

# A Summer Short Course on Quantum Dynamics & Spectroscopy (2019)

2019/8/15

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.

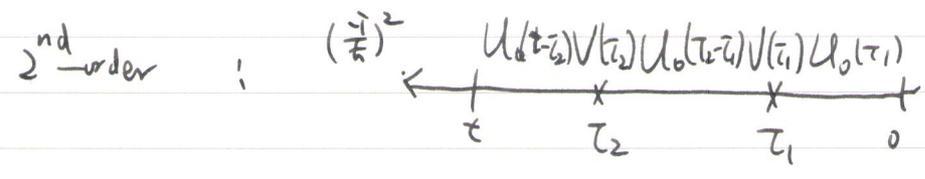
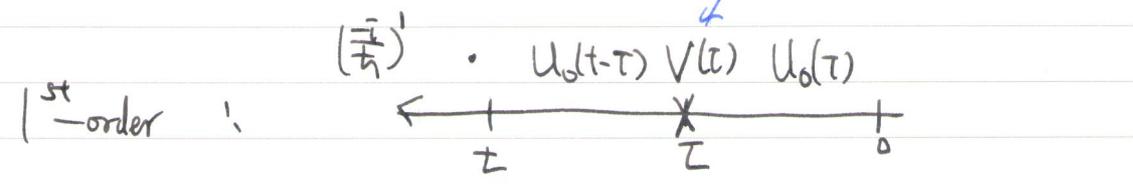
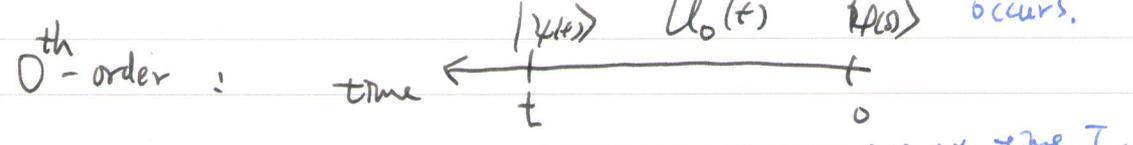
"Golden Rule No. 2". The formula is actually originally derived by Paul Dirac.

"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  
timeless

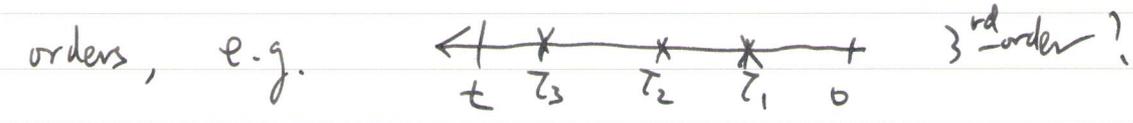


This expansion has a graphic

representation: recall  $|\psi(t)\rangle = U(t) |\psi(0)\rangle$   
 all propagated by  $U_0(t)$ ,  
 no interaction with  $V(t)$  occurs.



This can be easily generalized to higher

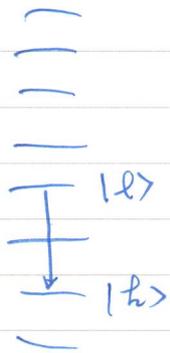


⇒ Basically these are a kind of Feynman diagram.

# \* First-order time-dependent perturbation theory (3) (4)

⇒ transition ~~prob~~ 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  $|l\rangle \xrightarrow{H} |k\rangle$ .



This picture generally arises in the first-order perturbation theory, as being

demonstrated in the famous Fermi's Golden Rule —

Here we show an ~~ex~~ example, simple one,

by considering a system under constant, step function perturbation.

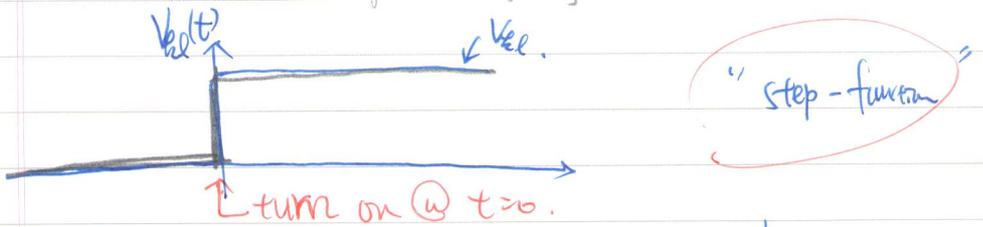
\* Constant, step function perturbation!

