Chapter 3

Time-Dependent Perturbation Theory

Suppose we have a time dependent Hamiltonian $H(t)$, then we know that the system under consideration will satisfy time-dependent Schrödinger equation

$$i\hbar \frac{d|\psi(t)\rangle}{dt} = H(t)|\psi(t)\rangle \quad \text{——(1)}$$

This equation can be integrated for the time part for a few simple systems such as: (i) when $H(t)$ is time independent, (ii) a two-level ($spin-\frac{1}{2}$) system coupled to a uniform magnetic field, and a radio-frequency magnetic field, and some other simple cases. However, for a vast majority of cases it is very difficult or essentially impossible to integrate Eqn (1), requiring the use of approximations. One such

approach is based upon perturbation theory, which is what we discuss next. For the purpose, we assume that the Hamiltonian $H(t)$ is of the form

$$H = H_0 + V(t) \qquad \text{——— (2)}$$

where H_0 is time independent, for which the Schrödinger equation has been solved

~~$H_0|\psi_n\rangle = E_n|\psi_n\rangle$~~ ———

$$H_0|\psi_n\rangle = E_n|\psi_n\rangle \qquad \text{— (3)}$$

we choose a compact notation for kets $|\psi_n\rangle \equiv |n\rangle$, so that

~~$H_0|\psi_n\rangle = E_n|\psi_n\rangle$~~ (1)

$$H_0|n\rangle = E_n|n\rangle \qquad \text{——— (4)}$$

Next, we develop a perturbation theoretic approach to obtain solutions of Eq.(1), for a Hamiltonian of the form of Eq.(2). ~~For this we will be~~ We provide two separate derivations for that, one based upon interaction picture, while the other one based upon ~~Dyson series~~ a linear combination of basis functions.

(i) Interaction Picture Derivation :

For the purpose we define a new state ket $|\tilde{\psi}(t)\rangle$, related to the ket $|\psi(t)\rangle$ (whose expression we have to obtain), by a unitary transformation

$$|\tilde{\psi}(t)\rangle = e^{iH_0 t/\hbar} |\psi(t)\rangle \quad \text{—(5)}$$

$$\Rightarrow \quad |\psi(t)\rangle = e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle \quad \text{—(6)}$$

Substituting this in Eq.(1) with the Hamiltonian of the form Eq.(2)

$$i\hbar \frac{d}{dt}\left(e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle\right)$$

$$= (H_0 + V(t)) e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle$$

$$\Rightarrow \quad i\hbar \left\{ -\frac{iH_0}{\hbar} e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle + e^{-iH_0 t/\hbar} \frac{d|\tilde{\psi}(t)\rangle}{dt} \right\}$$

$$= H_0 e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle + V(t) e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle$$

$$\Rightarrow \quad H_0 e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle + i\hbar e^{-iH_0 t/\hbar} \frac{d|\tilde{\psi}(t)\rangle}{dt}$$

$$= H_0 e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle + V(t) e^{-iH_0 t/\hbar} |\tilde{\psi}(t)\rangle$$

$$\Rightarrow \quad i\hbar\, e^{-iH_0 t/\hbar}\frac{d|\tilde{\psi}(t)\rangle}{dt} = V(t)\, e^{-iH_0 t/\hbar}|\tilde{\psi}(t)\rangle$$

$$\Rightarrow \quad i\hbar\frac{d|\tilde{\psi}(t)\rangle}{dt} = e^{iH_0 t/\hbar}\, V(t)\, e^{-iH_0 t/\hbar}|\tilde{\psi}(t)\rangle$$

$$\Rightarrow \quad \boxed{i\hbar\frac{d|\tilde{\psi}\rangle}{dt} = \tilde{V}(t)|\tilde{\psi}(t)\rangle} \qquad \text{---(7)}$$

where $$\boxed{\tilde{V}(t) = e^{iH_0 t/\hbar}\, V(t)\, e^{-iH_0 t/\hbar}} \qquad \text{---(8)}$$

Note that the modified state ket $|\tilde{\psi}(t)\rangle$ satisfies a modified Schrödinger equation (Eq. (7)), in which the modified perturbation potential $\tilde{V}(t)$ plays the role of Hamiltonian. This picture defined through unitary transformations of Eqs. (5) and (8), is called the "interaction picture".

