_{el}(\mathbf{r}; R) \psi_{el}(\mathbf{r}; R) = \epsilon_{el}(R) \psi_{el}(\mathbf{r}; R)$$

for one R we get one electronic energy.
 & then another R we get different electronic energy and so on.

$T_N = 0$ (Approximation)

$$V(R) = \underbrace{\epsilon_{el}(R)}_{T_e + V_{eN} + V_{ee}} + V_{NN}(R)$$

\swarrow PES

$$[\hat{T}_N(R) + \hat{V}(R)] \chi_N(R) = E \chi_N(R) \quad (\text{B.O.})$$

\downarrow

motion of nuclei

\downarrow

force field given by e^-

\downarrow

total energy of the system
(el + vib + rot)

It is difficult to solve numerically.

$$\psi(\mathbf{r}, R) = \sum_{i=1}^{\infty} \chi_N^i(R) \cdot \psi_{el}^i(\mathbf{r}; R)$$

Basis sets are known functions of Hermitian operator

dependent on R
 (unknown have to calculate)

independent on R
 (known set of fn)

Complete Schrodinger equation \rightarrow

$$\left(T_N(R) + H_e(r; R) + V_{NN}(R) \right) \sum_{i=1}^{\infty} \psi_N^i(R) \psi_{el}^i(r; R) = E \sum_{i=1}^{\infty} \psi_N^i(R) \psi_{el}^i(r; R)$$

$$\Rightarrow \sum_{i=1}^{\infty} (T_N + H_e + V_{NN}) \psi_N^i \psi_{el}^i = E \sum_{i=1}^{\infty} \psi_N^i \psi_{el}^i$$

$$\Rightarrow \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} -\frac{1}{2M_{\alpha}} \nabla_{\alpha}^r \{ \psi_N^i \psi_{el}^i \} + \sum_{i=1}^{\infty} (H_e + V_{NN}) \psi_N^i \psi_{el}^i = E \sum_{i=1}^{\infty} \psi_N^i \psi_{el}^i$$

$$\Rightarrow \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} -\frac{1}{2M_{\alpha}} \nabla_{\alpha} \left(\psi_N^i \nabla_{\alpha} \psi_{el}^i + \psi_{el}^i \nabla_{\alpha} \psi_N^i \right) + \sum_{i=1}^{\infty} V_{el}^i \psi_N^i \psi_{el}^i = E \sum_{i=1}^{\infty} \psi_N^i \psi_{el}^i$$

$$\Rightarrow \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} -\frac{1}{2M_{\alpha}} \left\{ \psi_N^i \nabla_{\alpha}^r \psi_{el}^i + \psi_{el}^i \nabla_{\alpha}^r \psi_N^i + (\nabla_{\alpha} \psi_{el}^i) \cdot (\nabla_{\alpha} \psi_N^i) + \psi_{el}^i \nabla_{\alpha}^r \psi_N^i + (\nabla_{\alpha} \psi_N^i) \cdot (\nabla_{\alpha} \psi_{el}^i) \right\} + \sum_{i=1}^{\infty} V_{el}^i \psi_N^i \psi_{el}^i = E \sum_{i=1}^{\infty} \psi_N^i \psi_{el}^i$$

$$\Rightarrow \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} -\frac{1}{2M_{\alpha}} \psi_{\ell}^i \nabla_{\alpha}^r \psi_N^i + \sum_{\ell=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} -\frac{1}{2M_{\alpha}} \left\{ 2(\nabla_{\alpha} \psi_{\ell}^i) (\nabla_{\alpha} \psi_N^i) + \psi_N^i \nabla_{\alpha}^r \psi_{\ell}^i \right\} + \sum_{\ell=1}^{\infty} v^{\ell} \psi_N^{\ell} \psi_{\ell}^{\ell} = E \sum_{\ell=1}^{\infty} \psi_N^{\ell} \psi_{\ell}^{\ell}$$

$$\Rightarrow \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} -\frac{1}{2M_{\alpha}} \langle \psi_{\ell}^j | \psi_{\ell}^i \rangle \nabla_{\alpha}^r \psi_N^i + \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} + \frac{1}{2M_{\alpha}} \left\{ 2 \langle \psi_{\ell}^j | \nabla_{\alpha} | \psi_{\ell}^i \rangle (\nabla_{\alpha} \psi_N^i) + \psi_N^i \langle \psi_{\ell}^j | \nabla_{\alpha}^r | \psi_{\ell}^i \rangle \right\} + \sum_{i=1}^{\infty} \langle \psi_{\ell}^j | \psi_{\ell}^i \rangle v^{\ell} \psi_N^i = E \sum_{i=1}^{\infty} \langle \psi_{\ell}^j | \psi_{\ell}^i \rangle \psi_N^i$$

