

CHAPTER 7: APPROXIMATION METHODS FOR TIME-DEPENDENT PROBLEMS

(From Cohen-Tannoudji, Chapter XIII)

A. STATEMENT OF THE PROBLEM

Consider a system with Hamiltonian \hat{H}_0 ; its eigenvalues and eigenvectors are

$$\hat{H}_0|\varphi_n\rangle = E_n|\varphi_n\rangle \quad (7.1)$$

(\hat{H}_0 is discrete and non-degenerate for simplicity.)

At $t = 0$, a perturbation is applied

$$\hat{H}(t) = \hat{H}_0 + W(t) = \hat{H}_0 + \lambda\hat{W}(t) \quad (7.2)$$

where $\lambda \ll 1$, and $\hat{W}(t) = 0$ for $t < 0$:

| | | |
|---------------------------|--|-------------------|
| $t < 0$ | $t = 0$ | $t > 0$ |
| stationary state | $W(t)$ | final state |
| $ \varphi_i\rangle$ | evolution starts | $ \psi(t)\rangle$ |
| eigenstate of \hat{H}_0 | ($ \varphi_i\rangle$ is not eigenstate of \hat{H}) | |

What is the probability $\mathcal{P}_{fi}(t)$ of finding the system in another eigenstate $|\varphi_f\rangle$ of \hat{H}_0 at time t ?

Treatment: solve the Schrödinger equation (S. E.)

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = [\hat{H}_0 + \lambda \hat{W}(t)] |\psi(t)\rangle \quad (7.3)$$

with the initial condition $|\psi(0)\rangle = |\varphi_i\rangle$

$$\Rightarrow \mathcal{P}_{fi}(t) = |\langle \varphi_f | \psi(t) \rangle|^2 \quad (7.4)$$

In generally this problem is not rigorously soluble!

\Rightarrow we need APPROXIMATION METHODS

B. APPROXIMATE SOLUTION OF THE SCHRÖDINGER EQUATION

1. The Schrödinger equation in the $\{|\varphi_n\rangle\}$ representation

We will use the $\{|\varphi_n\rangle\}$ representation which is convenient as $|\varphi_i\rangle$ and $|\varphi_f\rangle$ are eigenstates of \hat{H}_0 , and obtain the differential equations for the components of the state vector

$$|\psi(t)\rangle = \sum_n c_n(t) |\varphi_n\rangle \quad (7.5)$$

$$c_n(t) = \langle \varphi_n | \psi(t) \rangle \quad (7.6)$$

$$\hat{W}_{nk}(t) = \langle \varphi_n | \hat{W}(t) | \varphi_k \rangle \quad (7.7)$$

$$\text{and} \quad \langle \varphi_n | \hat{H}_0 | \varphi_k \rangle = E_n \delta_{nk} \quad (7.8)$$

We will project both sides of S.E. onto $|\varphi_n\rangle$ (and use $\sum_k |\varphi_k\rangle \langle \varphi_k| = \hat{1}$):

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = [\hat{H}_0 + \lambda \hat{W}(t)] |\psi(t)\rangle \quad (7.9)$$

$$\Rightarrow i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t) + \sum_k \lambda \hat{W}_{nk}(t) c_k(t) \quad (7.10)$$

Changing functions

If $\lambda \hat{W}(t) = 0$ then the equations decouple

$$i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t) \quad (7.11)$$

and yield simple solution

$$c_n(t) = b_n e^{-iE_n t/\hbar} \quad (7.12)$$

where b_n is a constant depending on the initial conditions.

If $\lambda \hat{W}(t) \neq 0$ and $\lambda \ll 1$, we expect the solutions $c_n(t)$ of the full equations to be very close to the solution above (for $\lambda \hat{W}(t) = 0$), and thus if we perform the change of function

$$c_n(t) = b_n(t) e^{-iE_n t/\hbar} \quad (7.13)$$

we can predict that $b_n(t)$ will be slowly varying functions of time.

