Lecture 2: Fermi's Golden Rule , the Density matrix Formalism.

* first-order time-dependent theory
* Fermi's golden rule.
* quantum statistical mechanisms.
* density matrix formalism.
* two-level system

The key of this lecture, of course, is

the Fermi's golden rule. The name is

given by Fermi dubbing the formula.

"Golden Rule No. 2". The formula is actually

originally derived by Paul Dirac.

"FGR" not only provides a simple expression

to evaluate transition rate (prob. of transition

per unit time), it has greater physical

content $\Rightarrow$ the basic form of coupling

strength and energy matching dominates
all types of quantum dynamics. Here we will
give a simple derivation of this great formula.

Now recall that in the last lecture we introduced
time-evolution operator, time-ordered exponential, and
interaction picture, The key $\mathbb{I}_3$, for

$$H = H_0 + V \qquad V_\mathcal{I}(t) = e^{\frac{i}{\hbar}H_0 t} \cdot V(t) \cdot e^{-\frac{i}{\hbar}H_0 t}$$

$$U_\mathcal{I}(t) \simeq 1 - \frac{i}{\hbar}\int_0^t d\tau \cdot V_\mathcal{I}(\tau) - \frac{1}{\hbar^2}\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \, V_\mathcal{I}(\tau_2)\, V_\mathcal{I}(\tau_1)$$
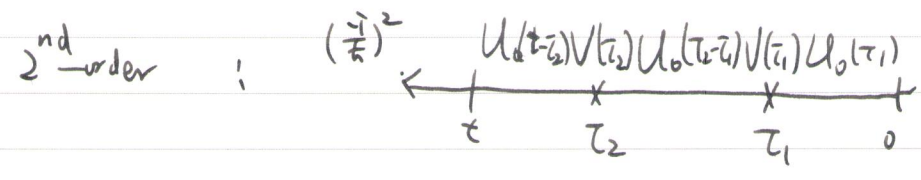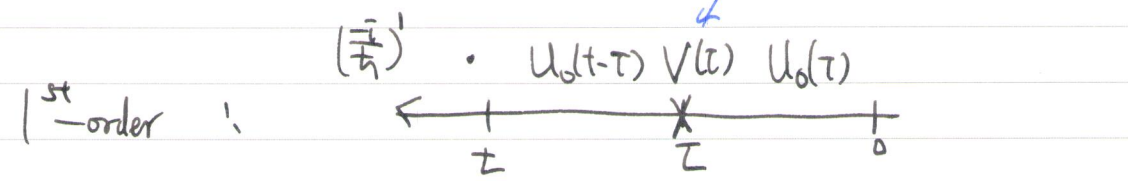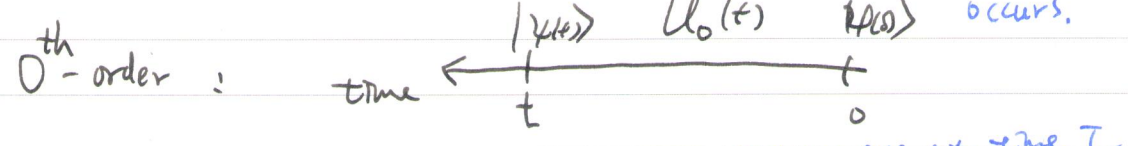
So, back to the Schrödinger picture $\quad U^\dagger(\tau) = U(-\tau)$

$$U(t) = U_0(t) U_\mathcal{I}(t) = U_0(t) - \frac{i}{\hbar} U_0(t)\int_0^t d\tau \cdot U_0^\dagger(\tau)\, V(\tau)\, U_0(\tau)$$

$$- \frac{1}{\hbar^2} U_0(t) \cdot \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \cdot U_0^\dagger(\tau_2) V(\tau_2)\, U(\tau_2)$$
$$\cdot U_0^\dagger(\tau_1)\, V(\tau_1)\, U_0(\tau_1)$$

0th order

$$\simeq U_0(t) - \frac{i}{\hbar}\int_0^t d\tau \cdot U_0(t-\tau)\cdot V(\tau)\cdot U_0(\tau)$$