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.

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

$\uparrow$  diagonal in  $\{|k\rangle\}$        $\uparrow$  off-diagonal couplings  
 $\uparrow$  turn on @  $t=0$



Assume we solved  $H_0$ , in the eigenbasis of

$$H_0 : \boxed{H_0 |k\rangle = E_k |k\rangle}$$

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?

∴  $|ψ(0)⟩ = |l⟩$ , we want to

calculate the prob. of finding the system

in  $|k⟩$  @ time  $t$ : (for  $k ≠ l$ )

$$P_k(t) = |\langle k | ψ(t) \rangle|^2 = |\langle k | U(t) | l \rangle|^2.$$

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

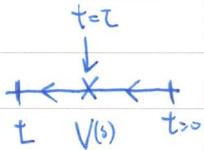
truncated in the first order —

$$A_z(t) = U_0^\dagger(t) A(z) U_0(t)$$

$$\approx e^{-\frac{i}{\hbar} H_0 t} \cdot \left[ 1 - \frac{i}{\hbar} \int_0^t dt' V_I(t') \right]$$

$$= e^{-\frac{i}{\hbar} H_0 t} \cdot \left[ 1 - \frac{i}{\hbar} \int_0^t dt' e^{\frac{i}{\hbar} H_0 t'} \cdot V(z) \cdot e^{-\frac{i}{\hbar} H_0 t'} \right]$$

↑ do not forget this



$$= e^{-\frac{i}{\hbar} H_0 t} - \frac{i}{\hbar} \int_0^t dt' e^{-\frac{i}{\hbar} H_0(t-t')} \cdot V(z) \cdot e^{-\frac{i}{\hbar} H_0 t'}$$

free prog. t-t'
highly
Free prog. t'

plug in:  $\frac{i}{\hbar} H_0 t$

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

$$\approx -\frac{i}{\hbar} \int_0^t dt' \langle k | e^{-\frac{i}{\hbar} H_0(t-t')} \cdot V(z) \cdot e^{-\frac{i}{\hbar} H_0 t'} | l \rangle dt'$$

$$= -\frac{i}{\hbar} \cdot e^{-\frac{i}{\hbar} E_k t} \int_0^t e^{\frac{i}{\hbar} (E_k - E_l) \tau} \times V_{kl} \cdot dt'$$

timeless

The integral is easy to evaluate, we

have:

$$\omega_{kl} = \frac{E_k - E_l}{\hbar}$$

$$b_{kl}(t) = - \frac{V_{kl}}{E_k - E_l} \cdot [e^{i\omega_{kl}t} - 1]$$

$$e^{i\theta} - 1 = 2ie^{i\theta/2} \sin \frac{\theta}{2} \quad = \quad \frac{-2i \cdot V_{kl} \cdot e^{i\frac{\omega_{kl} \cdot t}{2}}}{E_k - E_l} \times \sin(\omega_{kl} \cdot t/2)$$

$$\text{sinc} x = \frac{\sin x}{x}$$

$$\lim_{x \rightarrow 0} \text{sinc} x = 1$$

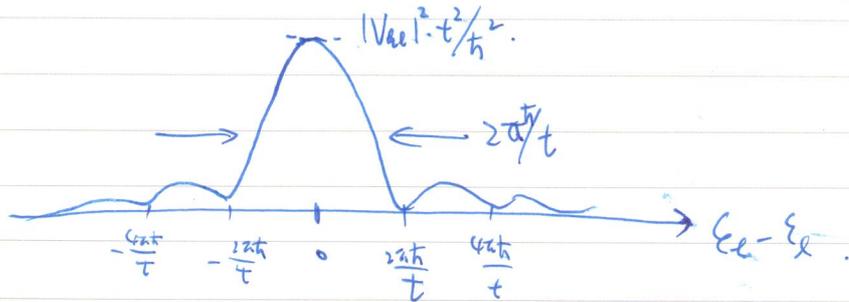
$$\therefore P_k(t) = |b_{kl}(t)|^2 = \frac{4|V_{kl}|^2}{|E_k - E_l|^2} \times \sin^2\left(\frac{\omega_{kl} \cdot t}{2}\right)$$

