Time dependent Perturbation Theory (TDPT)

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- Introduction:

to illustrate the meaning of TDPT, let us consider as an example a hydrogen atom. if we neglect all interactions except Coulomb interaction $\Rightarrow$ $\hat{H}_0 = \frac{p^2}{2m} - \frac{e^2}{r}$ with well know eigenenergies and eigenstates (stationary states) corresponding to bound states $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$ and $\Psi^{(0)}_{nlm}(\vec{r},t) = \psi_{nlm}(\vec{r})\, e^{-\frac{iE_n t}{\hbar}}$.

now suppose the atom in influenced by an electromagnetic wave. the electron then experiences oscillatory electromagnetic forces corresponding to a time-dependent potential energy term $H'(t)$ where $H = H_0 + H'(t)$. for such hamiltonian (H), stationary states do not exist and no longer possible to find exact solutions of the schrodinger equation. However, approximate solutions can be found using TDPT. in this theory, the $H'(t)$ is considered as a perturbation and our aim is to find out how this term affects the behavior of the system.

- for the unperturbed system, we have

$$i\hbar \frac{\partial \Psi^{(0)}_k(\vec{r},t)}{\partial t} = \hat{H}_0 \Psi^{(0)}_k(\vec{r},t) \quad \text{with solution} \quad \Psi^{0}_k(\vec{r},t) = \psi_k(\vec{r})\, e^{-\frac{iE_k t}{\hbar}}$$

this solution does not satisfy the schrodinger equation for the perturbed system

$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = [H_0 + H'(t)]\, \Psi(\vec{r},t)$$

Now ~~ass~~ let us assume that the system is prepared in one of the unperturbed solutions at $t=0$

i.e $\Psi(\vec{r},0) = \Psi_i^{(0)}(\vec{r},0) = \psi_i(\vec{r})$; i stands for initial

furthermore, we assume that the unperturbed states form a complet set of states. this however is usefull to expand our a unknow solution in terms of the unperturbed stationary states.

$$\Psi(r,t) = \sum_k a_k(t)\,\Psi_k^{(0)}(\vec{r},t) = a_i(t)\,\Psi_i^{(0)}(\vec{r},t) + \sum_{k\neq i} a_k(t)\,\Psi_k^{(0)}(\vec{r},t)$$

if the system starts with the initial state $\Psi(\vec{r},0)$

$\Psi(\vec{r},0) = a_i(0)\,\Psi_i^{(0)}(\vec{r},0)$ which must be equal to $\psi_i(\vec{r})$

$= \psi_i(\vec{r}) \Rightarrow a_i(0) = 1$ and all other coefficients are equal to zero

where $a_i(0)$ is the probability amplitude of finding the system in the initial state $\psi_i^{(0)}(\vec{r},0)$.

Now because the unperturbed state $\psi_i^{(0)}(\vec{r},0)$ is not a solution of the perturbed system; of the schrodinger eq^n $i\hbar \dfrac{\partial \Psi(\vec{r},t)}{\partial t} = H\,\Psi(\vec{r},t)$; then the coefficient $a_i(0)$ will decrease from 1 as time goes, while some of the other coefficients (amplitudes) a_k will start to increase from zero, taking into account that

$\sum_k |a_k(t)|^2 = 1$; where $|a_k(t)|^2$ is transition probability

Thus, if the system was at $t=0$ in the unperturbed state $\psi_i^{(0)}(\vec{r})$, then there is a finite probability that the system will be found at later time t in excited state $\psi_k^{(0)}$ of the unperturbed system ~~so~~ to with probability of $|a_k(t)|^2$. notice that both initial and final states are eigen states of H_0, so the role of H' is to induce this transition.

- Formulation of TDPT:

Again for the unperturbed system $\hat{H}_0$, we have

$$i\hbar \frac{\partial}{\partial t} |\Psi_n^{(0)}(t)\rangle = \hat{H}_0 |\Psi_n^{(0)}(t)\rangle$$ with solution of

the form $|\Psi_n^{(0)}(t)\rangle = e^{-\frac{iE_n t}{\hbar}} \underline{|\Psi_n\rangle}$ stationary states solution of time independent schrodinger equation

now with perturbation H'

$\hat{H} = \hat{H}_0 + \hat{H}'$, we have

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = (H_0 + H'(t)) |\Psi(t)\rangle \quad \text{--- (1)}$$

now expand $|\Psi(t)\rangle$ in terms $|\Psi_n^{(0)}(t)\rangle$

$$|\Psi(t)\rangle = \sum_n a_n(t) |\Psi_n^{(0)}(t)\rangle = \sum_n a_n(t) e^{-\frac{iE_n t}{\hbar}} |\Psi_n\rangle \quad \text{--- (2)}$$

with $a_n(t) = \langle \Psi_n^{(0)}(t) | \Psi(t) \rangle$ amplitude of finding the system in the unperturbed state $|\Psi_n^{(0)}(t)\rangle$ at a time t.