Substituted into the equation gives

$$\begin{aligned} & i\hbar e^{-iE_n t/\hbar} \frac{d}{dt} b_n(t) + E_n b_n(t) e^{-iE_n t/\hbar} \\ = & E_n b_n(t) e^{-iE_n t/\hbar} + \sum_k \lambda \hat{W}_{nk}(t) b_k(t) e^{-iE_k t/\hbar} \end{aligned} \quad (7.14)$$

Multiplying both sides by $e^{iE_n t/\hbar}$ and introducing the Bohr frequency $\omega_{nk} = \frac{E_n - E_k}{\hbar}$ gives

$$i\hbar \frac{d}{dt} b_n(t) = \lambda \sum_k e^{i\omega_{nk} t} \hat{W}_{nk}(t) b_k(t) \quad (7.15)$$

2. Perturbation equations

In general, the solution is not known exactly and, for $\lambda \ll 1$, we try to determine this solution in the form of a power series in λ

$$b_n(t) = b_n^{(0)}(t) + \lambda b_n^{(1)}(t) + \lambda^2 b_n^{(2)}(t) + \dots \quad (7.16)$$

and substitute it into the equation, and set equal the coefficients of λ^r on both sides of the equation

$$\text{i) } r = 0 : \quad i\hbar \frac{d}{dt} b_n^{(0)}(t) = 0 \quad (7.17)$$

$$\text{ii) } r \neq 0 : \quad i\hbar \frac{d}{dt} b_n^{(r)}(t) = \sum_k e^{i\omega_{nk}t/\hbar} \hat{W}_{nk}(t) b_k^{(r-1)}(t) \quad (7.18)$$

RECURRENCE!

3. Solution to the first order in λ

a. The state of the system at time t

$$t < 0 : \quad |\varphi_i\rangle \text{ i.e. } b_i(t) \neq 0, b_k(t) = 0 \forall k \neq i \quad (7.19)$$

$$t = 0 : \quad \hat{H}_0 \rightarrow \hat{H}_0 + \lambda \hat{W} \text{ and solution of S.E. is continuous at } t = 0 \quad (7.20)$$

$$\Rightarrow b_n(t = 0) = \delta_{ni} \forall \lambda \quad (7.21)$$

$$\Rightarrow b_n^{(0)}(t = 0) = \delta_{ni} \quad (7.22)$$

$$\Rightarrow b_n^{(r)}(t = 0) = 0 \text{ if } r \geq 1 \quad (7.23)$$

and with $i\hbar \frac{d}{dt} b_n^{(0)}(t) = 0$ we get

$$0^{\text{th}}\text{-order solution: } b_n^{(0)}(t) = \delta_{ni} \text{ for all } t > 0$$

$$1^{\text{st}} \text{ - order: } i\hbar \frac{d}{dt} b_n^{(1)}(t) = \sum_k e^{i\omega_{nk}t} \hat{W}_{nk}(t) \delta_{ki} \quad (7.24)$$

$$= e^{i\omega_{ni}t} \hat{W}_{ni}(t) \quad (7.25)$$

$$\text{By integration } b_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{ni}t'} \hat{W}_{ni}(t') dt' \quad (7.26)$$

$$c_n(t) = b_n(t) e^{-iE_n t/\hbar} \approx \left(b_n^{(0)}(t) + \lambda b_n^{(1)}(t) \right) e^{-iE_n t/\hbar} \quad (7.27)$$

to the first order time-dependent perturbation theory we get the state of the system at time t calculated to the first order:

$$|\psi(t)\rangle \approx \sum_n c_n(t) |\varphi_n\rangle \quad (7.28)$$

b. The transition probability $\mathcal{P}_{if}(t)$

$$|c_f(t)|^2 = |\langle \varphi_f | \psi(t) \rangle|^2 = \mathcal{P}_{if}(t) \quad (7.29)$$

$$c_f(t) = b_f(t) e^{-iE_f t / \hbar} \quad (7.30)$$

$$\Rightarrow \mathcal{P}_{if}(t) = |b_f(t)|^2 \quad (7.31)$$

where $b_f(t) = b_f^{(0)}(t) + \lambda b_f^{(1)}(t) + \dots$

Let us assume $|\varphi_i\rangle$ and $|\varphi_f\rangle$ are different (i.e. we are concerned only with transition induced by $\lambda \hat{W}$ between two distinct stationary states of \hat{H}_0):