$$= \frac{|V_{kl}|^2}{\hbar^2} \times t^2 \times \frac{1}{\left(\frac{E_k - E_l}{\hbar} \times \frac{1}{2} \times t\right)^2} \times \sin^2\left(\frac{\omega_{kl} \cdot t}{2}\right)$$

$$= \frac{|V_{kl}|^2 \cdot t^2}{\hbar^2} \times \text{sinc}^2\left[\frac{(E_k - E_l)t}{2\hbar}\right]$$

$P_k(t)$  depends on  $E_k - E_l$ , max. @  $E_k = E_l$

↑ resonance



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

timeless

$P_2(t)$  depends on  $t$  in a complex way, however, with enough time it "converged" to a linear behavior!

notice that  $\lim_{a \rightarrow \infty} \frac{\sin^2(\frac{ax}{2})}{ax^2} = \frac{\pi}{2} \cdot \delta(x)$

We have  $\lim_{t \rightarrow \infty} P_2(t) = \frac{2\pi |V_{ee}|^2}{\hbar} \cdot \delta(E_2 - E_1) \cdot t$

\* population grows linear in  $t$  as  $t \rightarrow \infty$  "long enough"

\* physically,  $P_2(t) < 1$ , <sup>must</sup> so the result is also only valid at a sufficiently short time.

⑧ ⑩

Therefore we can define a

"rate" for the process:  
Stationary

$$P_{\text{res}} = \frac{dP_a}{dt} = \frac{2\pi |V_{ba}|^2}{\hbar} \times \delta(E_a - E_b).$$

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 ~~can~~ provides a

basic picture for all quantum dynamics.

Dynamics  $\hat{=}$  coupling + energy matching.

## \* Applications of FGR

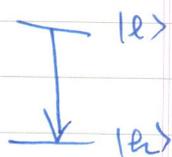
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the first-order perturbation does not treat the depletion of  $|e\rangle$ , so we  $P_e(t)$  directly:

$$P_e(t) \approx \frac{2\pi}{\hbar} |V_{ee}|^2 \delta(\epsilon_e - \epsilon_e) \cdot t$$

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

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



~~$$\frac{dP_e(t)}{dt} = -\Gamma_{e \rightarrow g} P_e(t)$$~~

$$\frac{dP_e(t)}{dt} = -\Gamma_{e \rightarrow g} P_e(t)$$

$$\therefore P_e(t) \approx e^{-\Gamma_{e \rightarrow g} t}$$

It often gives very good results.

\* check additional info in Tokmarkoff'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 & have 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!!

# Ensemble average

(1) (2) (4)

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

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

microcanonical  $\rightarrow (N, E, V)$  i.e. gives

canonical  $\rightarrow (N, T, V)$  similar

grand canonical  $\rightarrow (V, T)$  macroscopic

Subsystem view: If the "system" can be decomposed into many independent sub-systems, then we can ~~not~~ think the ensemble as a collection of subsystems <sup>each</sup> ~~many~~ can be in a different sense.  $\dots$

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

Exp. observable often requires averaging over ~~the~~ an ensemble of states:  $\langle O \rangle = \frac{\sum P_{ij} O_{ij}}{\Omega}$   
for <sup>thermal</sup> equilibrium  $\Rightarrow P_{ij} = \frac{e^{-\beta E_{ij}}}{Z}$

timeless

# \* Statistical mixture

(12) (14) (18)

