Change of states with time

Lets consider an apparatus which just "contains" the particular state from time t_1 to t_2. In other words I want to see how states change with the dimension time. The amplitude is given

$$\langle \chi \mid U(t_1, t_2) \mid \phi \rangle$$

$$= \sum_i \langle \chi | i \rangle \langle i | U(t_1, t_2) | j \rangle \langle j | \phi \rangle$$

generally $t_1 \to -\infty$ $t_2 \to \infty$ is what scientists calculate

$\langle i | S | j \rangle$ called as S matrix

How to analyse (Non relativistically)?

we know $U(t_3, t_1) = U(t_3, t_2) \cdot U(t_2, t_1)$

Therefore we first analyse $U(t+\Delta t, t)$ and then multiply piecewise upto any range of t we want.

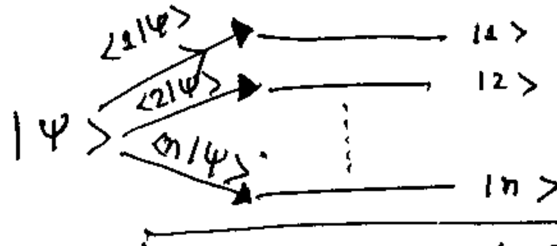
Now lets consider the effect of $U(t+\Delta t, t)$ on $|\Psi(t)\rangle$

$$\boxed{|\Psi(t+\Delta t)\rangle = U(t+\Delta t, t)\,|\Psi(t)\rangle}$$

$\boxed{\text{like } |\chi\rangle = A|\phi\rangle}$

~~Remember: like/ take/taking~~

IDEA: we say that the base states dont change with time. Its the amplitude $\langle i | \Psi \rangle$ which changes with time.

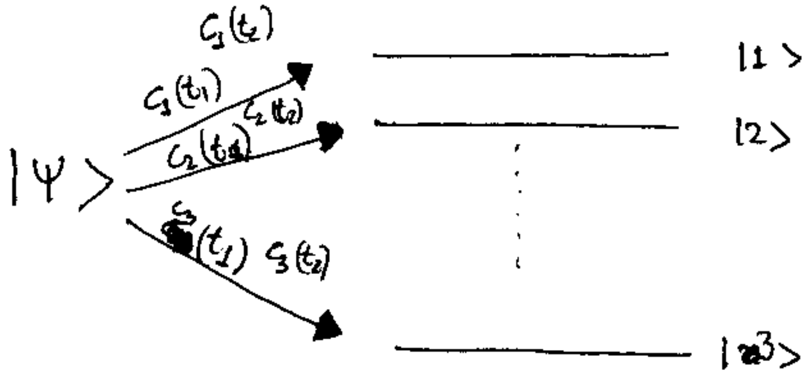


Thus $$\boxed{|\Psi(t)\rangle = \sum_i C_i(t)\,|i\rangle}$$

also we must put the constraint that $\boxed{\sum_i |C_i(t)|^2 = 1}$ ②

There-fore if $|C_1(t)|$ increases $|C_i(t)|$ for some i should decrease.

<u>My Concept</u>



now if $|C_1(t_1)| > |C_1(t_2)|$ && $|C_3(t_1)| > |C_3(t_2)|$ that means $|C_2(t_1)| < |C_2(t_2)|$ thus we can say that from the time span of t_1 to t_2 there must have been the amplitude to go from $|3\rangle \to |2\rangle$ and $|1\rangle \to |2\rangle$. Let those amplitudes be

$$\cancel{\boxed{\langle 2 | U(t_2, t_1) | 3\rangle = H'_{32} \qquad \langle 2 | U(t_2, t_1) | 1\rangle = H'_{12}}}$$