$|a_n(t)|^2$ is the corresponding probability

- given that both H_0 and $H'(t)$ are Hermitian, then $|\Psi(t)\rangle$ stays normalized for all times

$$\sum_n |a_n(t)|^2 = 1$$

let us substitute the solution (2) into schrodinger eq^n (1)

$$i\hbar \frac{d}{dt}|\Psi(t)\rangle = (H_0 + H'(t))|\Psi(t)\rangle$$

$$\sum_n \left(i\hbar \frac{da_n}{dt}|\Psi_n^{0}(t)\rangle + a_n \underbrace{i\hbar \frac{d}{dt}|\Psi_n^{(0)}(t)\rangle}_{E_n |\Psi_n^{(0)}(t)\rangle} \right) = \sum_n a_n \left(H_0 |\Psi_n^{(0)}(t)\rangle + H'(t)|\Psi_n^{(0)}(t)\rangle \right)$$

$$\sum_n i\hbar \frac{da_n}{dt}|\Psi_n^{(0)}(t)\rangle + \cancel{\sum_n a_n E_n |\Psi_n^{(0)}(t)\rangle} = \cancel{\sum_n a_n E_n |\Psi_n^{(0)}(t)\rangle}$$
$$+ \sum_n a_n H'(t)|\Psi_n^{(0)}(t)\rangle$$

$$\sum_n i\hbar \frac{da_n}{dt}|\Psi_n^{(0)}(t)\rangle = \sum_n a_n H'(t)|\Psi_n^{(0)}(t)\rangle$$

multiply by $\langle \Psi_k^{(0)}(t)|$ and using $\langle \Psi_k^{(0)}(t)|\Psi_n^{(0)}(t)\rangle = \langle \Psi_k|\Psi_n\rangle = \delta_{kn}$

$$i\hbar \frac{d}{dt} a_k(t) = \sum_n a_n(t) \langle \Psi_k^{(0)}(t)| H'(t) |\Psi_n^{(0)}(t)\rangle$$
$$= \sum_n a_n(t)\, e^{\frac{iE_k t}{\hbar}} e^{-\frac{iE_n t}{\hbar}} \langle \Psi_k | H' | \Psi_n \rangle$$

$$i\hbar \frac{d}{dt} a_k(t) = \sum_n a_n(t)\, e^{i\omega_{kn} t} H'_{kn} \; ; \quad \omega_{kn} = (E_k - E_n)/\hbar$$

Bhor frequency

the last eq^n is a set of coupled equations

untill now we have made no approximations. the last eq^n can be written as in matrix form,

$$i\hbar \frac{d}{dt}\begin{pmatrix} a_1(t) \\ a_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} e^{i\omega_{12} t} & \cdots \\ H_{21} e^{-i\omega_{12} t} & H_{22} & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \\ \vdots \end{pmatrix}$$

note that if the perturbation is set to zero, then $a_k(t)$ keeps the value it had at $t=0$ and the system remains in the same initial state $|\psi_i^{(0)}(t)\rangle$;

i.e $a_k(0) = \delta_{ki}$, then $a_k(t) = \delta_{ki}$ with no perturbation

$$\therefore i\hbar \frac{d}{dt} a_k(t) = \sum_n e^{i\omega_{kn} t} H'_{kn} a_n(t) \quad --- \quad (3)$$

Now, we already assumed that the perturbation H' is small. this means that the coefficients $a_k(t)$ change slowly from their initial values. further, we assumed that the system was prepared in the unperturbed state $|\psi_i\rangle$ at $t=0$, so that $a_k(0) = \delta_{ki}$. So as a first approximation, we can set $a_n(t)$ to $a_n(0) = \delta_{ni}$

