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

$$\hat{H}_0|\varphi_n\rangle = E_n|\varphi_n\rangle \tag{7.1}$$

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

At $t = 0$, a perturbation is applied

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

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.)

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\varphi(t)\rangle = \left[\hat{H}_0 + \lambda\hat{W}(t)\right]|\psi(t)\rangle \tag{7.3}$$

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

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

In generally this problem is not rigorously soluble!

⇒ we need APPROXIMATION METHODS

B. APPROXIMATE SOLUTION OF THE SCHRÖDINGER EQUATION

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

$$
\begin{aligned}
|\psi(t)\rangle &= \sum_n c(t)|\varphi_n\rangle && (7.5)\\
c_n(t) &= \langle\varphi_n|\psi(t)\rangle && (7.6)\\
\hat{W}_{nk}(t) &= \langle\varphi_n|\hat{W}(t)|\varphi_k\rangle && (7.7)\\
\text{and} \quad & \langle\varphi_n|\hat{H}_0|\varphi_k\rangle = E_n\delta_{nk} && (7.8)
\end{aligned}
$$

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

$$
\begin{aligned}
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle &= \left[\hat{H}_0 + \lambda\hat{W}(t)\right]|\psi(t)\rangle && (7.9)\\
\Rightarrow i\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_n(t) &= E_n c_n(t) + \sum_k \lambda\hat{W}_{nk}(t)c_k(t) && (7.10)
\end{aligned}
$$

Changing functions

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

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

and yield simple solution

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

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

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

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

Substituted into the equation gives

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

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

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

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

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

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

$$\text{i) } r = 0 : \qquad i\hbar \frac{\mathrm{d}}{\mathrm{d}t} b_n^{(0)}(t) = 0 \tag{7.17}$$

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

RECURRENCE!

3. Solution to the first order in λ

a. The state of the system at time t

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

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

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

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

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

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

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

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

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

$$\text{By integration } b_n^{(1)}(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{ni}t'}\hat{W}_{ni}\left(t'\right)\mathrm{d}t' \tag{7.26}$$

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

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

$$|\psi(t)\rangle \approx \sum_n c_n(t)|\varphi_n\rangle \tag{7.28}$$

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

$$\begin{aligned} \left|c_f(t)\right|^2 &= \left|\langle\varphi_f|\psi(t)\rangle\right|^2 = \mathcal{P}_{if}(t) && (7.29) \\ c_f(t) &= b_f(t)e^{-iE_f t/\hbar} && (7.30) \\ \Rightarrow \mathcal{P}_{if}(t) &= \left|b_f(t)\right|^2 && (7.31) \end{aligned}$$

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

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

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

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

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

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

$\hat{W}(t) = \hat{W} \sin \omega t$ 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 $|\varphi_f\rangle$.)

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

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

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

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

The transition probability becomes

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

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

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

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

Constant perturbation $\omega = 0$

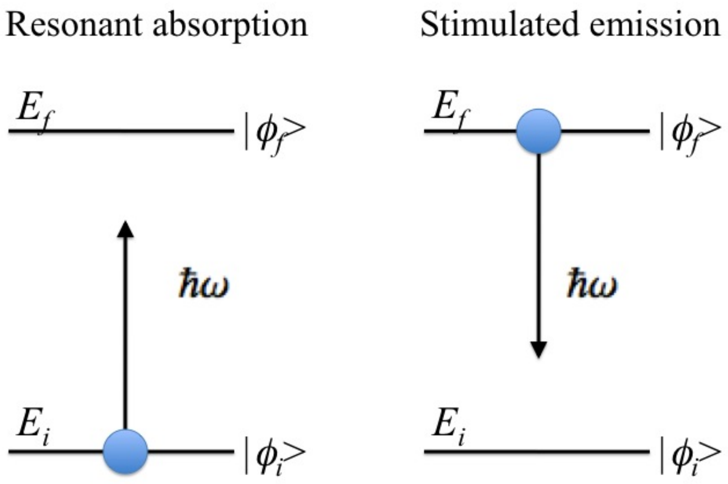
$$\mathcal{P}_{if}(t;\omega) = \frac{\left|W_{fi}\right|^2}{\hbar^2\omega_{fi}^2}\left|1 - e^{i\omega_{fi}t}\right|^2 = \frac{\left|W_{fi}\right|^2}{\hbar^2}F\left(t;\omega_{fi}\right) \tag{7.39}$$