$\cancel{C_2(t_2) = C_2(t_1)}$

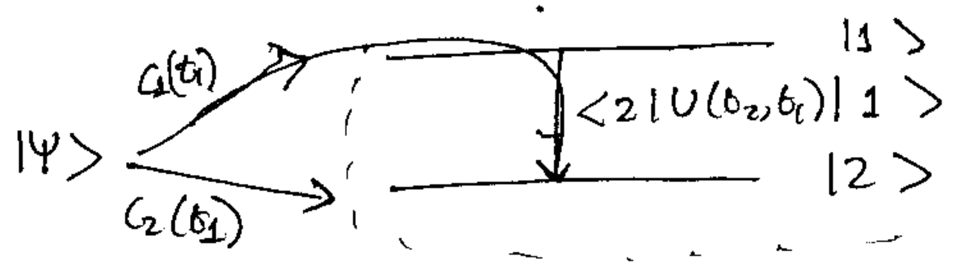
Let $\boxed{t_2 \to t_1 + \Delta t}$

Then

$$C_1(t_2) = \cancel{C_1(t_1)} + C_1(t_1)\langle 1 | U(t_2, t_1) | 1\rangle + C_2(t_1)\langle 1 | U(t_2, t_1) | 2\rangle \cdots C_n(t_1)\langle 1 | U(t_2, t_1) | n\rangle$$

⟨amp to remain in $|1\rangle$ in (t_2) | amp to exist in $|1\rangle$⟩ in (t_1)

⟨amp to exist in $|1\rangle$ at t_2 | amp to exist in $|2\rangle$ at t_1⟩



$$\therefore \quad C_2(t_2) = \cancel{C_2(t_1)} + C_2(t_1)\langle 2|U(t_2 t_1)|2\rangle + C_1(t_1)\langle 2|U(t_2 t_1)$$

$$C_1(t+\Delta t) - \cancel{C_1(t)} = C_1(t_1)\langle 1|U(t+\Delta t, t)|1\rangle + C_2(t_1)\langle 1|U(t+\Delta t, t)|2\rangle \cdots$$

Lets define

$$\boxed{\begin{aligned}\langle i|U(t+\Delta t, t)|j\rangle &= -\frac{i}{\hbar} H_{ij}\Delta t \quad \text{if } i \neq j \\ &= 1 - \frac{i}{\hbar} H_{ij}\Delta t \quad \text{if } i = j\end{aligned}}$$

It follows

$$\boxed{H_{ij}^* = H_{ji}}$$

Symmetry ??

$$C_1(t+\Delta t) = C_1(t)\left[1 - \frac{i}{\hbar} H_{11}\Delta t\right] + \sum_{j=2} C_j(t)\left(-\frac{i}{\hbar} H_{1j}\Delta t\right)$$

$$C_1(t+\Delta t) - C_1(t) = -\frac{i}{\hbar} \sum_{j=1} H_{1j}\, C_j(t)\, \Delta t$$

$$i\hbar\, \frac{\Delta C_1}{\Delta t} = \sum H_{1j}\, C_j(t)$$

$$i\hbar\, \frac{dC_i}{dt} = \sum H_{ij}(t)\, C_j(t)$$

Lets see mathmetically (Feynman type)

$$|\Psi(t+\Delta t)\rangle = U(t+\Delta t, t)\,|\Psi(t)\rangle$$

$$\langle i|\Psi(t+\Delta t)\rangle = \sum_j \langle i|U(t+\Delta t, t)|j\rangle \langle j|\Psi(t)\rangle$$

$$\boxed{C_i(t+\Delta t) = \sum_j \langle i|U(t+\Delta t, t)|j\rangle\, C_j(t)}$$

$$U_{ij} = \delta_{ij} + K_{ij}\,\Delta t$$ ⇒ Taylor's expansion

$$= \delta_{ij} - \frac{i}{\hbar} H_{ij}\,\Delta t$$

$$C_i(t+\Delta t) = \sum_j \left(\delta_{ij} - \frac{i}{\hbar} H_{ij}\,\Delta t\right) C_j(t)$$