$b_f^{(0)}(t) = 0$ and consequently

$$\mathcal{P}_{if}(t) = \lambda^2 |b_f^{(1)}(t)|^2 \quad (7.32)$$

and using the formula for $b_n^{(1)}(t)$ we get

$$\mathcal{P}_{if}(t) = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{fi}t'} \underbrace{W_{fi}(t')}_{W(t)=\lambda\hat{W}} dt' \right|^2 \quad (7.33)$$

Consider the function $\tilde{W}_{fi}(t')$ which is zero for $t' < 0$ and $T' > t$ and is equal to $W_{fi}(t')$ for $0 \leq t' \leq t$.

$\tilde{W}_{fi}(t')$ is the matrix element of the perturbation “seen” by the system between the time $t = 0$ and the measurement time t , when we try to determine if the system is in the state $|\varphi_f\rangle$.

$\mathcal{P}_{if}(t)$ is proportional to the square of the modulus of the Fourier transform of the perturbation actually “seen” by the system, $\tilde{W}_{fi}(t)$.

C. SPECIAL CASE: A SINUSOIDAL OR CONSTANT PERTURBATION

$$\hat{W}(t) = \hat{W} \sin \omega t \text{ or}$$

$$\hat{W}(t) = \hat{W} \cos \omega t$$

\hat{W} is a time independent observable and ω a constant angular frequency.

(Example: electromagnetic wave of angular frequency ω .)

$\mathcal{P}_{if}(t)$ is the probability, induced by monochromatic radiation, of a transition between the initial state $|\varphi_i\rangle$ and the final state $|\varphi_f\rangle$.)

$$\hat{W}_{fi}(t) = \hat{W}_{fi} \sin \omega t = \frac{\hat{W}_{fi}}{2i} (e^{i\omega t} - e^{-i\omega t}) \quad (7.34)$$

\hat{W}_{fi} is a time independent complex number and

$$b_n^{(1)}(t) = -\frac{\hat{W}_{ni}}{2\hbar} \int_0^t [e^{i(\omega_{ni}+\omega)t'} - e^{i(\omega_{ni}-\omega)t'}] dt' \quad (7.35)$$

$$= \frac{\hat{W}_{ni}}{2i\hbar} \left[\frac{1 - e^{i(\omega_{ni}+\omega)t}}{\omega_{ni} + \omega} - \frac{1 - e^{i(\omega_{ni}-\omega)t}}{\omega_{ni} - \omega} \right] \quad (7.36)$$

The transition probability becomes

$$\mathcal{P}_{if}(t; \omega) = \lambda^2 \left| b_f^{(1)}(t) \right|^2 = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi}+\omega)t}}{\omega_{fi} + \omega} - \frac{1 - e^{i(\omega_{fi}-\omega)t}}{\omega_{fi} - \omega} \right|^2 \quad (7.37)$$

(\mathcal{P}_{if} depends on the frequency of the perturbation)

If $\hat{W}_{fi}(t) = \hat{W}_{fi} \cos \omega t$,

$$\mathcal{P}_{if}(t; \omega) = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi}+\omega)t}}{\omega_{fi} + \omega} + \frac{1 - e^{i(\omega_{fi}-\omega)t}}{\omega_{fi} - \omega} \right|^2 \quad (7.38)$$

Constant perturbation $\omega = 0$

$$\mathcal{P}_{if}(t; \omega) = \frac{|W_{fi}|^2}{\hbar^2 \omega_{fi}^2} \left| 1 - e^{i\omega_{fi}t} \right|^2 = \frac{|W_{fi}|^2}{\hbar^2} F(t; \omega_{fi}) \quad (7.39)$$