For sufficiently short times, we have

$$\frac{d}{dt} a_k(t) = -\frac{i}{\hbar} \sum_n e^{i\omega_{kn} t} H'_{kn}(t)\, \delta_{ni} = -\frac{i}{\hbar} e^{i\omega_{ki} t} H'_{ki}(t)$$

integrate

$$a_k(t) \simeq \delta_{ki} - \frac{i}{\hbar} \int_0^t e^{i\omega_{ki} t} H'_{ki}(t)\, dt$$ see back

relabel let $k \to f$

$$a_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_0^t e^{i\omega_{fi} t} H'_{fi}(t)\, dt$$

for $f \neq i$, $a_f(t) = -\frac{i}{\hbar} \int_0^t e^{i\omega_{fi} t} H'_{fi}\, dt$

this is a transition amplitude from initial state to final state which is first order in H'_{fi}. However, the transition probability is of second order in H'_{fi}

$$|a_f(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t dt\, e^{i\omega_{fi} t} H'_{fi} \right|^2$$

notice that the probability of finding the system in the initial state (after perturbation is applied) is

$$|a_i(t)|^2 = 1 - \sum_{f\neq i} |a_{f=i}(t)|^2 = 1 - O(H'^2_{fi})$$

so it deviates from 1 only to 2^{nd} order in perturbation.

- principle of detailed balance:

for the process $i \to f$, we found

$$H'_{fi}(t) = \langle \psi_f | H' | \psi_i \rangle = \langle \psi_i | H' | \psi_f \rangle^* = H'^*_{if}(t) \quad ; \quad H' = H'^{\dagger} \text{ hermitian}$$

so for the reversed process $f \to i$ i.e at $t=0$, the system in the final state and after a time t, the system will be in the initial state

$$a_{f\to i}(t) = -\frac{i}{\hbar}\int_0^t H'_{if}(t)\, e^{i\omega_{if}t}\, dt = -\frac{i}{\hbar}\int_0^t H'^*_{fi}(t)\, e^{-i\omega_{fi}t}\, dt$$

where $\omega_{if} = -\omega_{fi}$

$$= -a^*_{i\to f}(t)$$

$|a_{f\to i}|^2 = |a_{i\to f}|^2 \Rightarrow$ transition probability from $i \to f$ is the same as for the reverse process $f \to i$

This is called principle of detailed balance

the reverse process is similar to Relaxation process.

- Second order expansion:

we found for first order that

$$a_k(t) = \delta_{ki} - \frac{i}{\hbar}\sum_n \int_0^t dt\, e^{i\omega_{kn}t} H'_{kn}\, a_n(t) \quad \text{--- (4)}$$

notice that a appears on both sides ; iterative equation

Now to get an expression to $a_n(t)$ on the right hand side of equation (4), let me relabel $k \to n$ and $n \to m$

$$a_n(t) = \delta_{ni} - \frac{i}{\hbar} \sum_m \int_0^t dt' \, e^{i\omega_{nm} t'} H'_{nm} \, a_m(t')$$ see back

Now substituting the last equation in the right hand side of eqn (4) gives to second order

$$a_k(t) = \delta_{ki} - \frac{i}{\hbar} \sum_n \int_0^t dt \, e^{i\omega_{kn} t'} H'_{kn} \Big[\delta_{ni} - \frac{i}{\hbar} \sum_m \int_0^t dt' \, e^{i\omega_{nm} t'} H'_{nm} \, a_m(t') \Big]$$

$$= \delta_{ki} - \frac{i}{\hbar} \int_0^t dt \, e^{i\omega_{ki}} H'_{ki}$$

$$+ \left(\frac{1}{i\hbar}\right)^2 \sum_n \int_0^t dt \, e^{i\omega_{kn} t} H_{kn} \sum_m \int_0^t dt' \, e^{i\omega_{nm} t'} H'_{nm} \, a_m(t')$$

if we break it to second order, then we set

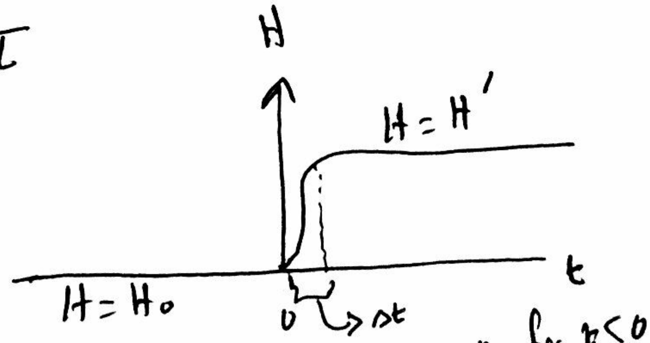
$$a_m(t' = 0) = \delta_{mi}$$

Note that in most problems we stop at first order only.