$$\Rightarrow \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} -\frac{1}{2M_{\alpha}} \delta_{ji} \nabla_{\alpha}^r \psi_N^i - \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} \frac{1}{2M_{\alpha}} \left\{ 2 \langle \psi_{\ell}^j | \nabla_{\alpha} | \psi_{\ell}^i \rangle (\nabla_{\alpha} \psi_N^i) + \psi_N^i \langle \psi_{\ell}^j | \nabla_{\alpha}^r | \psi_{\ell}^i \rangle \right\} + \sum_{i=1}^{\infty} v^{\ell} \delta_{ji} v^{\ell} \psi_N^i$$

$$= E \sum_{i=1}^{\infty} \delta_{ji} \psi_N^i$$

Now $j=i$

$$\Rightarrow \sum_{\alpha=1}^{n_{\alpha}} \nabla_{\alpha}^r \psi_N^j - \sum_{i=1}^{\infty} \sum_{\alpha=1}^{n_{\alpha}} \frac{1}{2M_{\alpha}} \left\{ 2 \langle \psi_{\ell}^j | \nabla_{\alpha} | \psi_{\ell}^i \rangle (\nabla_{\alpha} \psi_N^i) + \psi_N^i \langle \psi_{\ell}^j | \nabla_{\alpha}^r | \psi_{\ell}^i \rangle \right\} + v^j \psi_N^j = E \psi_N^j$$

$$\Rightarrow \sum_{\alpha=1}^{n_{\alpha}} \left[-\frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 + v^j - E \right] \psi_N^j$$

$$= \sum_{e^0=1}^{\alpha} \sum_{\alpha=1}^{n_{\alpha}} \left[\frac{1}{2M_{\alpha}} \left\{ 2 \langle \psi_{ee}^i | \nabla_{\alpha} | \psi_{ee}^j \rangle \cdot \nabla_{\alpha} \nabla_N^e + \langle \psi_{ee}^j | \nabla_{\alpha} | \psi_{ee}^i \rangle \psi_N^i \right\} \right]$$

kinetic coupling / non-adiabatic coupling

for adiabatic approximation these are zero.

~~for non-adiabatic approximation~~

for (degeneracy state) $\frac{1}{v_e^i - v_j}$ or b/w two same type electronic state almost zero so the term will be singular. we have to do another representation.

(using Hellmann-Feynman theorem prove the coupling term is singular)

We are trying to fix this analytically

adiabatic representation: -

ψ_N^i

Afternoon session

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = H\Psi(x,t) \text{ Here we need initial } \Psi.$$

$$|N| = \frac{1}{\int \Psi^* \Psi dx} \text{ square integrable function}$$

$H\Psi(x,t) = E\Psi(x,t)$ This is eigen value problem

$$AxAP_x \text{ with } [Ax, AP_x] = i\hbar$$

General quantisation Rule

$$\oint p dq = nh$$

$E = nh\nu$ Planck
 $mvr = nh/2\pi$ Bohr

$$|\Psi(x,t)\rangle = e^{-iHt/\hbar} \Psi(x,t=0)$$

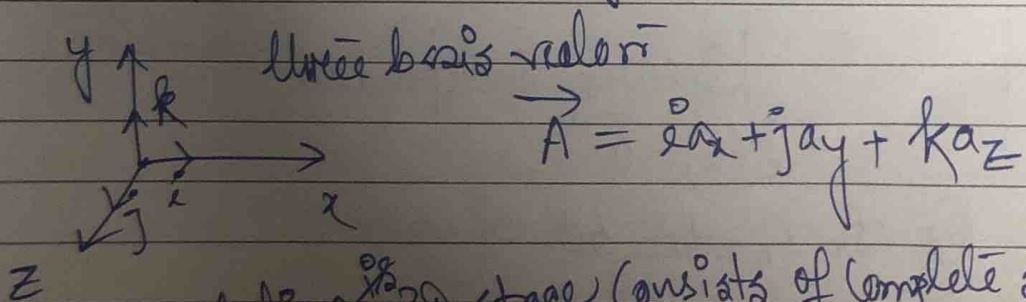
$$e^{\hat{A}+\hat{B}} \neq e^{\hat{A}} \cdot e^{\hat{B}} + (i\hbar)^{n+1}$$

error accumulated when splitting

$$e^{\hat{A}+\hat{B}} \neq e^{\hat{A}} \cdot e^{\hat{B}}$$

unless these operators commute each other prove.