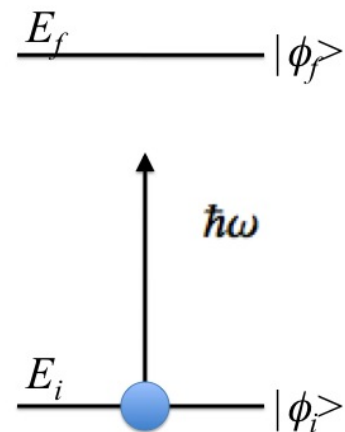
$$F(t; \omega_{fi}) = \left[\frac{\sin(\omega_{fi}t/2)}{\omega_{fi}/2} \right]^2 \quad (7.40)$$

2. Sinusoidal perturbation which couples discrete states: resonance

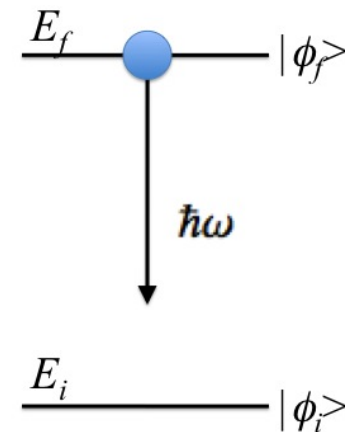
a. Resonant nature of the transition probability

When t is fixed, $\mathcal{P}_{if}(t; \omega)$ is a function of one variable ω . This function has a maximum for $\omega \simeq \omega_{fi}$ or $\omega \simeq -\omega_{fi}$; this is a resonance phenomenon (choose $\omega \geq 0$)

Resonant absorption



Stimulated emission



$$\mathcal{P}_{if}(t; \omega) = \frac{|\hat{W}_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\underbrace{\omega_{fi} + \omega}_{A_+}} - \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\underbrace{\omega_{fi} - \omega}_{A_-}} \right|^2 \quad (7.41)$$

$$A_+ = -ie^{i(\omega_{fi} + \omega)t/2} \frac{\sin [(\omega_{fi} + \omega)t/2]}{\underbrace{(\omega_{fi} + \omega)/2}} \quad (7.42)$$

goes to zero for $\omega = -\omega_{fi}$

This term is anti-resonant for $\omega = \omega_{fi}$ (and resonant for $\omega = -\omega_{fi}$)