Next, we obtain a perturbation theoretic solution of Eq. (7). For the purpose

we integrate Eq.(7) between the limits t_0 (some initial time) and t, to obtain

$$|\tilde{\psi}(t)\rangle = |\tilde{\psi}(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt' \tilde{V}(t')|\tilde{\psi}(t')\rangle \quad \text{—(9)}$$

Because this equation has the unknown solution $|\tilde{\psi}\rangle$ on the right hand side, it cannot be further integrated. Therefore, we develop an iterative solution by setting $|\tilde{\psi}(t')\rangle \approx |\tilde{\psi}(t_0)\rangle$ on the RHS

$$|\tilde{\psi}(t)\rangle = |\tilde{\psi}(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt' \tilde{V}(t')|\psi(t_0)\rangle$$

$$= \left(1 + \frac{1}{i\hbar}\int_{t_0}^{t} dt' \tilde{V}(t')\right)|\psi(t_0)\rangle$$

— (10)

This solution is correct up to first order terms in perturbation on $V(t)$. To obtain solution up to second order, we substitute Eq.(10) on the RHS of Eq(9), to obtain

$$|\tilde{\psi}(t)\rangle = |\tilde{\psi}(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\, \tilde{V}(t')\cdot|\psi(t_0)\rangle$$

$$+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, \tilde{V}(t')\,\tilde{V}(t'')\,|\psi(t_0)\rangle$$

(11)

if we define a time ordered product as

$$T[\tilde{V}(t')\tilde{V}(t'')] = \tilde{V}(t')\tilde{V}(t'') \quad \text{if } t' \geq t''$$

$$= \tilde{V}(t'')\tilde{V}(t') \quad \text{if } t' \leq t''$$

(12)

i.e. the term with the "later" time will be on the right, we can show

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, \tilde{V}(t')\tilde{V}(t'') = \frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\, T[\tilde{V}(t')\tilde{V}(t')]$$

(13)

so that to the second order

$$|\tilde{\psi}(t)\rangle = T\left[1 + \frac{1}{i\hbar}\int_{t_0}^{t} \tilde{V}(t')\,dt' + \frac{1}{2}\frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\, \tilde{V}(t')\tilde{V}(t'')\right]|\tilde{\psi}(t_0)\rangle$$

by iterating the procedure an infinite number of times, we obtain

$$|\tilde{\psi}(t)\rangle = \tilde{U}(t,t_0)\,|\psi(t_0)\rangle \qquad \text{——— (14)}$$

where $\tilde{U}(t,t_0)$ can be seen as the time evolution operator in the interaction representation, defined as

$$\tilde{U}(t,t_0) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t}\cdots\int_{t_0}^{t} dt_1' \cdots dt_n'$$

$$\times\, T\left[\tilde{V}(t_1')\,\tilde{V}(t_2')\cdots\tilde{V}(t_n')\right]$$

$$= T\, e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'\,\tilde{V}(t')\,dt'} \qquad \text{——— (15)}$$

In case we want to do k-th order perturbation theory, we can expand Eq (15) up to k-th order, and perform various calculations.

Eqns. (14) and (15) form the Dyson series solution of the time dependent perturbation theory.

(ii) Linear Combination of Eigenfunctions Approach:

In this approach we expand $|\psi(t)\rangle$ in terms of eigenfunctions of H_0 as

$$|\psi(t)\rangle = \sum_j a_j(t) e^{-iE_j t/\hbar} |j\rangle \quad \text{—(16)}$$

note that $e^{-iEnt/\hbar}$ describe the time dependence of $|\psi(t)\rangle$ with respect to H_0, therefore, the influence of $V(t)$ is contained in time dependent linear coefficients $a_j(t)$. Substituting (16) in (1), with $H(t)$ given by Eqn. (2), we have

$$i\hbar \sum_j \left\{ -\frac{iE_j}{\hbar} a_j(t) e^{-iE_j t/\hbar} + \frac{da_j}{dt} e^{-iE_j t/\hbar} \right\} |j\rangle$$

$$= \sum_j \left(H_0 a_j(t) |j\rangle + V(t) a_j(t) |j\rangle \right)$$

$$\sum_j E_j a_j(t) e^{-iE_j t/\hbar} |j\rangle + \sum_j \frac{da_j}{dt} e^{-iE_j t/\hbar} |j\rangle$$

$$= \sum_j E_j a_j(t) e^{-iE_j t/\hbar}$$

using $H_0 a_j(t)|j\rangle = a_j(t) H_0 |j\rangle$

$= E_j a_j(t)|j\rangle$, we have

$$\sum_j E_j a_j(t) e^{-iE_j t/\hbar}|j\rangle + i\hbar \sum_j \frac{da_j}{dt} e^{-iE_j t/\hbar}|j\rangle$$