- <u>sudden perturbation:</u>

in this case the hamiltonian goes from H_0 to H' very fast during a time interval Δt which is much shorter than any of natural periods of the system, τ

i.e $\Delta t \ll \tau \equiv \frac{2\pi}{\omega_{fi}} = \frac{2\pi\hbar}{\epsilon_f - \epsilon_i}$



we can set $H_0 = 0$ for $t < 0$ as it is a constant

so

$$|a_f(t)|^2 = |a_{i \to f}(t_0 + \Delta t)|^2$$

$$= \frac{1}{\hbar^2} \left| \int_0^{\Delta t} dt \, e^{i\omega_{fi} t} H'_{fi} \right|^2$$

$\therefore \left| a_{i\to f}(t_0+\Delta t) \right|^2 \sim \left| \frac{1}{\hbar} H'_{fi} \Delta t \right|^2 << \left| \frac{2\pi H'_{fi}}{E_f - E_i} \right|^2$; for $f \neq i$
see back

when the phase factor $e^{i\omega_{fi}\Delta t} \approx 1$ for $\omega_{fi}\Delta t << 1$
where ~~ta~~ also we assumed that H'_{fi} is almost constant for sudden permanent perturbation as shown in the schematic graph in the previous page;

so if the matrix elements H'_{fi} are not much larger than the energies of the system i.e

i.e $2\pi H'_{fi} < E_f - E_i$ $\Rightarrow$ then these probabilities will be much smaller than 1. this means that the leakage to other states is very small, indicating that the probability of finding the system in the original initial state is practically unchanged i.e $\left| a_i(t_0+\Delta t) \right|^2 \approx \left| a_i(t_0) \right|^2 = 1$

meaning the wavefunction of the initial state is unable to react immediately to the sudden change in H

- Adiabatic Perturbation!

Here the Hamiltonian changes very slowly compared to natural periods of the system

i.e $t_1 >> \tau \equiv \frac{2\pi}{\omega_{fi}}$

$H' = 0$ for $t < 0$ and $t > t_1$

now the transition amplitude for $t > t_1$

$$a_{f\neq i}(t) = \frac{-i}{\hbar}\int_0^{t_1} e^{i\omega_{fi}t} H'_{fi}(t)\, dt$$

so $H'_{fi}(t)$ is a very slowly varing function compared to the oscillations of the exponential term. the rapid oscillating term $e^{i\omega_{fi}t}$ average out to zero as $e^{i\omega_{fi}t} = \cos\omega_{fi}t + i\sin\omega_{fi}t$ indicating that the transition amplitude $a_{f\neq i}(t) \to 0$.
thus for Adiabatic approximation, the transition probabilities are negligible.

Harmonic Perturbation and Fermi's Golden Rule:

consider a harmonic perturbation described by

$$H'(\vec{r},t) = H'_{fi}(\vec{r})\, e^{-i\omega t} + H^{\dagger\prime}_{fi}(\vec{r})\, e^{i\omega t}$$

$$\text{shortly} = H'_{fi}\, e^{-i\omega t} + H^{\dagger\prime}_{fi}\, e^{i\omega t} = H'_{fi}\, e^{-i\omega t} + H^{*\prime}_{if}\, e^{i\omega t} \quad \text{--- (5)}$$

an example of this periodic perturbation is an electromagnetic wave with frequency ω incident on an atom. a resonance occurs when the frequency of the incident wave matches energy difference (gap) between two levels in the atom.

notice that in eq^n (5), we have used the fact that H' is hermitian ; where $H' = H^{\dagger\prime}$