$$\boxed{i\hbar \frac{dC_i(t)}{dt} = \sum_j H_{ij}(t)\, C_j(t)}$$

Relation between H and E

Lets say there is only one base state

[Let H_{11} be independent of t] [Same physical conditions]

$$i\hbar \frac{dC_1}{dt} = H_{11} C_1$$

$$\boxed{C_1 = (\text{constant})\, e^{-\frac{i}{\hbar} H_{11} t}}$$

Case Study

1) Ammonia Molecule (NH_3)

a) First approximation

NH_3 only one base state $|1\rangle$

$\therefore \quad C_1 = a\, e^{-\frac{i E_0 t}{\hbar}}$

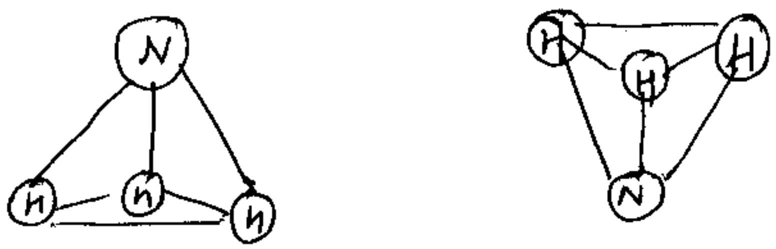
(Uncertainty $\Delta p = 0$ (at rest)

$\Delta x \to \infty$)

single energy state

b) Second approximation

sp^3 hybridization pyramidal geometry



(two possible orientation)

$|1\rangle$ $\quad$ $|2\rangle$

$$|\psi\rangle = \langle 1|\psi\rangle |1\rangle + \langle 2|\psi\rangle |2\rangle$$

$$i\hbar \frac{dC_1}{dt} = C_1 H_{11} + C_2 H_{12}$$

$$i\hbar \frac{dC_2}{dt} = C_1 H_{21} + C_2 H_{22}$$

case I

Consider there is no transitions in $|1\rangle \to |2\rangle$ or $|2\rangle$ to $|1\rangle$ in time i.e

$$\langle 2| U(t+\Delta t, t)|1\rangle = \langle 1| U(t+\Delta t, t)|2\rangle = 0$$

or $H_{21} = H_{12} = 0$

then $C_1 = a_1 e^{-i/\hbar\, H_{11} t}$ $C_2 = a_2 e^{i/\hbar\, H_{22} t}$

since physical conditions are same there is no difference in H_{11} or H_{22}

$\therefore H_{11} = H_{22} = E_0$

Case II

In reality $\langle 1 | U(t+\Delta t, t) | 2 \rangle$ and $\langle 2 | U(t+\Delta t, t) | 1 \rangle$ are non zero. There is some amplitude for transition

If both $|1\rangle$ and $|2\rangle$ are symmetric then

$$H_{21} = H_{12} = -A$$

[can differ only by a phase]

$$\therefore \begin{cases} i\hbar \dfrac{dC_1}{dt} = H_{11} C_1 - A C_2 \\ i\hbar \dfrac{dC_2}{dt} = H_{22} C_2 - A C_1 \end{cases}$$

[add and substract get eq in C_1+C_2 and C_1-C_2]

$$\begin{cases} C_1(t) = \dfrac{a}{2} e^{-\frac{i}{\hbar}[E_0 - A]t} + \dfrac{b}{2} e^{-\frac{i}{\hbar}[E_0 + A]t} \\ C_2(t) = \dfrac{a}{2} e^{-\frac{i}{\hbar}[E_0 - A]t} - \dfrac{b}{2} e^{-i/\hbar [E_0 + A]t} \end{cases}$$

$$\therefore \boxed{|\psi(t)\rangle = C_1(t)\,|1\rangle + C_2(t)\,|2\rangle}$$

~~ahday~~ we see that by mere considering A there is split in energy. We get two energy levels. If b is 0 then again there is one energy level $(E_0 - A)$ and so on

2)