QM is probabilistic theory



- Euclidean \mathbb{R}^3 space consists of complete space vector.
- Hilbert space is set of complex vector space is ∞ dim extension set of scalar

Norm is preserved.

Length of the

In Euclidean space

$$\|\vec{A}\| = \sqrt{a_x^2 + a_y^2 + a_z^2}$$

length of the vector preserves direction will change.

$$\begin{array}{ccc}
 (a_x \ a_y \ a_z) & \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} & \rightarrow 1 \\
 \swarrow & \searrow & \\
 1 \times 3 & & 3 \times 1 \\
 \swarrow & & \searrow \\
 & & = (1, 1) \\
 & & = \text{scalar product}
 \end{array}$$

In Hilbert space norm is preserved.

$$\boxed{\|\psi\| \Rightarrow \sqrt{\langle \psi | \psi \rangle} = 1}$$

eigenfn of Hermitian operator Complete orthonormal set

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad \text{Basis set has to be this properly.}$$

$$\begin{cases}
 \vec{i} \cdot \vec{i} = \vec{j} \cdot \vec{j} = \vec{k} \cdot \vec{k} = 1 \\
 \vec{i} \cdot \vec{j} = \vec{j} \cdot \vec{k} = \vec{k} \cdot \vec{i} = 0
 \end{cases}$$

This holds in Euclidean space.

$$|\Psi(x, t)\rangle = \sum_i c_i(t) |\phi_i(x)\rangle$$

Coefficient changes with time

Linearly independent

$$c_i(t) = 0$$

In Complete set of vector any set of vector is not expressed as a linear combination of other's set.

$$\langle \psi(x,t) | \psi(x,t) \rangle = \sum_i c_i^2 \langle \alpha$$

which defines probability

Basis properly \rightarrow Basis for ψ linearly independent. $\text{---} \textcircled{1}$
 Dimension depends on no of basis for $\text{---} \textcircled{2}$
 orthonormal $\text{---} \textcircled{3}$

span $\text{---} \textcircled{4}$
 over the entire space.

$\checkmark \textcircled{1}$
 $\checkmark \textcircled{2}$
 $\checkmark \textcircled{3}$

It does not span $\times \textcircled{4}$

$i, j, k \rightarrow \textcircled{1}, \textcircled{2}, \textcircled{3}, \textcircled{4} \checkmark$

$\checkmark \textcircled{1}, \checkmark \textcircled{2}, \checkmark \textcircled{3}, \checkmark \textcircled{4} \rightarrow \times$

linearly dependent

square integrability
 in functional space

square summability
 in discrete space

mapping b/w f.s to d.s
 $\&$ evaluate integrals

$|\phi\rangle \langle \phi| \rightarrow$ operator
 In general we get matrix
 Hilbert space
 is expressed
 in matrix form

$|\phi_n\rangle \langle \phi_n| = \hat{P}_n$ projection operator

$$\hat{i} \cdot \vec{A} = a_x \quad \text{projecting}$$

$$\hat{i} \cdot \hat{i} \cdot \vec{A} = \hat{i} a_x$$

$$\Rightarrow \hat{i} \cdot \hat{i} \vec{A} + \hat{j} \cdot \hat{j} \vec{A} + \hat{k} \cdot \hat{k} \vec{A} = \vec{A}$$

$$|\psi\rangle = a_1 |\phi_1\rangle + a_2 |\phi_2\rangle + a_3 |\phi_3\rangle$$

$$\langle \phi_1 | \psi \rangle = a_1$$

$$\Rightarrow |\phi_1\rangle \langle \phi_1 | \psi \rangle = a_1 |\phi_1\rangle$$

$$\sum_n |\phi_n\rangle \langle \phi_n| = \text{Identity operator/matrix}$$

n goes to
dimensional
of the
space

This is "Completeness" relation.

$$\langle \phi_m | \phi_n \rangle = \delta_{mn}$$

$$\sum_n |\phi_n\rangle \langle \phi_n| = \hat{1}$$

$$\sum_i |c_i|^2 \langle \alpha | \alpha \rangle \text{ space}$$

$$\int_{-\infty}^{+\infty} dx |f(x)|^2 \langle \alpha | \alpha \rangle \text{ space}$$

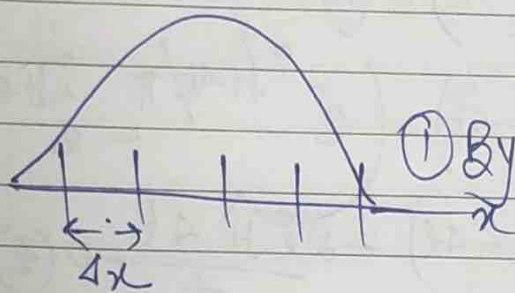
$$\int_{-\infty}^{+\infty} dk |f(k)|^2 \text{ identical with momentum space}$$

$$\sum_n f_n^*(x) f_n(x') = \delta(x-x')$$

↓
Dirac delta

$$\Psi(x,t) = e^{-i\hat{H}t/\hbar} \Psi(x,t=0)$$

time evolution operator
it is integral part of TDSE.