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

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 $\omega \geq 0$)



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

$$A_+ = -ie^{i\left(\omega_{fi}+\omega\right)t/2}\frac{\sin\left[\left(\omega_{fi}+\omega\right)t/2\right]}{\underbrace{\left(\omega_{fi}+\omega\right)/2}_{\text{goes to zero for } \omega=-\omega_{fi}}} \tag{7.42}$$

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

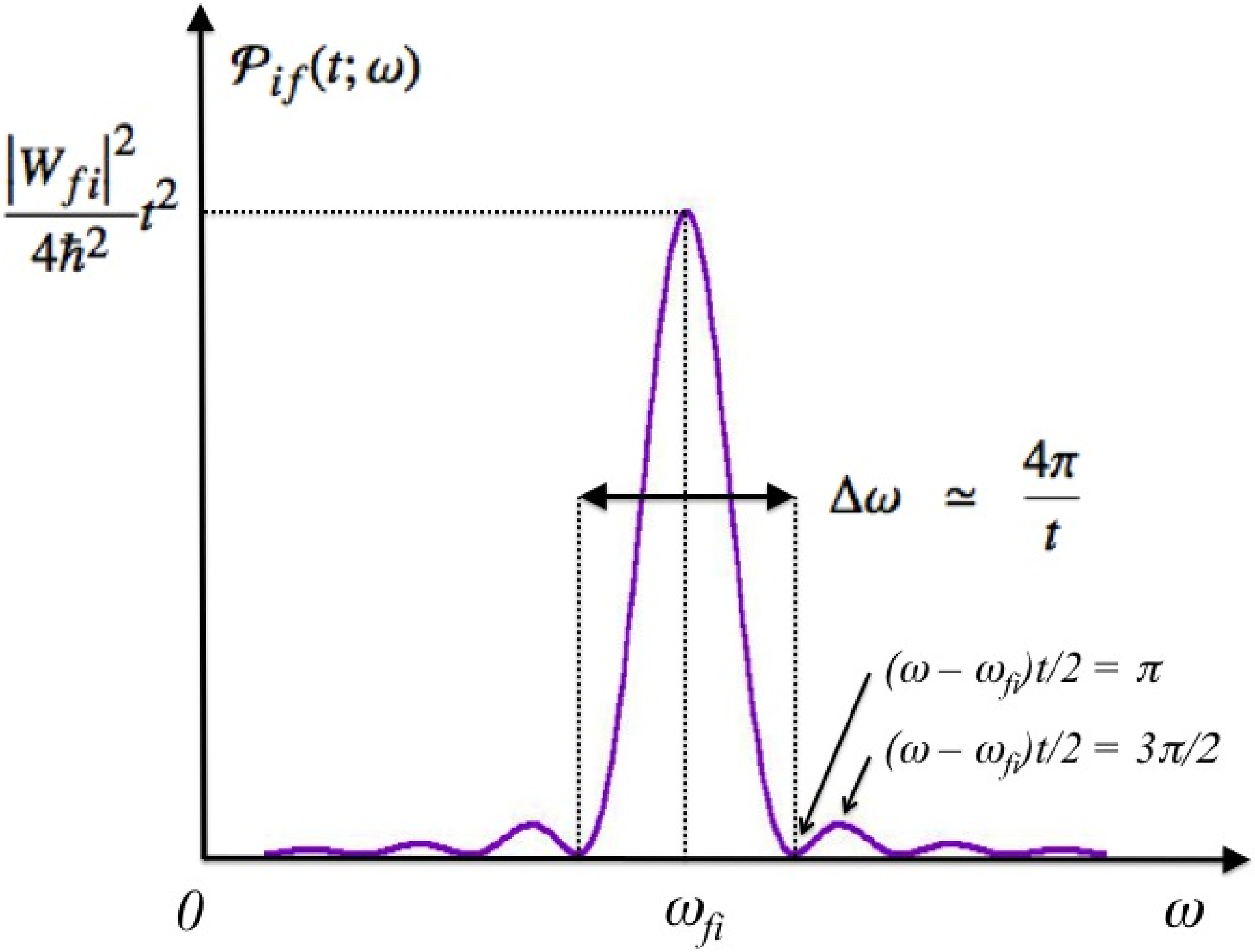
Resonant term

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

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

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

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


$\mathcal{P}_{if}(t;\omega)$
$\frac{|W_{fi}|^2}{4\hbar^2}t^2$
$\Delta\omega \simeq \frac{4\pi}{t}$
$(\omega - \omega_{fi})t/2 = \pi$
$(\omega - \omega_{fi})t/2 = 3\pi/2$
0
ω_{fi}
ω