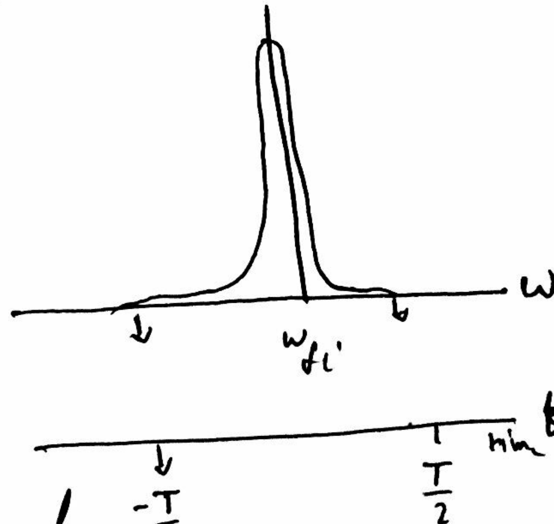
i.e $H'_{fi} = \langle \psi_f | H' | \psi_i \rangle = \langle \psi_i | H^{\dagger\prime} | \psi_f \rangle^* = H^{*\prime}_{if}$ see back

- Now the first order transition amplitude (for $i \neq f$) is given by

$$a_{i\to f}(t) = \frac{1}{i\hbar} H'_{fi} \int e^{i(\omega_{fi}-\omega)t}\, dt + \frac{1}{i\hbar} H^{*\prime}_{if} \int e^{i(\omega_{fi}+\omega)t}\, dt$$

what are the limits of the integrals ??

the interaction of the incident EM wave occurs during a very short period of time like a strik in the frequency domain that can be represented by a delta function



Now using

$$\int_{-\infty}^{\infty} dt\, e^{i(\omega_{fi}-\omega)t} = 2\pi\, \delta(\omega_{fi}-\omega)$$

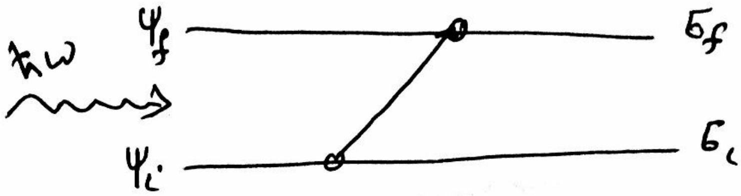
this integral vanish unless

$$\omega_{fi} = \omega \Rightarrow \frac{E_f - E_i}{\hbar} = \omega$$

$$E_f = E_i + \hbar\omega$$

we see that this transisition corresponds with $T \to \infty$

to absorption of energy $\hbar\omega$ (photon absorption)



for the second integral

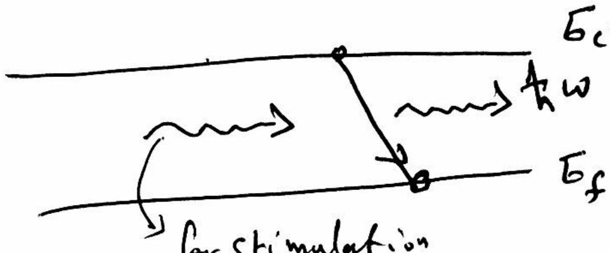
$$\int_{-\infty}^{\infty} dt\, e^{i(\omega_{fi}+\omega)} = 2\pi\, \delta(\omega_{fi}+\omega)$$

absorption

this integral vanish unless $\omega_{fi} = -\omega$

$$\frac{E_f - E_i}{\hbar} = -\omega \quad \Rightarrow \quad E_f = E_i - \hbar\omega$$

this corresponds to an emission of energy $\hbar\omega$
which is mostly called
stimulated emission of photon



both processes are equally probable
- the transition probabilities of both processes depend on how closely the resonance condition is satisfied.
- let us calculate the transition probability for each process separately

a) for absorption

$$|a_{i\to f}(t)|^2 = \left| \frac{1}{(i\hbar)^2} \int_{-\infty}^{\infty} H'_{fi}\, e^{i(\omega_{fi}-\omega)t}\, dt \right|^2$$

$$= \frac{|H'_{fi}|^2}{\hbar^2} \underline{\left| 2\pi\, \delta(\omega_{fi}-\omega) \right|^2}$$

let us see how do we calculate this quantity now $\lim_{T\to\infty} \int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t} dt = 2\pi\,\delta(\omega_{fi}-\omega)$

$$\Rightarrow |2\pi\,\delta(\omega_{fi}-\omega)|^2 = \left| \lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{i(\omega_{fi}-\omega)t} \right|^2$$