Apply boundary conditions

$C_1(0) = 1 = \frac{a+b}{2}$ $\qquad$ $C_2(0) = 0 = \frac{a-b}{2}$

thus $\quad C_1(t) = e^{-i/\hbar \, E_0 t} \cos(At/\hbar)$

$\quad C_2(t) = e^{-i/\hbar \, E_0 t} \sin(At/\hbar)$

Note

1) when $a=0$ or $b=0$ only ① energy state (E_0+A) or (E_0-A) respectively. Therefore (E_0+A), (E_0-A) are stationary Energy states

2) when $a=b$ only ① energy state E_0

3) when $a \neq b$ only two energy states E_0-A and E_0+A

A Deeper look into Hamilton,

$$\boxed{i\hbar \frac{dC_i}{dt} = \sum_j C_j H_{ij}}$$

now what is H_{ij} ??

From previous discussions we defined

$$\cancel{H_{ij} = \langle i | U(t+\Delta t, t) | j \rangle / \hbar}$$

$$\boxed{\langle i | U(t+\Delta t, t) | j \rangle = \delta_{ij} - \frac{i}{\hbar} H_{ij} \Delta t} \qquad \in \Delta t \to 0$$

Thus H_{ij} seems like a <u>part of amplitude (if not whole)</u>; of a base state $|j\rangle$ to exist in other base state $|i\rangle$ after a period of time Δt. The question is which part of the amplitude?

For example

1) if $|\psi\rangle = C_1 |1\rangle$

$$i\hbar \frac{dC_1}{dt} = C_1 H_{11}$$

$$\boxed{C_1 = a_0 e^{-\frac{i H_{11} t}{\hbar}}}$$

<u>and from de broglie's hypothesis H_{11} = Energy</u>

So we conclude for <u>one basis</u> system H_{11} is the energy of the system. (That doesnt mean that H_{ij} is the energy)

2) if $|\psi\rangle = C_1 |1\rangle + C_2 |2\rangle$

i)
$$\begin{bmatrix} H_{11} = E_1 & H_{12} = 0 \\ H_{21} = 0 & H_{22} = E_0 \end{bmatrix}$$

then
$$\boxed{\begin{aligned} C_1 &= a_0 e^{-iE_1 t/\hbar} \\ C_2 &= b_0 e^{-iE_2 t/\hbar} \end{aligned}}$$

$\therefore \quad |\Psi\rangle = a_0 e^{-iE_1 t/\hbar} |1\rangle + b_0 e^{-iE_2 t/\hbar} |2\rangle$

$\langle 1 | \Psi \rangle = a_0 e^{-iE_1 t/\hbar}$

$|\langle 1 | \Psi \rangle|^2 =$ constant over time.

thus $|1\rangle$ is a <u>stationary state</u> of Energy E_1 (The freq)

~~since~~ Thus H_{11} is the energy of state $|1\rangle$

similarly $|2\rangle$ is also a stationary state with Energy E_2

<u>Conclusion</u> $\Rightarrow$ if $\boxed{H_{ij} = C(i,j)\,\delta_{ij}}$ i.e diagonal then H_{ij} represent the energy of the ($i = j$'th) state which is also stationary state.

ii) $H_{ij\,(i \neq j)} \neq 0$

Let $|\Psi\rangle = C_1 |1\rangle + C_2 |2\rangle$

$$\begin{bmatrix} H_{11} = A_1 & H_{12} = -A_1 \\ H_{21} = -A_2 & H_{22} = A_2 \end{bmatrix}$$

Here we are not having diagonal matrix

from differential equations we get

$C_1 = \frac{a}{2} e^{-iE_1 t/\hbar}$

ii) $H_{ij\,(i\neq j)} \neq 0$

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle$$

Let $\begin{bmatrix} H_{11} = E_0 & H_{12} = -A \\ H_{21} = -A & H_{22} = E_0 \end{bmatrix}$ [superposition principle assumed]

$$c_1 = \frac{a}{2}e^{-\frac{i(E_0-|A|)t}{\hbar}} + \frac{b}{2}e^{-\frac{i(E_0+|A|)t}{\hbar}}$$

$$c_2 = \frac{a}{2}e^{-\frac{i(E_0-|A|)t}{\hbar}} - \frac{b}{2}e^{-\frac{i(E_0+|A|)t}{\hbar}}$$