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 $\frac{\left(\omega-\omega_{fi}\right)t}{2} = \frac{3\pi}{2}$ we get the transition probability $\frac{\left|W_{fi}\right|^2 t^2}{9\pi^2\hbar^2}$ 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

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

The resonant approximation is justified on the condition

$$2\left|\omega_{fi}\right| >> \Delta\omega \tag{7.48}$$

that is

$$\underbrace{t}_{\text{duration of the perturbation}} >> \frac{1}{\left|\omega_{fi}\right|} \simeq \underbrace{\frac{1}{\omega}}_{\text{oscillation period}} \tag{7.49}$$

b) Limits of the first-order calculations

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

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

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

$$t \quad \ll \quad \frac{\hbar}{\left|W_{fi}\right|} \tag{7.51}$$

3. Coupling with the states of the continuum

E_f belongs to a continuous part of the spectrum of $\hat{H}_0$
$\Downarrow$
We cannot measure the probability of finding the system in a well-defined state $|\varphi_f\rangle$ at time t
$\Downarrow$
We have to integrate over probability density $\left|\langle\varphi_f|\psi(t)\rangle\right|^2$ 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

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

The probability density

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

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 $\vec{p}_f$ $(\delta\Omega_f, \delta E_f)$

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

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

$$\rho(E) = p^2\frac{\mathrm{d}p}{\mathrm{d}E} = p^2\frac{m}{p} = m\sqrt{2mE} \qquad (7.55)$$

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

b) The general case

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

$$\langle \alpha | \alpha' \rangle = \delta(\alpha - \alpha') \tag{7.57}$$

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

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

Change variables and introduce density of final states

$$\mathrm{d}\alpha = \rho(\beta, E)\mathrm{d}\beta\mathrm{d}E \tag{7.59}$$

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

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)

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

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

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

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

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

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

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

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

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.

$\Rightarrow$ 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) $E_i \in \delta E_f$

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

(b) $E_i \notin \delta E_f$

$$\delta\mathcal{P}\left(\varphi_i, \alpha_f, t\right) \;=\; 0 \tag{7.66}$$

⇒ 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 $\delta\mathcal{W}\left(\varphi_i, \alpha_f\right)$

$$\delta\mathcal{W}\left(\varphi_i, \alpha_f\right) = \frac{\mathrm{d}}{\mathrm{d}t}\delta\mathcal{P}\left(\varphi_i, \alpha_f, t\right) \tag{7.67}$$

  which is time independent

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

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

Fermi's Golden Rule

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

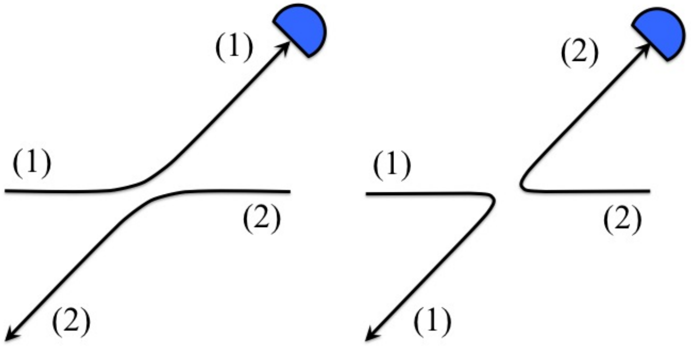
Assume that W is a sinusoidal perturbation which couples a state $|\varphi_i\rangle$ to the continuum of states $|\beta_f, E_f\rangle$ with energies E_f close to $E_i + \hbar\omega$. We can carry out the same procedure as above:

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

CHAPTER 8: SYSTEMS OF IDENTICAL PARTICLES

(From Cohen-Tannoudji, Chapter XIV)

Consier scattering of two quantum particles



as the particles are indistinguishable, we cannot determine the path they followed.
→ Problems: exchange degeneracy (removed by the symmetrization postulate)