1st order

2nd-order

$$- \frac{1}{\hbar^2}\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \, U_0(t-\tau_2)\cdot V(\tau_2) \cdot U_0(\tau_2-\tau_1)\cdot V(\tau_1)\cdot U_0(\tau_1)$$
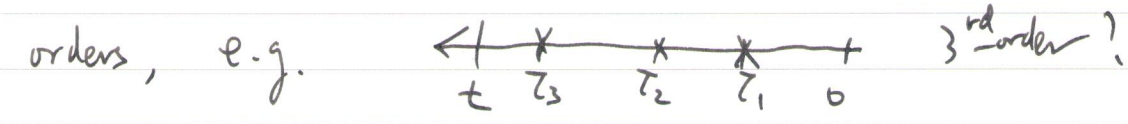
This expansion has a graphic

representation : recall $|\psi(t)\rangle = U(t) |\psi(0)\rangle$

all propagated by $U_0(t)$,
no interaction with $V(t)$
occurs.

0th - order :   time $\longleftarrow$

$|\psi(t)\rangle \quad U_0(t) \quad |\psi(0)\rangle$

$$\begin{array}{ccc} & U_0(t) & \\ t & & 0 \end{array}$$

Interact once at time τ

1st - order : $\left(\frac{-i}{\hbar}\right)^1 \cdot U_0(t-\tau) V(\tau) U_0(\tau)$

$$\begin{array}{ccc} t & \tau & 0 \end{array}$$

2nd - order : $\left(\frac{-i}{\hbar}\right)^2 \quad U_0(t-\tau_2) V(\tau_2) U_0(\tau_2-\tau_1) V(\tau_1) U_0(\tau_1)$

$$\begin{array}{cccc} t & \tau_2 & \tau_1 & 0 \end{array}$$

This can be easily generalized to higher

orders, e.g.

$$\begin{array}{ccccc} t & \tau_3 & \tau_2 & \tau_1 & 0 \end{array}$$

3rd-order ?

$\Rightarrow$ Basically these are a kind of

Feynman diagram.

* First-order ~~time~~-dependent perturbation ~~theory~~.   ③   ⑤

$\Rightarrow$ transition ~~proper~~ probabilities per unit time.

A lot of important phenomena in quantum physics can be described by a rate process, i.e. we want to know the rate of transition from $|\ell\rangle \xrightarrow{k} |k\rangle$.
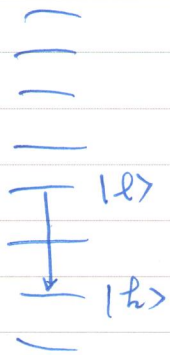
This picture generally arises in the first-order perturbation theory, as being demonstrated in the famous Fermi's Golden Rule —

$\overline{}$
$\overline{}$
$\overline{}$
$\top\ |\ell\rangle$
$\downarrow\ |k\rangle$

Here we show an ~~exp~~ example, simple one, by considering a system under constant, step function perturbation...
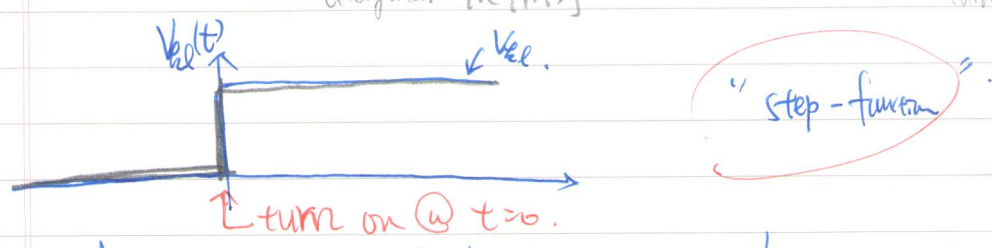
* <u>Constant, step function perturbation!</u>

Consider a molecule with known spectrum $\{|k\rangle\}$, i.e. eigenstates are not coupled to each other, and has a constant perturbation turning on the couplings at $t=0$, i.e.

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \quad , \quad \hat{V}_0(t) = \hat{V} \cdot \theta(t)$$

↑ diagonal in $\{|k\rangle\}$

↑ H-diagonal couplings

↳ turn on @ $t=0$.

"Step-function".

↳ turn on @ $t=0$.

Assume we solved H_0, in the eigenbasis of H_0:

$$H_0 |k\rangle = E_k \cdot |k\rangle$$

We want to know : if the system is initially prepared in a state $|l\rangle$, what is the rate of it making a transition to $|k\rangle$ after the perturbation is turned on?