$$= \underbrace{\lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{i(\omega_{fi}-\omega)t}} \lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{-i(\omega_{fi}-\omega)t}$$

$$= 2\pi\,\delta(\omega_{fi}-\omega) \lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{-i(\omega_{fi}-\omega)t}$$

requires $\omega_{fi} = \omega$

$$= 2\pi\,\delta(\omega_{fi}-\omega)\,[T/2 - (-T/2)]$$

$$= 2\pi\,\delta(\omega_{fi}-\omega)\,T$$

$$\Rightarrow |a_{i\to f}(t)|^2 = \frac{2\pi}{\hbar^2} |H'_{fi}|^2\, \delta(\omega_{fi}-\omega)\, T$$

here we define the transition rate for absorption as

$$W_{i\to f} = \frac{|a_{i\to f}(t)|^2}{T} = \frac{2\pi}{\hbar^2} |H'_{fi}|^2\, \delta(\omega_{fi}-\omega)$$ time independent

$$= \frac{2\pi}{\hbar^2} |H'_{fi}|^2\, \delta\left(\frac{E_f - E_i}{\hbar} - \omega\right)$$

$$= \frac{2\pi}{\hbar^2} |H'_{fi}|^2\, \delta\left(\frac{E_f - E_i - \hbar\omega}{\hbar}\right)$$

using $\delta(ax) = \frac{\delta(x)}{|a|}$ ←

$$= \frac{2\pi}{\hbar^2} |H'_{fi}|^2\, \hbar\, \delta(E_f - E_i - \hbar\omega)$$

$$= \frac{2\pi}{\hbar} |H'_{fi}|^2\, \delta(E_f - E_i - \hbar\omega)$$

the last equation is called Fermi's Golden Rule.

Note: life time of the final state is $\tau = \frac{1}{W_{i\to f}}$

b) for stimulated emission:

$$|a_{i\to f}(t)|^2 = \left| \frac{1}{(i\hbar)^2} \int_{-\infty}^{\infty} H'^*_{if}\, e^{i(\omega_{fi}+\omega)t}\, dt \right|^2$$

$$= \frac{|H'^*_{if}|^2}{\hbar^2} \left| 2\pi\, \delta(\omega_{fi}+\omega) \right|^2$$

Again $\left|2\pi\,\delta(\omega_{fi}+\omega)\right|^2 = \left| \lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{i(\omega_{fi}+\omega)t} \right|^2$

$$= \lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{i(\omega_{fi}+\omega)t} \lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{-i(\omega_{fi}+\omega)t}$$

$$= 2\pi\,\delta(\omega_{fi}+\omega) \lim_{T\to\infty} \int_{-T/2}^{T/2} dt\, e^{-i(\omega_{fi}+\omega)t}$$

requires $\omega_{fi} = -\omega$

$$= 2\pi\,\delta(\omega_{fi}+\omega)\, T$$

$$\Rightarrow |a_{i\to f}(t)|^2 = \frac{2\pi}{\hbar^2} |H'^*_{if}|^2\, \delta(\omega_{fi}+\omega)\, T$$

and $$W_{i\to f} = \frac{2\pi}{\hbar} |H'^*_{if}|^2\, \delta(E_f - E_i + \hbar\omega)$$

Now since the two delta function appearing in the absorption and emission formulas are equal i.e

$$\delta(\omega_{fi}-\omega) = \delta(-(\omega-\omega_{fi})) = \frac{\delta(\omega-\omega_{fi})}{|-1|} = \delta(\omega-\omega_{fi})$$

and $\delta(-x) = \delta(x)$ even function

$\Rightarrow$ we come to the conclusion: with harmonic perturbation, for any two states (ψ_i, ψ_f), the first order transition rate for absorption equals to that of emission

$$W_{i\to f} = W_{f\to i}$$

Example 1: scattering on static Potential ($\omega = 0$)

here the particles are unbound before and after scattering i.e we have continuous → continuous scattering spectrum. and let us assume that two particles collide together and the interaction potential is $V(\vec{r_1} - \vec{r_2}) = V(|\vec{r}|) = V(r)$. this scattering problem can be separated to center of mass and relative coordinate equations. the hamiltonian of the reduced particle is $H = \frac{p^2}{2\mu} + V(r) = H_0 + V(r)$