Permutation operators

a) Two particle systems

$$\mathcal{E}(1) \otimes \mathcal{E}(2) \tag{8.1}$$

$$\left\{|1 : u_i; 2 : u_j\rangle\right\} \tag{8.2}$$

Note

$$|1 : u_j; 2 : u_i\rangle \neq |1 : u_i; 2 : u_j\rangle \qquad \text{if } i \neq j \tag{8.3}$$

The permutation operator

$$\begin{aligned} \hat{P}_{21}|1 : u_i; 2 : u_j\rangle &= |2 : u_i; 1 : u_j\rangle && (8.4) \\ &= |1 : u_j; 2 : u_i\rangle && (8.5) \end{aligned}$$

The order of the vectors in a tensor product is of no importance.

b)The permutation operator P_{21}

$$\begin{aligned} \left(\hat{P}_{21}\right)^2 &= \hat{1} && (8.6) \\ \hat{P}^{\dagger}_{21} &= \hat{P}_{21} \text{ (self adjoint)} && (8.7) \\ \hat{P}^{\dagger}_{21}\hat{P}_{21} &= \hat{P}_{21}\hat{P}^{\dagger}_{21} = \hat{1} \text{ (unitary)} && (8.8) \end{aligned}$$

c) Symmetric and antisymmetric kets

Symmetrizer and antisymmetrizer
$\hat{P}^{\dagger}_{21} = \hat{P}_{21} \Rightarrow$ the eigenvalues of $\hat{P}_{21}$ must be real
$(\hat{P}_{21})^2 = \hat{1} \Rightarrow$ the eigenvalues are

$$+1 \text{ (symmetric)} \qquad -1 \text{ (antisymmetric)} \tag{8.9}$$

$$\hat{P}_{21}|\psi_S\rangle = |\psi_S\rangle \qquad \hat{P}_{21}|\psi_A\rangle = -|\psi_A\rangle \tag{8.10}$$

Consider the operators

$$\text{symmetrizer: } \hat{S} = \frac{1}{2}\left(\hat{1} + \hat{P}_{21}\right) \qquad \hat{S}^2 = \hat{S},\ \hat{S}^\dagger = \hat{S} \tag{8.11}$$

$$\text{antisymmetrizer: } \hat{A} = \frac{1}{2}\left(\hat{1} - \hat{P}_{21}\right) \qquad \hat{A}^2 = \hat{A},\ \hat{A}^\dagger = \hat{A} \tag{8.12}$$

which are projectors onto orthogonal subspaces

$$\hat{S}\hat{A} = \hat{A}\hat{S} = 0 \tag{8.13}$$

that are complementary

$$\hat{S} + \hat{A} = \hat{1} \tag{8.14}$$

If $|\psi\rangle$ is an arbitrary ket in $\mathcal{E}$,
$\hat{S}|\psi\rangle$ is a symmetric ket and
$\hat{A}|\psi\rangle$ is an antisymmetric ket

$$\hat{P}_{21}\hat{S}|\psi\rangle = \hat{S}|\psi\rangle \qquad \hat{P}_{21}\hat{A}|\psi\rangle = -\hat{A}|\psi\rangle \tag{8.15}$$

Transformation of observables by permutation

$\hat{B}(1)$ – defined in $\mathcal{E}(1)$, and extended to $\mathcal{E}$

$\{|u_i\rangle\}$ – the basis in $\mathcal{E}(1)$ from eigenvectors of $\hat{B}(1)$ (with eigenvalues b_i)

$$\begin{aligned}
\hat{P}_{21}\hat{B}(1)\hat{P}^{\dagger}_{21}|1:u_i;2:u_j\rangle &= \hat{P}_{21}\hat{B}(1)|1:u_j;2:u_i\rangle && (8.16)\\
&= b_j\hat{P}_{21}|1:u_j;2:u_i\rangle && (8.17)\\
&= b_j|1:u_i;2:u_j\rangle && (8.18)
\end{aligned}$$

$$\begin{aligned}
\hat{P}_{21}\hat{B}(1)\hat{P}^{\dagger}_{21} &= \hat{B}(2) && (8.19)\\
\hat{P}_{21}\hat{B}(2)\hat{P}^{\dagger}_{21} &= \hat{B}(1) && (8.20)\\
\hat{P}_{21}\left[\hat{B}(1)+\hat{C}(2)\right]\hat{P}^{\dagger}_{21} &= \hat{B}(2)+\hat{C}(1) && (8.21)\\
\hat{P}_{21}\hat{B}(1)\hat{C}(2)\hat{P}^{\dagger}_{21} &= \hat{B}(2)\hat{C}(1) && (8.22)
\end{aligned}$$