$$= \sum_j E_j a_j(t) e^{-iE_j t/\hbar}|j\rangle + \sum_j V(t) a_j(t) \times e^{-iE_j t/\hbar}|a_j\rangle$$

$$i\hbar \sum_j \frac{da_j}{dt} e^{-iE_j t/\hbar}|j\rangle = \sum_j e^{-iE_j t/\hbar} V(t) a_j(t)|j\rangle \quad (17)$$

on taking the inner product of this equation with $|i\rangle$, and using $\langle i|j\rangle = \delta_{ij}$, we have

$$i\hbar \sum_j \frac{da_j}{dt} e^{-iE_j t/\hbar}\langle i|j\rangle = \sum_j \langle i|V(t)|j\rangle a_j(t) \times e^{-iE_j t/\hbar}$$

$$\Rightarrow i\hbar \sum_j \delta_{ij} \frac{da_j}{dt} e^{-iE_j t/\hbar} = \sum_j V_{ij}(t) a_j(t) e^{-iE_j t/\hbar}$$

$$i\hbar \frac{da_i}{dt} e^{-iE_i t/\hbar} = \sum_j V_{ij}(t) e^{-iE_j t/\hbar} a_j(t)$$

$$i\hbar \frac{da_i}{dt} = \sum_j V_{ij}(t) e^{i(E_i - E_j)t/\hbar} a_j(t)$$

using $E_j = \hbar\omega_j$ and $\omega_{ij} = \omega_i - \omega_j$, we have

$$i\hbar \frac{da_i}{dt} = \sum_j V_{ij}(t) e^{i\omega_{ij}t} a_j(t) \quad \text{---(18)}$$

defining

$$\tilde{a} = \begin{pmatrix} a_1(t) \\ \vdots \\ a_n(t) \end{pmatrix} \quad \text{---(19)}$$

$$\tilde{V}_{ij}(t) = \begin{pmatrix} V_{11}(t) & \cdots & V_{1n}(t) e^{i\omega_{1n}t} \\ \vdots & & \\ V_{n1}(t) e^{i\omega_{n1}t} & \cdots & V_{nn}(t) \end{pmatrix} \quad \text{---(20)}$$

where ~~$V_{ij}(t) = \langle \phi_i | V(t) | \phi_j$~~

$$V_{ij}(t) = \langle i | V(t) | j \rangle \quad \text{---(21)}$$

we obtain the matrix form of time dependent Schrödinger equation

$$\boxed{i\hbar \frac{d\tilde{a}}{dt} = \tilde{V}(t)\,\tilde{a}(t)} \quad \text{---(21)}$$

Eq. (21), using perturbation theory, we introduce a perturbation parameter λ similar to the case of time independent perturbation theory, to write

$$H_0 + V(t) \longrightarrow H_0 + \lambda V(t)$$

$$\tilde{a}(t) = \tilde{a}^{(0)}(t) + \lambda \tilde{a}^{(1)}(t) + \lambda^2 \tilde{a}^{(2)}(t) + \cdots \quad (22)$$

and eventually we will set $\lambda = 1$.

Substituting (22) in (21), we have

$$i\hbar \left\{ \frac{d\tilde{a}^{(0)}}{dt} + \lambda \frac{d\tilde{a}^{(1)}}{dt} + \lambda^2 \frac{d\tilde{a}^{(2)}(t)}{dt} + \cdots \right\}$$

$$= \lambda \tilde{V}(t) \left\{ a^{(0)}(t) + \lambda \tilde{a}^{(1)}(t) + \lambda^2 \tilde{a}^{(2)}(t) + \cdots \right\}$$

on comparing terms order by order in powers of λ, we have

$$i\hbar \frac{d\tilde{a}^{(0)}}{dt} = 0 \quad \text{---} (23)$$

$$i\hbar \frac{d\tilde{a}^{(1)}}{dt} = \tilde{V}(t) \tilde{a}^{(0)}(t) \quad \text{---} (24)$$

$$i\hbar \frac{d\tilde{a}^{(2)}}{dt} = \tilde{V}(t) \tilde{a}^{(1)}(t)$$

or in general

$$i\hbar \frac{d\tilde{a}^{(k+1)}}{dt} = \tilde{V}(t) \tilde{a}^{(k)}(t) \quad \text{---} (25)$$