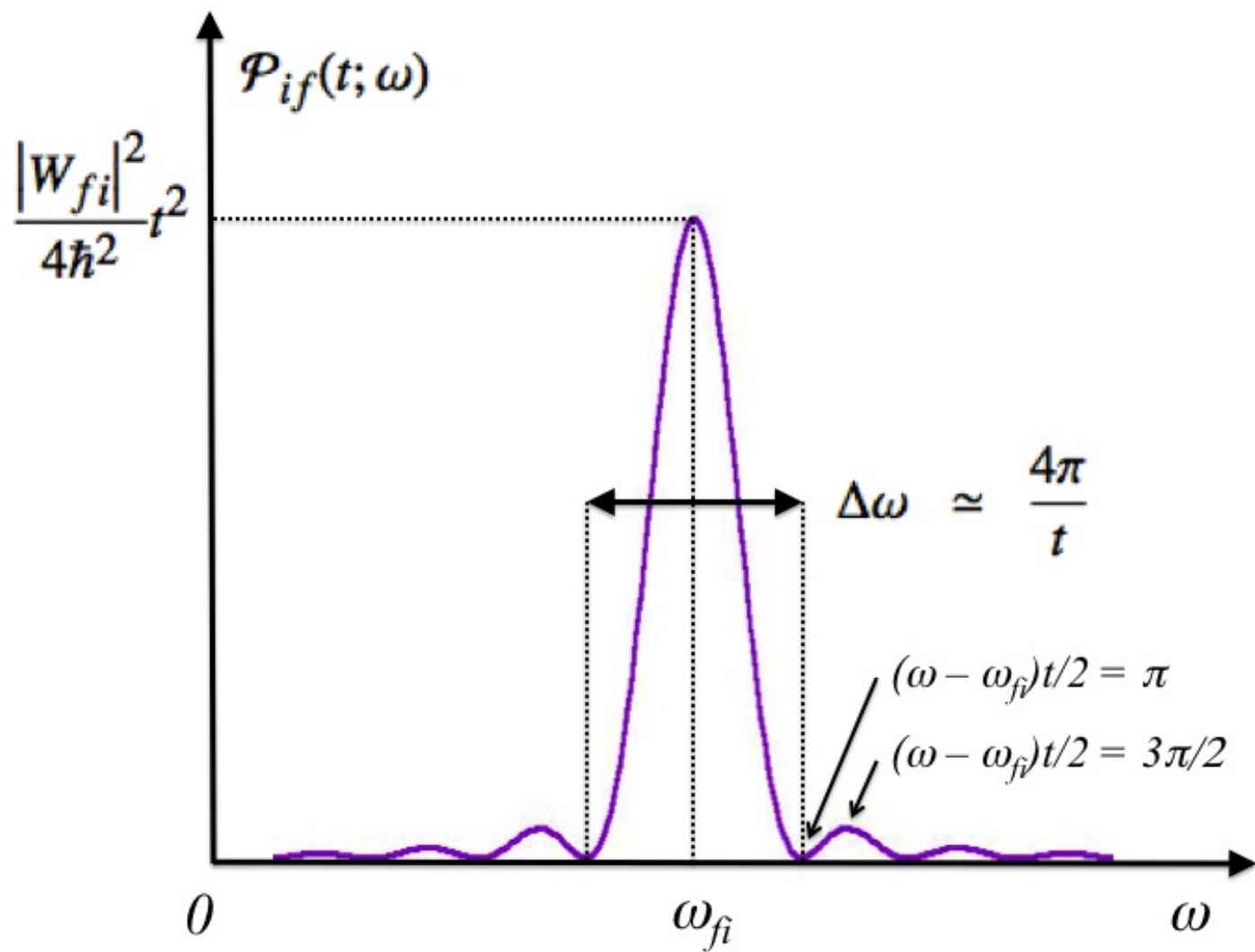
Resonant term

$$A_- = -ie^{i(\omega_{fi}-\omega)t/2} \frac{\sin [(\omega_{fi} - \omega) t/2]}{(\omega_{fi} - \omega) / 2} \quad (7.43)$$

Consider the case $|\omega - \omega_{fi}| \ll \omega_{fi}$ (this is the resonant approximation):
1st order transition probability:

$$\mathcal{P}_{if}(t; \omega) = \frac{|W_{fi}|^2}{4\hbar^2} F(t; \omega - \omega_{fi}) \quad (7.44)$$

$$\underbrace{F(t; \omega - \omega_{fi})}_{\text{sinc function}} = \left\{ \frac{\sin [(\omega_{fi} - \omega) t/2]}{(\omega_{fi} - \omega) / 2} \right\}^2 \quad (7.45)$$



b. The resonance width and time-energy uncertainty relation

The most of the resonant peak is concentrated around the resonant frequency ω_{fi} , for example at $\frac{(\omega - \omega_{fi})t}{2} = \frac{3\pi}{2}$ we get the transition probability $\frac{|W_{fi}|^2 t^2}{9\pi^2 \hbar^2}$ which is approximately 5% of the transition probability at the resonance.

We can define the width of the resonant peak as the difference between the frequencies of the minima of \mathcal{P}_{if} around the resonant frequency, see the figure, then

$$\Delta\omega \simeq \frac{4\pi}{t} \tag{7.46}$$

which is analogous to the time-energy uncertainty relation $\Delta E = \hbar\Delta\omega \simeq \frac{\hbar}{t}$

c. Validity of the perturbation treatment

a) Discussion of the resonant approximation

A_+ has been neglected relative to A_- :