Generalization

$$\hat{P}_{21}\hat{O}(1,2)\hat{P}_{21}^{\dagger} = \hat{O}(2,1) \tag{8.23}$$

where $\hat{O}(1,2)$ is any observable in $\mathcal{E}$ which can be expressed in terms of observables of the type $\hat{B}(1)$ and $\hat{C}(2)$.

Symmetric observables commute with the permutation operators:

$$\hat{O}_S(1,2) = \hat{O}_S(2,1) \tag{8.24}$$

$$\hat{P}_{21}\hat{O}_S(1,2) = \hat{O}_S(1,2)\hat{P}_{21} \tag{8.25}$$

$$\Rightarrow \left[\hat{O}_S(1,2), \hat{P}_{21}\right] = 0 \tag{8.26}$$

An arbitrary number of particles

Example 3 particles

$$\left\{ |1 : u_i; 2 : u_j; 3 : u_k\rangle \right\} \tag{8.27}$$

Six permutations

$$\hat{P}_{123}, \hat{P}_{321}, \hat{P}_{231}, \hat{P}_{132}, \hat{P}_{213}, \hat{P}_{312} \tag{8.28}$$

$$\hat{P}_{npq}|1 : u_i; 2 : u_j; 3 : u_k\rangle = |n : u_i; p : u_j; q : u_k\rangle \tag{8.29}$$

(N! permutation operators in a system of N particles with the same spin.)

Any permutation operator can be broken down into a product of transposition (i.e. pairwise exchange) operators, for example

$$\hat{P}_{312} = \underbrace{\hat{P}_{132}\hat{P}_{213}}_{\text{even parity of } \hat{P}_{312}} = \hat{P}_{321}\hat{P}_{132} = \ldots \tag{8.30}$$

$$\text{even:} \quad \hat{P}_{123}, \hat{P}_{321}, \hat{P}_{231} \tag{8.31}$$

$$\text{odd:} \quad \hat{P}_{132}, \hat{P}_{213}, \hat{P}_{321} \tag{8.32}$$

For any N, there are always as many even permutations as there are odd.

Permutation operators are unitary and constitute a group.

Completely symmetric or antisymmetric kets. Symmetrizer and antisymmetrizer.

Completely symmetric

$$\hat{P}_\alpha |\psi_S\rangle = |\psi_S\rangle \qquad \text{for any } \hat{P}_\alpha \tag{8.33}$$

Completely antisymmetric

$$\hat{P}_\alpha |\psi_A\rangle = \underbrace{\varepsilon_\alpha}_{+1 \text{ for even, } -1 \text{ for odd}} |\psi_S\rangle \qquad \text{for any } \hat{P}_\alpha \tag{8.34}$$

$$\text{Symmetrizer} \qquad \hat{S} = \frac{1}{N!} \sum_\alpha \hat{P}_\alpha \text{ projects onto } \mathcal{E}_S \tag{8.35}$$

$$\text{Antisymmetrizer} \qquad \hat{A} = \frac{1}{N!} \sum_\alpha \varepsilon_\alpha \hat{P}_\alpha \text{ projects onto } \mathcal{E}_A \tag{8.36}$$

The symmetrization postulate

When a system includes several identical particles, only certain kets of its state space can describe its physical states. Physical kets, depending on the nature of the identical particles, are either

completely symmetric (bosons – integral spin)
or
completely antisymmetric (fermions – half-integral spin)

with respect to permutation of these particles.

Construction of physical kets

(i) number the particles arbitrarily, and construct the ket $|u\rangle$ corresponding to the physical state considered and to the numbers given to the particles

(ii) apply $\hat{S}$ or $\hat{A}$ to $|u\rangle$, depending on whether identical particles are bosons or fermions

(iii) normalize the ket so obtained.