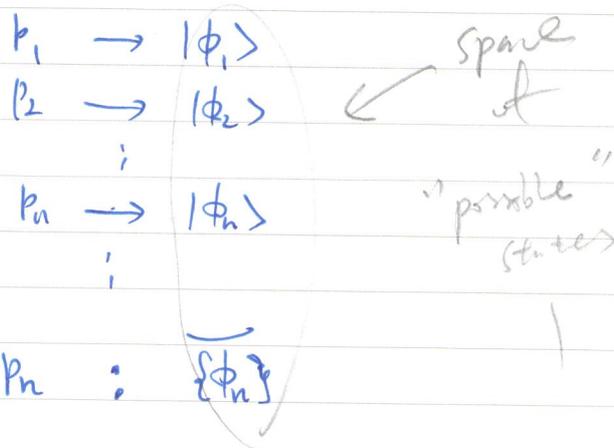
In QM, this means a system can be in

many states  $\Rightarrow$  i.e. many wave functions,

we do not know at a given time in which

state the system is, but we know the

statistics  $\Rightarrow$  a statistical mixture of states.



It is incorrect to ~~use~~ represent the

~~system~~ 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~~

timeless

\* How can we describe a statistical mixture?

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

⇒ think about observable ~~to~~ <sup>for</sup> an ensemble of wavefunctions ⇒ observables are all that matters -

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

$$= \text{Tr} \sum_n p_n \langle \phi_n | \hat{O} | \phi_n \rangle$$

↓ trick ←

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

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

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.

\*  $\rho$  is: ① trace 1, ②  $\text{Tr} \rho^2 = 1$  ③ Hermitian ④ positive semi-definite <sup>to</sup> i.e. eigenvalues  $\geq 0$ .

# Some example ~~of~~ density matrices

## ① 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.

$$|\psi\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \quad \therefore \rho = |\psi\rangle\langle\psi| = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

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

coherence (off-diagonal), populations (diagonal)

## ② statistical mixture

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

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

no coherence !!

## ③ thermal equilibrium

Suppose we know the eigenstate of a system

$$H|\phi_n\rangle = \epsilon_n|\phi_n\rangle$$

in equilibrium  $\rho_{eq} = \sum_n p_n \cdot |\phi_n\rangle\langle\phi_n| = \frac{1}{Z} \sum_n e^{-\beta\epsilon_n} |\phi_n\rangle\langle\phi_n|$

$$= \frac{1}{Z} \begin{pmatrix} e^{-\beta\epsilon_1} & & 0 \\ & e^{-\beta\epsilon_2} & \\ 0 & & \dots \end{pmatrix} = \frac{1}{Z} \cdot e^{-\beta H}$$

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

timeless

## pure state vs. mixture

(14)

(10)

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

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

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

$$\text{Tr}\rho^2 \leftarrow \text{purity}$$

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

EqM for  $\rho$ :

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

$\uparrow$  Quantum Liouville equation,

Example : (Extra material, self reading) (15) (4)

for a TLS:

①  $|z\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$   $\rightarrow$   $\rho = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}$

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

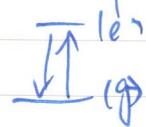
$\Rightarrow \rho = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$

coherence

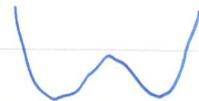
population

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 

③ double-well potential



④ light polarization ...

$|L\rangle$   $|R\rangle$

and many more.

# time-independent TLS

chosen a basis, TLS Hamiltonian is

$$H = \begin{pmatrix} |1\rangle & |2\rangle \\ h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} = \begin{pmatrix} \epsilon_1 & J \\ J^* & \epsilon_2 \end{pmatrix}$$

$$= \frac{\epsilon_1 + \epsilon_2}{2} \cdot I + \frac{\epsilon_1 - \epsilon_2}{2} \cdot \begin{pmatrix} 1 & \frac{2J}{\epsilon_1 - \epsilon_2} \\ \frac{2J^*}{\epsilon_1 - \epsilon_2} & -1 \end{pmatrix}$$

coupling.  
electronic energy

if we define

$$\tan 2\theta = \frac{2|J|}{\epsilon_1 - \epsilon_2} \quad \text{mixing angle.}$$