$|A_-(\omega)|^2$ sinc function

$$|A_+(\omega)|^2 = |A_-(-\omega)|^2 \ll |A_-(\omega_{fi})|^2 \quad (7.47)$$

The resonant approximation is justified on the condition

$$2|\omega_{fi}| \gg \Delta\omega \quad (7.48)$$

that is

$$\underbrace{\text{duration of the perturbation}}_t \gg \frac{1}{|\omega_{fi}|} \simeq \underbrace{\frac{1}{\omega}}_{\text{oscillation period}} \quad (7.49)$$

b) Limits of the first-order calculations

If t becomes too large, the first-order approximation can cease to be valid (i.e. giving infinite transition probability which is physically a nonsense):

$$\lim_{t \rightarrow \infty} \mathcal{P}_{if}(t; \omega = \omega_{fi}) = \lim_{t \rightarrow \infty} \frac{|W_{fi}|^2}{4\hbar^2} t^2 = \infty \quad (7.50)$$

For the first-order approximation to be valid at resonance, $\mathcal{P}_{if}(t; \omega = \omega_{fi}) \ll 1$:

$$t \ll \frac{\hbar}{|W_{fi}|} \quad (7.51)$$

3. Coupling with the states of the continuum

E_f belongs to a continuous part of the spectrum of \hat{H}_0

⇓

We cannot measure the probability of finding the system in a well-defined state $|\varphi_f\rangle$ at time t

⇓

We have to integrate over probability density $|\langle\varphi_f|\psi(t)\rangle|^2$ over a certain group of final states.

a. Integration over a continuum of final states; density of states

a) Example

- spinless particle of mass m
- scattering by a potential $W(\vec{r})$

$E = \vec{p}^2/2m$, $|\psi(t)\rangle$ can be expanded in terms of $|\vec{p}\rangle$
The corresponding wavefunctions are plane waves

$$\langle \vec{r} | \vec{p} \rangle = \left(\frac{1}{2\pi\hbar} \right)^{3/2} e^{i\vec{p}\cdot\vec{r}/\hbar} \quad (7.52)$$

The probability density

$$|\langle \vec{p} | \psi(t) \rangle|^2 \quad (7.53)$$

Detector gives a signal when the particle is scattered with the momentum \vec{p}_f but since it has a finite aperture it really gives the signal when the particle has momentum in a domain D_f of \vec{p} -space around \vec{p}_f ($\delta\Omega_f, \delta E_f$)

$$\delta\mathcal{P}(\vec{p}_f, t) = \int_{\vec{p}_f \in D_f} d^3\vec{p} |\langle \vec{p} | \psi(t) \rangle|^2 \quad (7.54)$$

$$d^3\vec{p} = p^2 dp \underbrace{d\Omega}_{\text{solid angle around } \vec{p}_f} = \underbrace{\rho(E)}_{\text{density of final states}} dE d\Omega$$

$$\rho(E) = p^2 \frac{dp}{dE} = p^2 \frac{m}{p} = m \sqrt{2mE} \quad (7.55)$$

$$\delta\mathcal{P}(\vec{p}_f, t) = \int_{\Omega \in \delta\Omega_f, E \in \delta E_f} d\Omega dE \rho(E) |\langle \vec{p} | \psi(t) \rangle|^2 \quad (7.56)$$

b) The general case

Eigenstates of \hat{H}_0 , labeled by a continuous set of indices

$$\langle \alpha | \alpha' \rangle = \delta(\alpha - \alpha') \quad (7.57)$$

at time t : $|\psi(t)\rangle$

$$\delta\mathcal{P}(\alpha_f, t) = \int_{\alpha \in D_f} d\alpha |\langle \alpha | \psi(t) \rangle|^2 \quad (7.58)$$

Change variables and introduce density of final states

$$d\alpha = \rho(\beta, E) d\beta dE \quad (7.59)$$

$$\delta\mathcal{P}(\alpha_f, t) = \int_{\beta \in \delta\beta_f, E \in \delta E_f} d\beta dE \rho(\beta, E) |\langle \beta, E | \psi(t) \rangle|^2 \quad (7.60)$$

Fermi's Golden Rule

Let $|\psi(t)\rangle$ be the normalized state vector of the system at time t .