Example: 2 particle system

(i) $|u\rangle = |1:\varphi; 2:\chi\rangle$

(ii) If particles are bosons, symmetrize $|u\rangle$

$$\hat{S}|u\rangle = \frac{1}{2}\left[|1:\varphi; 2:\chi\rangle + |1:\chi; 2:\varphi\rangle\right] \tag{8.37}$$

If they are fermions, antisymmetrize $|u\rangle$

$$\hat{A}|u\rangle = \frac{1}{2}\left[|1:\varphi; 2:\chi\rangle - |1:\chi; 2:\varphi\rangle\right] \tag{8.38}$$

(iii) normalize

$$|\varphi;\chi\rangle = \frac{1}{\sqrt{2}}\left[|1:\varphi; 2:\chi\rangle + \epsilon|1:\chi; 2:\varphi\rangle\right] \tag{8.39}$$

$\epsilon = +1$ for bosons, -1 for fermions

Assume that the individual states $|\varphi\rangle$, $|\chi\rangle$ are identical

$$|\varphi\rangle = |\chi\rangle \tag{8.40}$$

then

$$|u\rangle = |1:\varphi;2:\varphi\rangle \tag{8.41}$$

is already symmetric.

If the two particles are bosons, the ket $|u\rangle = |1:\varphi;2:\varphi\rangle$ is the physical ket associated with the states in which the two bosons are in the same individual state $|\varphi\rangle$.

If the two particles are fermions,

$$\hat{A}|u\rangle = \frac{1}{2}\left[|1:\varphi;2:\varphi\rangle - |1:\varphi;2:\varphi\rangle\right] \quad = \quad 0 \tag{8.42}$$

There is no ket of $\mathcal{E}_A$ able to describe the physical state in which two fermions are in the same individual state $|\varphi\rangle$.

Pauli's exclusion principle

Two fermions cannot be in the same individual state.

Generalization to an arbitrary $N > 2$

Example $N = 3$

$$|u\rangle = |1:\varphi; 2:\chi; 3:\omega\rangle \tag{8.43}$$

α) Bosons

$$\begin{aligned}
\hat{S}|u\rangle &= \frac{1}{3!}\sum_{\alpha}\hat{P}_{\alpha}|u\rangle && (8.44)\\
&= \frac{1}{6}\left[|1:\varphi; 2:\chi; 3:\omega\rangle + |1:\omega; 2:\varphi; 3:\chi\rangle\right. && (8.45)\\
&\quad +|1:\chi; 2:\omega; 3:\varphi\rangle + |1:\varphi; 2:\omega; 3:\chi\rangle && (8.46)\\
&\quad \left.+|1:\chi; 2:\varphi; 3:\omega\rangle + |1:\omega; 2:\chi; 3:\varphi\rangle\right] && (8.47)
\end{aligned}$$

Normalization

1) $|\varphi\rangle, |\chi\rangle, |\omega\rangle$ are orthogonal

replace $1/6$ by $1/\sqrt{6}$

2) If two states are the same and are orthogonal then

$$\begin{aligned} |\varphi;\varphi;\omega\rangle &= \frac{1}{\sqrt{3}}\left[|1:\varphi;2:\varphi;3:\omega\rangle + |1:\varphi;2:\omega;3:\varphi\rangle\right. && (8.48)\\ &\left.+|1:\omega;2:\varphi;3:\varphi\rangle\right] && (8.49)\end{aligned}$$

3) If three states are the same

$$|\varphi;\varphi;\varphi\rangle = |1:\varphi;2:\varphi;3:\varphi\rangle \tag{8.50}$$

β) Fermions

$$\hat{A}|u\rangle \quad = \quad \frac{1}{3!}\sum_{\alpha} \varepsilon_{\alpha}\hat{P}_{\alpha}|1:\varphi;2:\chi;3:\omega\rangle \tag{8.51}$$

The signs of the various terms are determined by the same rule as those of a 3×3 determinant

Slater determinant

$$\hat{A}|u\rangle \quad = \quad \frac{1}{3!}\begin{vmatrix} |1:\varphi\rangle & |1:\chi\rangle & |1:\omega\rangle \\ |2:\varphi\rangle & |2:\chi\rangle & |2:\omega\rangle \\ |3:\varphi\rangle & |3:\chi\rangle & |3:\omega\rangle \end{vmatrix} \tag{8.52}$$

Pauli exclusion principle:

$\hat{A}|u\rangle$ is zero if two of the individual states coincide since the determinant then has two identical columns.

Normalization:
If the three individual states are orthogonal replace $1/3!$ by $1/\sqrt{3!}$.