(kind of Beats formation)
(A is complex. General derivation done later)
(A is taken (supposed) real here)

Now we can no longer say $|1\rangle$, $|2\rangle$ stationary states. $|\langle 1|\psi\rangle|^2$, $|\langle 2|\psi\rangle|^2$ are time dependent which is due to the fact that $\langle 1|U(t+\Delta t, t)|2\rangle$ and $\langle 2|U(t+\Delta t, t)|1\rangle$ are non zero.

Conclusion: In non diagonal matrix H_{11}, H_{22} etc are no more the energy of stationary states.

But we can go from one base states (basis) to other

Consider $|I\rangle = \frac{1}{\sqrt{2}}[|1\rangle - |2\rangle]$ $|II\rangle = \frac{1}{\sqrt{2}}[|1\rangle + |2\rangle]$

$$|\psi\rangle = \frac{c_1}{\sqrt{2}}[|I\rangle + |II\rangle] + \frac{c_2}{\sqrt{2}}[-|I\rangle + |II\rangle]$$

$$= \frac{1}{\sqrt{2}}[c_1 - c_2]|I\rangle + \frac{1}{\sqrt{2}}[c_1 + c_2]|II\rangle$$

$$\boxed{|\psi\rangle = c_I|I\rangle + c_{II}|II\rangle}$$

now $c_I = \text{Const} \times e^{-\frac{i(E_0+|A|)t}{\hbar}}$

$c_{II} = \text{Const} \times e^{-\frac{i(E_0-|A|)t}{\hbar}}$

Thus here $|I\rangle$ and $|II\rangle$ represent stationary States or Energy basis with (E_0+A) and (E_0-A) energies respectively. ④

~~let~~ $H_{11} /\!/ H_{21}$ $H_{12} /\!/ H$

$$i\hbar \frac{dC_1}{dt} = (E_0 \,\cancel{+}\,)C_1 - AC_2 \quad -①$$

$$i\hbar \frac{dC_2}{dt} = -AC_1 + (E_0 \,\cancel{\;}\,)C_2 \quad -②$$

adding ①, ②

$$i\hbar \frac{d}{dt}(C_1+C_2) = (E_0-A)(C_1+C_2) \cancel{\neq (E_0-A)C_1}$$

$$i\hbar \frac{d}{dt}(C_1-C_2) = (E_0+A)(C_1-C_2)$$

$$\boxed{i\hbar \frac{dC_{II}}{dt} = (E_0-A)C_{II} \qquad i\hbar \frac{dC_I}{dt} = (E_0+A)C_I}$$

~~again~~ thus

$$\begin{bmatrix} H_{II} = E_0+A = E_I & H_{I\,II} = 0 \\ H_{II\,I} = 0 & H_{II\,II} = E_0-A = E_{II} \end{bmatrix}$$

again we get diagonal matrix giving the energy of stationary states.

* Also we see that $|1\rangle$ and $|2\rangle$ are not the energy states. A particle in $|1\rangle$ has 1/2 probability to exist in energy state of (E_0+A) and 1/2 probability to exist in (E_0-A) energy.

but when $A=0$ then $|1\rangle$ and $|2\rangle$ are energy states also consider general case of (ii)

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

$H_{11} \neq H_{22} \neq H_{12} \neq H_{21} \neq 0$

$$|\psi\rangle = C_1 |1\rangle + C_2 |2\rangle$$

$$\boxed{\begin{aligned} i\hbar \frac{dC_1}{dt} &= H_{11} C_1 + H_{12} C_2 \quad - (1) \\ i\hbar \frac{dC_2}{dt} &= H_{21} C_1 + H_{22} C_2 \quad - (2) \end{aligned}}$$