$\therefore \, |\mathcal{H}(0)\rangle = |\ell\rangle$, we want to

calculate the prob. of finding the system

in $|k\rangle$ @ time t : (for $k \neq \ell$)

$$P_k(t) = |\langle k | \mathcal{H}(t)\rangle|^2 = |\langle k | U(t) | \ell \rangle|^2 .$$

$$U(t) = U_0(t) \cdot U_I(t)$$

truncated in the
first order —

$\boxed{A_I(t) = U_0^{\dagger}(t) \cdot A(t) \cdot U_0(t)}$

$$\simeq e^{-\frac{i}{\hbar} H_0 t} \cdot \left[1 - \frac{i}{\hbar} \int_0^t d\tau \cdot V_I(\tau) \right]$$

do not forget this

$$= e^{-\frac{i}{\hbar} H_0 t} \cdot \left[1 - \frac{i}{\hbar} \int_0^t d\tau \cdot e^{\frac{i}{\hbar} H_0 \tau} \cdot V(0) \cdot e^{-\frac{i}{\hbar} H_0 \tau} \right]$$

$t = \tau$

$t \quad V(0) \quad t > 0$

$$= e^{-\frac{i}{\hbar} H_0 t} - \frac{i}{\hbar} \int_0^t e^{-\frac{i}{\hbar} H_0 (t - \tau)} \cdot V(0) \cdot e^{-\frac{i}{\hbar} H_0 \tau} \cdot d\tau .$$

free prop.   hit by   free prop. "τ"
$t - \tau$!

plug in : $\frac{i}{\hbar} k$ ℓ

$$b_{k\ell} = \langle k | U(t) | \ell \rangle$$

$$\simeq -\frac{i}{\hbar} \int_0^t \langle k | e^{-\frac{i}{\hbar} H_0 (t - \tau)} \cdot V(0) \cdot e^{-\frac{i}{\hbar} H_0 \tau} | \ell \rangle \, d\tau$$

$$= -\frac{i}{\hbar} \cdot e^{-\frac{i}{\hbar} \xi_k t} \cdot \int_0^t e^{\frac{i}{\hbar} (\xi_\ell - \xi_k) \tau} \times V_{k\ell} \cdot d\tau .$$
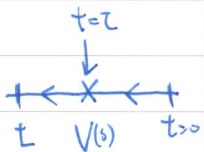
The integral is easy to evaluate, we

have :

$$\boxed{w_{k\ell} = \frac{\mathcal{E}_k - \mathcal{E}_\ell}{\hbar}}$$

$$b_{k\ell}(t) = -\frac{V_{k\ell}}{\mathcal{E}_k - \mathcal{E}_\ell} \cdot \left[e^{i w_{k\ell} t} - 1 \right]$$

$$\boxed{e^{i\theta} - 1 = 2i e^{i\theta/2} \sin \frac{\theta}{2}} \qquad = \frac{-2i \cdot V_{k\ell} \cdot e^{\frac{i w_{k\ell} \cdot t}{2}}}{\mathcal{E}_k - \mathcal{E}_\ell} \times \sin\left(w_{k\ell} \cdot t/2 \right).$$

$$\boxed{\text{sinc}\, x = \frac{\sin x}{x}} \qquad \therefore P_k(t) = \left| b_{k\ell}(t) \right|^2 = \frac{4 |V_{k\ell}|^2}{|\mathcal{E}_k - \mathcal{E}_\ell|^2} \times \sin^2\left(\frac{w_{k\ell} \cdot t}{2} \right).$$

$$= \frac{|V_{k\ell}|^2}{\hbar^2} \times t^2 \times \frac{1}{\left(\frac{\mathcal{E}_k - \mathcal{E}_\ell}{\hbar} \times \frac{1}{2} \times t \right)^2} \times \sin^2\left(\frac{w_{k\ell} \cdot t}{2} \right)$$

$$\boxed{\lim_{x \to 0} \text{sinc}\, x = 1} \qquad = \frac{|V_{k\ell}|^2 \cdot t^2}{\hbar^2} \times \text{sinc}^2\left[\frac{(\mathcal{E}_k - \mathcal{E}_\ell) t}{2\hbar} \right].$$

$P_k(t)$ depends on $\mathcal{E}_k - \mathcal{E}_\ell$, max. @ $\underline{\mathcal{E}_k = \mathcal{E}_\ell}$

resonance ↗

Note that as $t \uparrow$, the peak narrows !!