Clearly, Eqs (25) represent a heirarchy of equations which can be solved iteratively. Clearly Eq. (23) can be integrated right away

$$\Rightarrow \quad \tilde{a}^{(0)} = \tilde{c} \equiv \text{constant} \qquad \text{--- (26)}$$

where $$\tilde{c} = \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix}$$

Substituting (26) in (24), we have

$$i\hbar \frac{d\tilde{a}^{(1)}}{dt} = \tilde{V}(t)\,\tilde{c}$$

or

$$i\hbar \frac{d\tilde{a}_i^{(1)}}{dt} = \sum_j V_{ij}(t)\, e^{-i\omega_{ji}t}\, c_j$$

$$\tilde{a}_i^{(1)}(t) = \frac{1}{i\hbar} \sum_j \int_{t_0}^{t} dt'\, c_j\, e^{-i\omega_{ji}t}\, V_{ij}(t')$$

(27)

similarly higher order equations can be solved.

Examples:

(1.) Constant Perturbation - Fermi's Golden Rule:

Let us assume that the time dependent potential $V(t)$ is of the form

$$V(t) = \begin{cases} 0 & \text{for } t < 0 \\ V & \text{for } t \geq 0 \end{cases} \qquad \text{---------- (28)}$$

that is the potential $V(t)$ is turned on abruptly at $t = t_0 = 0$, and its value V is time independent, although it may be dependent on other variables such as $\vec{p}, \vec{r}$ etc. We also assume that at the initial time $t = 0$, the system was in one of the eigenstates $|n\rangle$ of H_0, i.e.,

$$\boxed{c_n^{(0)} = c_i = \delta_{ni}} \qquad \text{---- (29)}$$

Using (28) and (29) in (27), we have

$$\tilde{a}_i^{(1)}(t) = \frac{1}{i\hbar}\int_0^t dt' \, e^{i\omega_{in}t'} \langle i|V|n\rangle$$

or $$\tilde{a}_i^{(1)}(t) = -\frac{(e^{i\omega_{in}t} - 1)}{\hbar\omega_{in}} \langle i|V|n\rangle \quad \text{—(30)}$$

and we restrict ourselves to the first order in perturbation theory, i.e., we do not include terms $\tilde{a}_i^{(k)}(t)$ for $k \geq 2$. The transition probability from state n to some other state i, at time t is obviously

$$P_{n\to i}(t) = |\tilde{a}_i^{(1)}(t)|^2 = \frac{(e^{i\omega_{in}t} - 1)(e^{-i\omega_{in}t} - 1)}{\hbar^2\omega_{in}^2} |\langle i|V|n\rangle|^2$$

or

$$P_{n\to i}(t) = \frac{(2 - e^{i\omega_{in}t} - e^{-i\omega_{in}t})}{\hbar^2\omega_{in}^2} |\langle i|V|n\rangle|^2$$

$$= \frac{2(1 - \cos\omega_{in}t)}{\hbar^2\omega_{in}^2} |\langle i|V|n\rangle|^2$$

$$= \frac{4\sin^2\omega_{in}t/2}{\hbar^2\omega_{in}^2} |\langle i|V|n\rangle|^2$$

or

$$P_{n\to i}(t) = \left(\frac{\sin^2 \omega_{in} t/2}{\frac{\omega_{in}}{2}}\right)^2 \frac{|\langle i|V|n\rangle|^2}{\hbar^2} \quad \text{---}$$