Consider a system which is initially in an eigenstate $|\varphi_i\rangle$ of \hat{H}_0 (in discrete part of spectrum)

$$\delta\mathcal{P}(\varphi_i, \alpha_f, t) = ? \quad (7.61)$$

The calculations for the case of a sinusoidal or constant perturbation remain valid when the final state of the system belongs to the continuous spectrum of \hat{H}_0

For W constant

$$|\langle \beta, E | \psi(t) \rangle|^2 = \frac{1}{\hbar^2} |\langle \beta, E | W | \psi(t) \rangle|^2 F\left(t; \frac{E - E_i}{\hbar}\right) \quad (7.62)$$

E – energy of the state $|\beta, E\rangle$

E_i – energy of the state $|\varphi_i\rangle$

$$\delta\mathcal{P}(\varphi_i, \alpha_f, t) = \frac{1}{\hbar^2} \int_{\beta \in \delta\beta_f, E \in \delta E_f} d\beta dE \rho(\beta, E) |\langle \beta, E | W | \psi(t) \rangle|^2 F\left(t; \frac{E - E_i}{\hbar}\right) \quad (7.63)$$

$F\left(t; \frac{E - E_i}{\hbar}\right)$ varies rapidly about $E = E_i$; for sufficiently large t , this function can be approximated, to within a constant factor, by the δ -function $\delta(E - E_i)$:

$$\lim_{t \rightarrow \infty} F\left(t; \frac{E - E_i}{\hbar}\right) = \pi t \delta\left(\frac{E - E_i}{2\hbar}\right) = 2\pi\hbar t \delta(E - E_i) \quad (7.64)$$

The function $\rho(\beta, E) |\langle \beta, E | W | \psi(t) \rangle|^2$ varies much more slowly with E . We will assume that t is sufficiently large for the variation of this function over an energy interval of width $4\pi\hbar/t$ centered at $E = E_i$ to be negligible.

⇒ We can replace $F\left(t; \frac{E-E_i}{\hbar}\right)$ by $2\pi\hbar t \delta(E - E_i)$ which allows us to integrate over E immediately.

If, in addition, $\delta\beta_f$ is very small, integration over β is unnecessary and we get

(a) $E_i \in \delta E_f$

$$\delta\mathcal{P}(\varphi_i, \alpha_f, t) = \delta\beta_f \frac{2\pi}{\hbar} t |\langle \beta_f, E_f = E_i | W | \varphi_i \rangle|^2 \rho(\beta_f, E_f = E_i) \quad (7.65)$$

(b) $E_i \notin \delta E_f$

$$\delta\mathcal{P}(\varphi_i, \alpha_f, t) = 0 \quad (7.66)$$

\Rightarrow A constant perturbation can induce transitions only between states of equal energies, and thus (b) holds.

The probability (a) increases linearly with t .

⇒ We can define

- transition probability per unit time $\delta\mathcal{W}(\varphi_i, \alpha_f)$

$$\delta\mathcal{W}(\varphi_i, \alpha_f) = \frac{d}{dt}\delta\mathcal{P}(\varphi_i, \alpha_f, t) \quad (7.67)$$

which is time independent

- transition probability density per unit time and per unit interval of the variable β_f

$$w(\varphi_i, \alpha_f) = \frac{\delta\mathcal{W}(\varphi_i, \alpha_f)}{\delta\beta_f} \quad (7.68)$$

Fermi's Golden Rule

$$w(\varphi_i, \alpha_f) = \frac{2\pi}{\hbar} |\langle \beta_f, E_f = E_i | W | \varphi_i \rangle|^2 \rho(\beta_f, E_f = E_i) \quad (7.69)$$

Assume that W is a sinusoidal perturbation which couples a state $|\varphi_i\rangle$ to the continuum of states $|\beta_f, E_f\rangle$ with energies E_f close to $E_i + \hbar\omega$. We can carry out the same procedure as above:

$$w(\varphi_i, \alpha_f) = \frac{\pi}{2\hbar} |\langle \beta_f, E_f = E_i + \hbar\omega | W | \varphi_i \rangle|^2 \rho(\beta_f, E_f = E_i + \hbar\omega) \quad (7.70)$$