$P_{k}(t)$ depends on t in a complex way, however, with enough time it "converged" to a linear behavior:

notice that $\lim\limits_{a \to \infty} \frac{\sin^2(\frac{ax}{2})}{a x^2} = \frac{\pi}{2} \cdot \delta(x)$.

We have $\lim\limits_{t \to \infty} P_{k}(t) = \frac{2\pi |V_{kl}|^2}{\hbar} \cdot \delta(\mathcal{E}_k - \mathcal{E}_l) \cdot t$.

* population grows linear in t as t is "long enough"

* physically, $P_{k}(t) < 1$ ↙ must., so the result is also only valid at a sufficiently short time.

Therefore we can define a "rate" for the process :

Stationary

$$k_{l \leftarrow a} = \frac{dP_a}{dt} = \frac{2\pi |V_{kal}|^2}{\hbar} \times \delta(E_a - E_l).$$

This is the "state-to-state form" of the Fermi's Golden rule. The form is actually not limited to the step-function perturbation it is more general, and ~~then~~ provides a basic picture for all quantum dynamics.

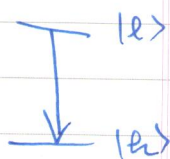Dynamics = coupling + energy matching .

* Applications of FGR.

the first-order perturbation does not treat the depletion of $|\ell\rangle$, so we use $P_k(t)$ directly:

$$P_k(t) \approx \frac{2\pi}{\hbar} |V_{k\ell}|^2 \, \delta(\mathcal{E}_k - \mathcal{E}_\ell) \cdot t$$

yields very bad results. Easily see when t is large the $P_k(t) > 1$ ⟸ wrong!!

However, if we ~~need~~ instead use the rate equation : (assume only two states).

$$\frac{dP_\ell(t)}{dt} = -\cancel{\sum_{k=\ell}^{} k \cdots}$$

$$\frac{dP_\ell(t)}{dt} = -k_{k\leftarrow\ell} \cdot P_\ell(t).$$

$$\therefore \quad P_\ell(t) \approx e^{-k_{k\leftarrow\ell} \cdot t}$$

It often gives very good results.

* check additional info in Tokmakoff's notes.

timeless

* quantum mechanics & ensemble theory.

Now everything up to here is for a "pure state" quantum system that can be exactly identified and characterized. However, this is not possible because we often (actually always) encounter "lack of information", the ~~experimentally~~ controllable parameters are ~~too~~ too few. Think about:

① the state of a molecule in a molecular beam generated from a ~~thermal~~-equilibrium gas chamber. We know the thermal distribution & that the molecule is a sample of it, but

② which one exactly is totally random and unknown.

③ the state of a cup of water! can't assign because too many degrees of freedom

\# statistical description is necessary!!

timeless

ensemble average

In physical chemistry, we often deal with systems that have well-defined "thermodynamic variables" i.e. $E, S, P, V, \mu, \ldots$ but likely to be in many "microstates" $\to$ ensemble.

state view: An ensemble is defined by the collection of microstates that all satisfy certain thermodynamical constraints.

$$\text{microcanonical} \to \Theta(N, E, V) \quad \text{i.e. gives}$$
$$\text{canonical} \to (N, V, T) \quad \text{similar}$$
$$\text{grand canonical} \to (V, T) \quad \text{macroscopic}$$

subsystem view: If the "system" can be decomposed into many independent sub-systems, then we can think the ensemble as a collection of subsystems, each can be in a different sense ...

$\uparrow$ very useful sometimes, think a collection of many many molecules.

Exp. observable often requires averaging over an ensemble of states: $\langle O \rangle = \sum_{\Theta \nu} P_{\Theta \nu} O_{\Theta \nu}$

for thermal equilibrium $\to P_{\Theta} = \dfrac{e^{\beta E_\nu}}{z}$

※ Statistical mixture

In QM, this means a system can be in
many (states) ⇒ i.e. many (wave functions),
we do not know at a given time in which
state the system is ⊗, but we know the
statistics ⇒ a statistical mixture of states.

$$P_1 \longrightarrow |\phi_1\rangle$$
$$P_2 \longrightarrow |\phi_2\rangle$$
$$\vdots$$
$$P_n \longrightarrow |\phi_n\rangle$$
$$\vdots$$
$$P_n : \{\phi_n\}$$

space
of
"possible"
states

It is incorrect to ~~write~~ represent the
system as a single wavefunction now.

$$|\psi\rangle \neq P_1|\phi_1\rangle + \dots + P_n|\phi_n\rangle + \dots$$

because mixture, no coherence,

~~How can we~~

* How can we describe a statistical mixture?