using the fact that

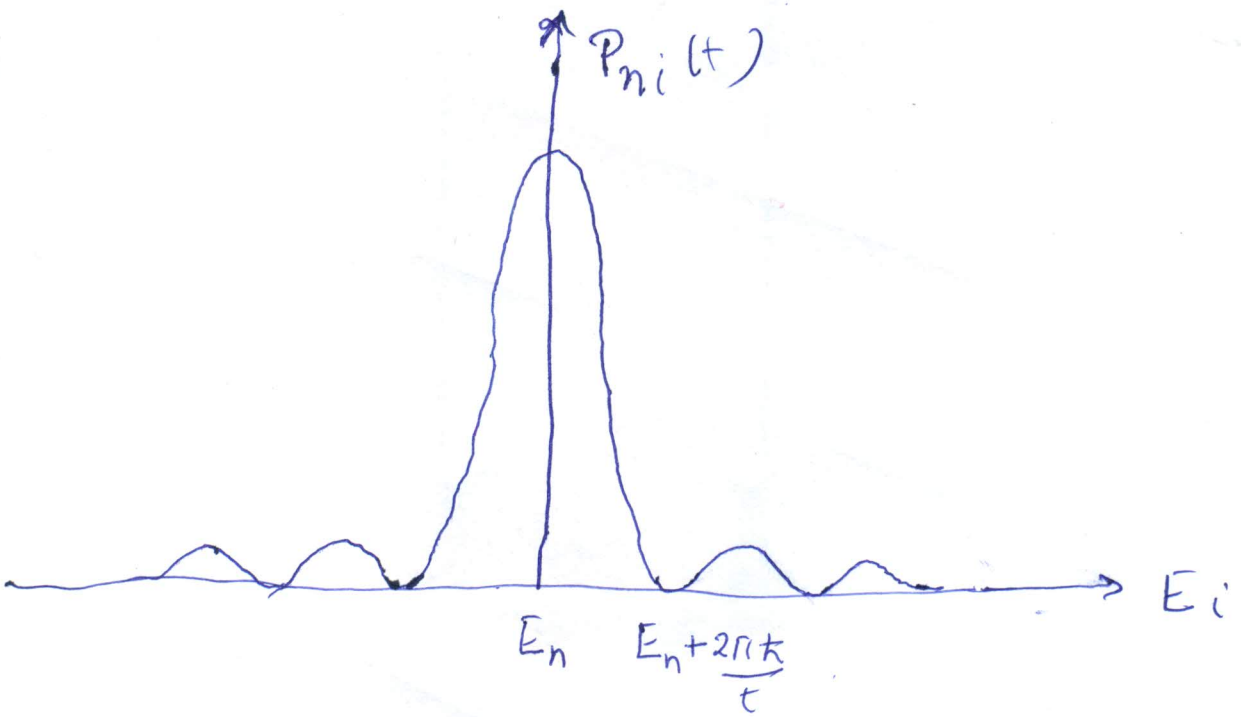
$$E_{in} = E_i - E_n = \hbar\omega_{in}$$

we can write

$$\boxed{P_{ni}(t) = \left(\frac{\sin E_{in} t/2\hbar}{E_{in}/2}\right)^2 |\langle i|V|n\rangle|^2}$$

(30)

if we assume that $|\langle i|V|n\rangle|^2$ changes slowly w.r.t. E_i, the plot of $P_{ni}(t)$ w.r.t. E_i looks as below



from this curve it is obvious that:

(i) most of the probability at a given t is contained within the central maximum

$$|E_i - E_n| \lesssim \frac{2\pi\hbar}{t}$$

(ii) the height of central peak grows as t^2 because for $E_n \to E_i$

$E_{in} \to 0 \Rightarrow \sin E_{in} t/2\hbar \sim \frac{E_{in}^2 t^2}{4\hbar^2}$

~~(iii) thus for $t \to \infty$~~

If we take $\Delta E = E_{in}$, then from point (i) it is obvious that the transition probability dominates for those states which satisfy

$$\Delta E \Delta t \sim 2\pi\hbar$$

where Δt is the time for which the perturbation V has been active.

From (i) it is also obvious that in the large time limit ($t \to \infty$) transition will happen only to those states with energies $E_i = E_n$, i.e. with energies

same as initial energies.

If final energies E_i form a continuum the total transition probability is

$$P_n(t) = \sum_i P_{n\to i}(t) = \int dE_i\, P(E_i) P_{n,i}(t)$$

where $P(E_i) \equiv$ density of states, ie. # of states per unit energy range

assuming that the matrix elements $\langle i|V|n\rangle$ does not vary with respect to E_i, much we have

$$P_n(t) = |\langle i|V|n\rangle|^2 \int dE_i\, P(E_i) \left(\frac{\sin E_{in} t/2\hbar}{E_{in}/2}\right)^2$$

(31)

if we take the long time limit $t \to \infty$, then using the result

$$\lim_{\alpha\to\infty} \frac{1}{\pi} \frac{\sin^2 \alpha x}{\alpha x^2} = \delta(x)$$

we obtain

$$\lim_{t\to\infty} \left(\frac{\sin E_{in} t/2\hbar}{E_{in}}\right)^2 \to \frac{\pi t}{2\hbar} \delta(E_{in})$$

(32)

on (32) → (31) we have

$$\Rightarrow \lim_{t\to\infty} P_n(t) = \frac{2\pi t}{\hbar} |\langle i|V|n\rangle|^2 \rho(E_i)\Big|_{E_i=E_n} \quad \text{—(33)}$$