Now let us go to the energy basis or stationary basis of Hamilton defined by

$$|I\rangle = a_1 |1\rangle + a_2 |2\rangle$$

$$|II\rangle = a_1' |1\rangle + a_2' |2\rangle$$

$$\Rightarrow |1\rangle = \frac{a_2' |I\rangle - a_2 |II\rangle}{a_1 a_2' - a_1' a_2} \qquad |2\rangle = \frac{a_1' |I\rangle - a_1 |II\rangle}{a_2 a_1' - a_1 a_2'}$$

Now $\boxed{|\psi\rangle = C_I |I\rangle + C_{II} |II\rangle}$

where $C_I = \dfrac{C_1 a_2' - C_2 a_1'}{a_1 a_2' - a_1' a_2}$ and $C_{II} = \dfrac{C_2 a_1 - C_1 a_2}{a_1 a_2' - a_1' a_2}$

now $|I\rangle$ and $|II\rangle$ are supposed to be stationary states

$$H_{II} = E_I \qquad H_{I\,II} = 0$$

$$H_{II\,I} = 0 \qquad H_{II\,II} = E_{II}$$

Thus $C_I = a_0 e^{-\frac{iE_I t}{\hbar}}$ $\quad C_{II} = b_0 e^{-\frac{iE_{II} t}{\hbar}}$

$$C_1 = a_0 a_1 e^{-iE_I t/\hbar} + b_0 a_1' e^{-\frac{iE_{II} t}{\hbar}}$$

$$C_2 = a_0 a_2 e^{-iE_I t/\hbar} + b_0 a_2' e^{-\frac{iE_{II} t}{\hbar}}$$

or

$$\boxed{\begin{aligned} C_1 &= a_1 C_I + a_1' C_{II} \\ C_2 &= a_2 C_I + a_2' C_{II} \end{aligned}}$$

now put these value of C_1 and C_2 in the differential equation (1) and compare cooficients of C_I and C_{II}

we get

$$\boxed{\begin{aligned} E_I a_1 &= H_{11} a_1 + H_{12} a_2 \\ E_{II} a_1' &= H_{11} a_1' + H_{12} a_2' \end{aligned}} \quad \begin{aligned} &-(3) \\ &-(4) \end{aligned}$$

simillarly from equation (2) we get

$$\boxed{\begin{aligned} E_I a_2 &= H_{21} a_1 + H_{22} a_2 \\ E_{II} a_2' &= H_{21} a_1' + H_{22} a_2' \end{aligned}} \quad \begin{aligned} &-(5) \\ &-(6) \end{aligned}$$

Eliminate a_1, a_2 from (3) and (5) we get

Quadratic

$$E_I = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H_{12} H_{21}}$$

similar expression is obtained for E_{II}

By convention $E_I \rightarrow (+)$

So here are the transformations

$$|\psi\rangle = C_1 |1\rangle + C_2 |2\rangle \implies C_I |I\rangle + C_{II} |II\rangle$$

$$\boxed{\begin{array}{ll} |I\rangle = a_1 |1\rangle + a_2 |2\rangle & C_I = \dfrac{C_1 a_2' - C_2 a_1'}{a_1 a_2' - a_1' a_2} \\ |II\rangle = a_1' |1\rangle + a_2' |2\rangle & \\ |1\rangle = \dfrac{a_2' |I\rangle - a_2 |II\rangle}{a_1 a_2' - a_1' a_2} & C_{II} = \dfrac{C_2 a_1 - C_1 a_2}{a_1 a_2' - a_1' a_2} \\ & C_1 = a_1 C_I + a_1' C_{II} \\ |2\rangle = \dfrac{a_1' |I\rangle - a_1 |II\rangle}{a_1' a_2 - a_2' a_1} & C_2 = a_2 C_I + a_2' C_{II} \end{array}}$$