when $H_0 = \frac{p^2}{2\mu}$; and $V(r)$ is considered as static perturbations

in this scattering (elastic) process, both energy and momentum are conserved $P_i = P_f$; $E_i = E_f$

$$\Rightarrow \psi_i(r) = \frac{1}{\sqrt{V_0}} e^{\frac{i\vec{P_i}\cdot\vec{r}}{\hbar}} \quad ; \quad \psi_f(r) = \frac{1}{\sqrt{V_0}} e^{\frac{i\vec{P_f}\cdot\vec{r}}{\hbar}} \quad ; \quad H'_{fi} = V_{fi}(r)$$

$$\text{so} \quad H'_{fi}(t) = H'_{fi} = \int \psi_f^*(r)\, H'_{fi}\, \psi_i(r)\, d^3r$$

$$= \frac{1}{V_0} \int e^{i(\vec{P_i} - \vec{P_f})\cdot\vec{r}/\hbar}\, V_{fi}(r)\, d^3r$$

$$\Rightarrow a_{i\to f}(t) = \frac{1}{i\hbar} H'_{fi} \int_{-\infty}^{\infty} e^{i\omega_{fi} t}\, dt$$

, here there is no absorption or emission

$$|a_{i\to f}(t)|^2 = \frac{|H'_{fi}|^2}{\hbar^2} \left| 2\pi\, \delta(\omega_{fi}) \right|^2 = \frac{2\pi\, |H'_{fi}|^2}{\hbar^2} \delta(\omega_{fi})\, T$$

transition rate $W_{i\to f}$

$$= (2\pi) \frac{|H'_{fi}|^2}{\hbar^2} \delta(\omega_{fi}) = \frac{2\pi}{\hbar^2} |H'_{fi}|^2 \delta(\omega_f - \omega_i)$$

$$= \frac{2\pi}{\hbar^2} |H'_{fi}|^2\, \hbar\, \delta(E_f - E_i) = \frac{2\pi}{\hbar} |H'_{fi}|^2 \delta(E_f - E_i)$$

this result is for scattering rate from an initial state ψ_i to one final state ψ_f. but our final state is really a set of continuum; infinite set of states so to find the total rate of transitions we have to sum over all final states

$$W_i = \sum_f w_{i \to f} = \sum_f \frac{2\pi}{\hbar} |H'_{fi}|^2 \delta(E_f - E_i)$$

this is converted to integral as

$$W_i = \int_{E_f} \frac{2\pi}{\hbar} |H'_{fi}|^2 \rho(E_f) dE_f \; \delta(E_f - E_i) \quad : \quad 0 \le E_f < \infty$$

$$= \frac{2\pi}{\hbar} |H'_{fi}|^2 \int_0^\infty \rho(E_f) \, \delta(E_f - E_i) \, dE_f$$

for static perturbation

notice that the delta function $\delta(E_f - E_i)$ ensures that the system can only have transitions between states with same energy, which is typical for elastic scattering

Example 2: Discrete to Continuous transitions;

Consider a monochromatic radiation with a photon energy $\hbar\omega$ incident on an atom (H atom for instance). if the initial state ψ_i is the ground state, this require photons with an energy higher than 13.6 eV. Then, the relevant final states ψ_f are continuum states for the emitted electron with an energy $E_f \approx \hbar\omega - 13.6$ eV.

Now the total rate of transitions W_i, from the initial state

$$W_i = \sum_f w_{i\to f}$$

, where the sum goes over all ψ_f states which are really infinite.

$$W_i = \sum_f \frac{2\pi}{\hbar} |H'_{fi}|^2 \, \delta(E_f - E_i - \hbar\omega)$$

: absorption only here

$$= \frac{2\pi}{\hbar} \sum_f |H'_{fi}|^2 \, \delta(E_f - E_i - \hbar\omega)$$

the sum here can be converted to an integral when the states belong to a continuous spectrum $\sum_f \to \int dE_f \underbrace{\rho(E_f)}_{\text{density of states}}$

where $dE_f\, \rho(E_f)$ is the # of states with energies between E_f and $E_f + dE_f$

$$\Rightarrow W_i = \frac{2\pi}{\hbar} \int_{E_f} dE_f \, \rho(E_f) \, |H'_{fi}|^2 \, \delta(E_f - E_i - \hbar\omega)$$

This is also a Fermi's Golden Rule