$J = |J| \cdot e^{i\phi}$

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

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

the characteristic equation is

$$\text{Det}[K - k \cdot I] = k^2 - 1 - \tan^2 2\theta = 0$$

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

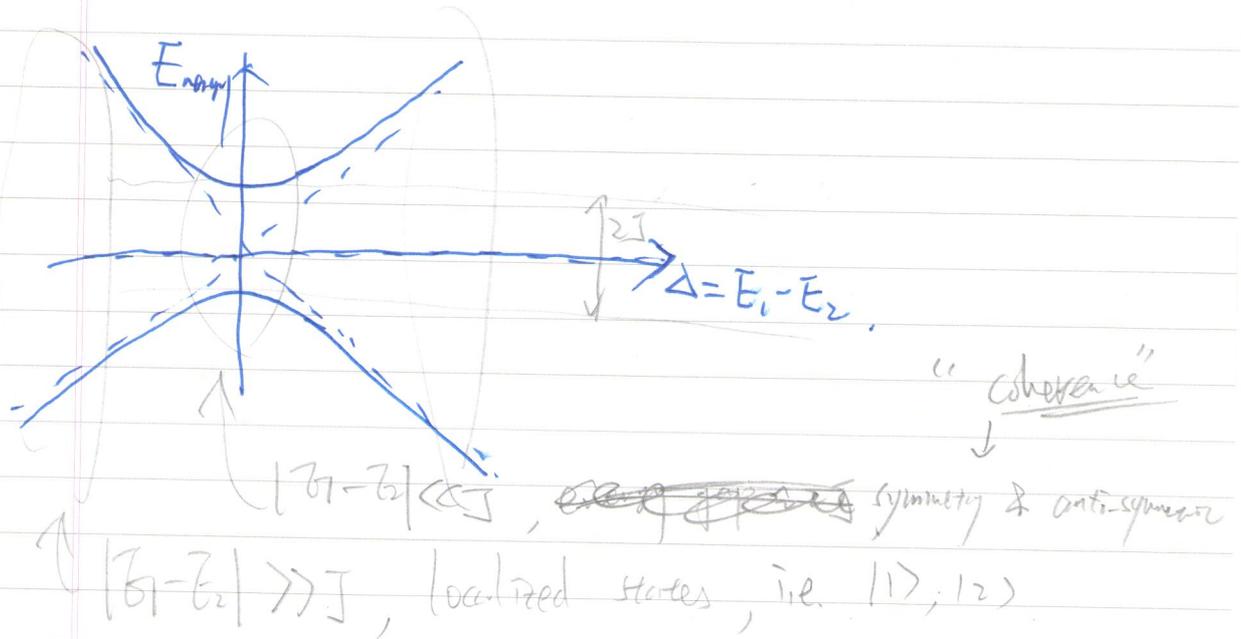
We can find

$$E_{\pm} = \frac{E_1 + E_2}{2} \pm \frac{1}{2} \sqrt{(E_1 - E_2)^2 + 4|J|^2}$$

and corresponding eigen functions:

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

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



(10) (14)

How about thermal equilibrium & time-evolution??

\* thermal equilibrium:

$$\rho_{\text{eq}} = \sum_{\alpha} \frac{e^{-\beta E_{\alpha}}}{Z} |\phi_{\alpha}\rangle \langle \phi_{\alpha}| \equiv \sum_{\alpha} \frac{e^{-\beta H}}{Z} \cdot |\phi_{\alpha}\rangle \langle \phi_{\alpha}|$$

↑ subover eigen states      eigen states

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

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

\* time-evolution.

$$U(t) = e^{-\frac{i}{\hbar} H \cdot t} = \begin{bmatrix} e^{-\frac{i}{\hbar} E_1 t} & 0 \\ 0 & e^{-\frac{i}{\hbar} E_2 t} \end{bmatrix}$$

In the eigenstate basis.

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

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

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

timeless

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

↑ diagonalization, transform basis to  $|H_\pm\rangle$ .

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

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

In the original basis  $\neq$