$$E_I = \frac{H_{11} + H_{22}}{2} + \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H_{12} H_{21}}$$

$$E_{II} = \frac{H_{11} + H_{22}}{2} - \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H_{12} H_{21}}$$

also

$$|a_1|^2 + |a_2|^2 = 1$$

$$|a_1'|^2 + |a_2'|^2 = 1$$

$$\frac{a_1}{a_2} = \frac{H_{12}}{E_I - H_{11}}$$

$$\frac{a_1'}{a_2'} = \frac{H_{12}}{E_{II} - H_{11}}$$

The final picture of Hamilton

$$\boxed{i\hbar \frac{dC_i}{dt} = \sum_j H_{ij} C_j} \quad -①$$

$$i\hbar \frac{d}{dt} \langle i|\Psi\rangle = \sum_j \langle i|\hat{H}|j\rangle\langle j|\Psi\rangle$$

$$i\hbar \frac{d}{dt} |\Psi\rangle = \sum_j \hat{H}|j\rangle\langle j|\Psi\rangle$$

$$\boxed{i\hbar \frac{d|\Psi\rangle}{dt} = \hat{H}|\Psi\rangle} \quad -②$$

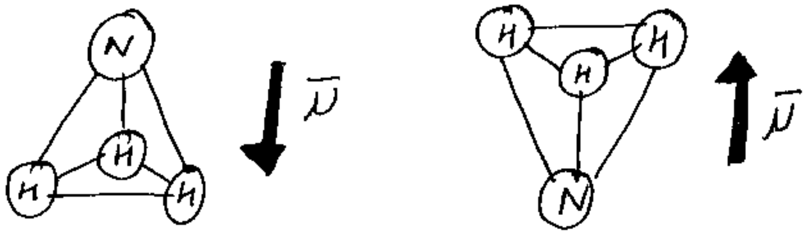
Equations ① and ② are same and convey same idea. The only difference is the method of representation. equation ② is as feynman says "Neater equation".

One can think of $\hat{H}$ as a apparatus through which if we input $|\Psi\rangle$ it changes like $i\hbar \frac{d|\Psi\rangle}{dt}$ (not sure ??)

Case Study

Ammonia molecule in an electric field

1) Constant electric field



$|1\rangle$ $|2\rangle$

Let there be no flip-flop i.e $A = 0$

Then in absence of electric field

$$\begin{bmatrix} H_{11} = E_0 & H_{12} = 0 \\ H_{21} = 0 & H_{22} = E_0 \end{bmatrix}$$

note $|1\rangle, |2\rangle$ are energy basis also

but in presence of ξ field we should get (as, $|1\rangle$, $|2\rangle$ represent stationary states)

$$\begin{bmatrix} H_{11} = E_0 + \mu\xi & H_{12} = 0 \\ H_{21} = 0 & H_{22} = E_0 - \mu\xi \end{bmatrix}$$

still $|1\rangle, |2\rangle$ are Energy basis

Now lets bring flip-flop nature. also assume that this flip-flop doesnot affect H_{11}, H_{22}. Only now $H_{12} = H_{21} = -A$

$$\begin{bmatrix} H_{11} = E_0 + \mu\xi & H_{12} = -A \\ H_{21} = -A & H_{22} = E_0 - \mu\xi \end{bmatrix}$$

now $|1\rangle, |2\rangle$ are no more stationary states

$$E_I = E_0 + \sqrt{A^2 + \mu^2\xi^2} \qquad E_{II} = E_0 - \sqrt{A^2 + \mu^2\xi^2}$$

Note:

1) At large ξ $\quad E_I \simeq E_0 + \mu\xi = H_{11} \qquad E_{II} \simeq E_0 - \mu\xi = H_{22}$

That means at large ξ the splitting depends on ξ ②
The flip flop amplitude has little role to play.

2) ① If we dont consider flip-flop then also there is splitting of energy due to electric field.