⇒ introduce a very useful tool in quantum statistical mechanics, "density matrix/operator"

⇒ think about observable for an ensemble of wavefunctions ⇒ observables are all that matters —

$$\langle O \rangle = \sum_n P_n \cdot \langle \phi_n | \hat{O} | \phi_n \rangle$$

$$= Tr \sum_n P_n \langle \phi_n | \hat{O} | \phi_n \rangle \qquad \downarrow trick$$

$$= Tr \sum_n P_n \cdot | \phi_n \rangle \langle \phi_n | \cdot \hat{O}$$

$$= Tr \, \rho \cdot \hat{O}$$

if we define $\rho = \sum_n P_n | \phi_n \rangle \langle \phi_n |$.

↳ density matrix determines all observables !!

↑ essential statistical property for a quantum system.

* ρ is: ① trace 1. $Tr\rho = 1$ ② Hermitian ③ positive semi-definite i.e. eigenvalues ≥ 0.

Some example of density matrices

① a pure state.

if $|\psi\rangle = \frac{1}{\sqrt{2}}|\phi_1\rangle + \frac{1}{\sqrt{2}}|\phi_2\rangle$, in $\begin{pmatrix}|\phi_1\rangle \\ |\phi_2\rangle\end{pmatrix}$ basis.

$$|\psi\rangle = \begin{pmatrix}\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}}\end{pmatrix} \qquad \therefore \rho_\psi = |\psi\rangle\langle\psi| = \begin{pmatrix}\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}}\end{pmatrix}\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right)$$

$$= \begin{pmatrix}\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2}\end{pmatrix}.$$

coherence, populations.
(off-diagonal), (diagonal)

② Statistical mixture

if $|\psi\rangle = \begin{cases}50\% & |\phi_1\rangle \\ 50\% & |\phi_2\rangle\end{cases}$

no coherence !!

$$\Rightarrow \rho = \frac{1}{2}|\phi_1\rangle\langle\phi_1| + \frac{1}{2}|\phi_2\rangle\langle\phi_2| \sim \begin{pmatrix}\frac{1}{2} & 0 \\ 0 & \frac{1}{2}\end{pmatrix}$$

③ thermal equilibrium.

Suppose we know the eigenstate of a system

$$H|\phi_n\rangle = \varepsilon_n|\phi_n\rangle$$

in equilibrium $\quad \rho_{eq} = \sum_n P_n \cdot |\phi_n\rangle\langle\phi_n| = \sum_n \frac{e^{-\beta \varepsilon_n}}{Z} \cdot |\phi_n\rangle\langle\phi_n|$

$$= \frac{1}{Z} \cdot \begin{pmatrix}e^{-\beta \varepsilon_1} & & 0 \\ & e^{-\beta \varepsilon_2} & \\ 0 & & \ddots\end{pmatrix} = \frac{1}{Z} \cdot e^{-\beta H}$$

clearly $\quad Z = \text{Tr } e^{-\beta H}$.

pure state   vs.   mixture

* if   a   system   can   be   described   as
a   single   wave function $|\psi\rangle$

$$\rho = |\psi\rangle\langle\psi|$$

then $\text{Tr}\,\rho = 1,$ $\text{Tr}\,\rho^2 = 1.$

~~Tr~~ $\text{Tr}\,\rho^2 \leftarrow$ purity .

* for   a   mixture $\to$ $\text{Tr}\,\rho^2 < 1.$

EOM for ρ:

$$\frac{d\rho}{dt} = \frac{d}{dt}\left[\sum P_n |\phi_n\rangle\langle\phi_n|\right] = -\frac{i}{\hbar}[H, \rho]$$

↑ Quantum Liouville equation,

Example: (Extra material, self reading) (LS) (H)

for a TLS:

① $|\psi\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \longrightarrow \rho = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}$ — coherence (population)

② system 50% in $|1\rangle$, 50% in $|2\rangle$

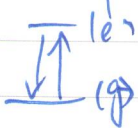$$\Longrightarrow \rho = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}.$$

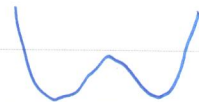## A little more on two-level systems:

many physically important system can be reduced to a TLS problem effectively.