① By discrete grid we are mapping continuous function

if grids are dense enough the calculation is accurate enough

② Discretization of time

both for numerical solution of time & space are required

$$\hat{U}(t, t_0) = e^{-i\hat{H}t/\hbar}$$

$$\hat{U}(t) = \prod_{n=0}^{n_{t_1}} \hat{U}[(n+1)\Delta t, n\Delta t]$$

when $n=0$

$$n=0 \quad U(t) = \hat{U}[\Delta t]$$

$$n=1 \quad U(t) = \hat{U}[2\Delta t, \Delta t]$$

$$\Delta t = \hbar/n_t$$

$$\hat{U} \hat{U}^\dagger = \hat{U}^\dagger \hat{U} = 1$$

evolve the system

unitarity ~~konform~~ norm is preserved

$$\Psi(x+\Delta t) = \hat{U}(\Delta t) \Psi(x)$$

$$\Psi(x-\Delta t) = \hat{U}^\dagger(\Delta t) \Psi(x)$$

$$\Psi(x+\Delta t) - \Psi(x-\Delta t) = \begin{pmatrix} e^{-i\hat{H}\Delta t/\hbar} & 2i\hat{H}\Delta t/\hbar \\ & -e \end{pmatrix} \Psi(x)$$

$$\Psi(x+\Delta t) = \Psi(x-\Delta t) - \frac{2i\hat{H}\Delta t}{\hbar} \Psi(x)$$

2nd order differentiation scheme

$$\Psi(x+\Delta t) = e^{i\hat{H}\Delta t/\hbar} \Psi(x) - \frac{2i\hat{H}\Delta t}{\hbar} \Psi(x)$$

$$= \begin{pmatrix} e^{i\hat{H}\Delta t/\hbar} & -\frac{2i\hat{H}\Delta t}{\hbar} \\ & \end{pmatrix} \Psi(x)$$

$$= \mathcal{O} \Psi(x)$$

$$\begin{pmatrix} e^{i\hat{H}\Delta t/\hbar} & -\frac{2i\hat{H}\Delta t}{\hbar} \\ & \end{pmatrix} = e^{-i\hat{H}\Delta t/\hbar} + \frac{2i\hat{H}\Delta t}{\hbar}$$

$$\hat{U}(\Delta t) = e^{-i(T+V)\Delta t/\hbar}$$

$$\approx e^{-iT\Delta t/\hbar} e^{-iV\Delta t/\hbar} + (\Delta t)^{n+1}$$

$\underbrace{e^{-iV\Delta t/\hbar}}_{\text{Coordinate space}} \underbrace{e^{-iT\Delta t/2\hbar}}_{\text{Momentum space}} \underbrace{e^{-iV\Delta t/\hbar}}_{\text{Coordinate space}} \underbrace{e^{-iT\Delta t/2\hbar}}_{\text{Momentum space}}$
 Kinetic energy is not local $\hat{U}(\Delta t)$

$$T = P^2/2m$$

Collocation

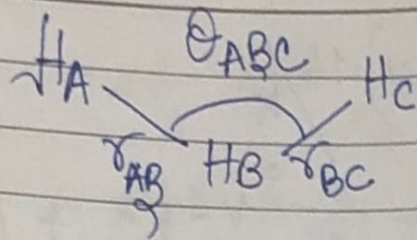
$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \bar{\Psi}(k) e^{ikx} dk$$

$$\bar{\Psi}(k) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x) e^{-ikx} dx$$

- 1) Kinetic reference split method
- 2) Potential reference split method

$$3) \hat{T} \Psi(x_j) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x_j)}{\partial x_j^2}$$

$$= -\frac{\hbar^2}{2m} \left[\frac{\Psi_j(x_{j+1}) + \Psi_j(x_{j-1}) - 2\Psi_j(x_j)}{(\Delta x_j)^2} \right]$$



When $\delta_{ABC} = 0^\circ$ then the system is collinear