① spin $\frac{1}{2}$, ② absorption & emission $|e\rangle$ $|g\rangle$

③ double-well potential

④ light polarization ... $|L\rangle$ $|R\rangle$

and many more.

timeless

time-independent TLS

chosen a basis, TLS Hamiltonian is.

$$
\begin{array}{cc} |1\rangle & |2\rangle \end{array}
$$

$$
H = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} = \begin{pmatrix} \varepsilon_1 & J \\ J^* & \varepsilon_2 \end{pmatrix}
$$

coupling.

electronic energy

$$
= \frac{\varepsilon_1 + \varepsilon_2}{2} \cdot I + \frac{\varepsilon_1 - \varepsilon_2}{2} \cdot \begin{pmatrix} 1 & \frac{2J}{\varepsilon_1 - \varepsilon_2} \\ \frac{2J^*}{\varepsilon_1 - \varepsilon_2} & -1 \end{pmatrix}.
$$

if we define

mixing angle

$$
\tan 2\theta = \frac{2|J|}{\varepsilon_1 - \varepsilon_2} \qquad\qquad J = |J| \cdot e^{i\varphi}
$$

then we want to first solve for the eigenvalues & eigenstates of the operator.

$$
K = \begin{pmatrix} 1 & \tan 2\theta \cdot e^{i\varphi} \\ \tan 2\theta \cdot e^{-i\varphi} & -1 \end{pmatrix}
$$

the characteristic equation is.

$$
\det [K - k \cdot I] = k^2 - 1 - \tan^2 2\theta = 0
$$

$$
\therefore \quad k_{\pm} = \pm \sqrt{1 + \tan^2 2\theta} = \pm \frac{1}{\cos 2\theta} . \quad \text{timeless}
$$

We can find.

$$E_{\pm} = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4|J|^2}\,.$$

and corresponding eigen functions:

$$|\psi_+\rangle = \cos\theta \cdot e^{\frac{i\varphi}{2}} \cdot |1\rangle + \sin\theta \cdot e^{\frac{-i\varphi}{2}} \cdot |2\rangle$$

$$|\psi_-\rangle = -\sin\theta \cdot e^{\frac{i\varphi}{2}} |1\rangle + \cos\theta \cdot e^{\frac{-i\varphi}{2}} \cdot |2\rangle.$$

$$\Delta = E_1 - E_2.$$

" coherence "

$|\varepsilon_1 - \varepsilon_2| \ll J$, (symmetry & anti-symmetric)

$|\varepsilon_1 - \varepsilon_2| \gg J$, localized states , i.e. $|1\rangle, |2\rangle$

timeless

How about thermal equilibrium & time-evolution ??

* thermal equilibrium:

$$\rho_{eq} = \sum_{i} \frac{e^{-\beta E_i}}{Z} \cdot |\phi_i\rangle\langle\phi_i| \equiv \sum_{i} \frac{e^{-\beta H}}{Z} \cdot |\phi_i\rangle\langle\phi_i|$$

eigen states

sum over eigen states

$$= \frac{1}{Z} \cdot e^{-\beta H}$$

whereas $Z = \mathrm{Tr}\, e^{-\beta H}$.

* time - evolution.

$$U(t) = e^{-\frac{i}{\hbar}H\cdot t} = \begin{bmatrix} e^{-\frac{i}{\hbar}E_+\cdot t} & 0 \\ 0 & e^{-\frac{i}{\hbar}E_-\cdot t} \end{bmatrix}$$

In the eigenstate basis.

$\Rightarrow$ back to $|1\rangle, |2\rangle$ basis ??

if we construct $W = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$

then $W^\dagger W = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, unitary.

timeless

$$\therefore \quad W^\dagger H W = \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}.$$

$\uparrow$ [diagonalization, transform basis to $|\psi_\pm\rangle$.

transform back? $\Rightarrow$ $H = W \cdot \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix} \cdot W^\dagger$

$$\therefore \quad U(t) = W \cdot \begin{bmatrix} e^{-\frac{i}{\hbar} E_+ t} & 0 \\ 0 & e^{-\frac{i}{\hbar} E_- t} \end{bmatrix} \cdot W^\dagger$$

In the original basis. $\#$