Thus the transition rate to the levels E_i will be independent of t and will be non zero only if $E_i = E_n$

$$\Gamma_n = \lim_{t\to\infty} \frac{dP_n(t)}{dt} = \frac{2\pi}{\hbar} |\langle i|V|n\rangle|^2 \rho(E_i = E_n)$$

— (34)

This is the famous Fermi's Golden Rule. To a single level E_i, this formula can be written as

$$\Gamma_{n\to i} = \frac{2\pi}{\hbar} |\langle i|V|n\rangle|^2 \delta(E_i - E_n)$$

— (35)

Note that Fermi's Golden Rule implies that under a time independent perturbation, the transitions are possible only to those final states for which the energy of the final state is same as that of the initial state

(ii) Harmonically Varying Perturbation

Let us assume a perturbation which was non-existent till time $t = t_0 = 0$, and varies sinusoidally thereon

$$V(t) = 0 \quad \text{for } t < 0$$

$$= V\cos\omega t \quad \text{for } t \geq 0 \quad -(36)$$

For $t > 0$, writing $V(t) = \frac{V}{2}(e^{i\omega t} + e^{-i\omega t})$ and assuming that at $t = 0$, system was in the state $|n\rangle$, we have from Eqn. (27)

$$\tilde{a}_i^{(1)}(t) = \frac{V_{in}}{i\hbar 2}\int_0^t dt' \left[e^{i\omega t'} + e^{-i\omega t'}\right] e^{i(\omega_{in})t'}$$

$$\tilde{a}_i^{(1)}(t) = \frac{\langle i|V|n\rangle}{2i\hbar}\int_0^t dt' \left[e^{i(\omega_{in}+\omega)t'} + e^{i(\omega_{in}-\omega)t'}\right]$$

$$= \frac{\langle i|V|n\rangle}{2i\hbar}\left[\frac{e^{i(\omega_{in}+\omega)t} - 1}{i(\omega_{in}+\omega)} + \frac{e^{i(\omega_{in}-\omega)t} - 1}{i(\omega_{in}-\omega)}\right] \quad -(37)$$

$$\Rightarrow P_{n\to i}(t) = |a_i^{(1)}(t)|^2$$

when we calculate this probability using Eq. (37), in addition to mod squared terms for the two terms, we will also have cross terms which will be oscillatory in the limit $t \to \infty$, and will average out to zero. Thus the transition rate will be just the sum of the mod squared of the 8 individual terms which will give rise to delta functions in the limit $t \to \infty$, as before, leading to

$$\Gamma_{n\to i} = \frac{2\pi}{\hbar} \frac{|\langle i|V|n\rangle|^2}{4} \left[\delta(E_i - E_n - \hbar\omega) + \delta(E_i - E_n + \hbar\omega)\right] \quad (38)$$

~~Proof~~ this rate also has the same form as Fermi's Golden rule, and the two delta functions enforce the conservation of total energy including those of photons of energy $\hbar\omega$. The first

term corresponds to absorption of a photon of energy $\hbar\omega$ by the system, while the second term corresponds to emission of a photon of energy $\hbar\omega$ by the system.

(iii) Interaction of Radiation with Matter:

Based upon the theory developed in the previous part, we will develop the formalism required to describe the interaction of radiation with matter. For us matter implies any system such as an atom, a molecule, a quantum dot, or a solid. In the present treatment we will restrict ourselves to treating finite systems, with discrete energy levels, although the treatment can be easily generalized to bulk systems which exhibit energy bands.

We assume that the time independent Hamiltonian H_0 describing the matter

satisfies

$$H_0|\psi_n\rangle = E_n|\psi_n\rangle$$

or $$H_0|n\rangle = E_n|n\rangle,$$

where H_0 is of the form

$$\boxed{H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) = \frac{p^2}{2m} + V(r)} \quad -(39)$$

This system is irradiated by light (electromagnetic radiation) whose vector potential is given by

$$\vec{A}(\vec{r},t) = A_0 \hat{e}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} + \text{c.c.} \quad -(40)$$

above c.c. implies complex conjugate, while $\hat{e}$ is the direction of polarization of the incident light. From Eq. (40) it is obvious that we are assuming linearly polarized (or plane polarized) light. Note that this amounts to a semi-classical theory in which the matter is treated quantum mechanically, while the radiation is treated classically.

We include the interaction of radiation with matter using "minimal substitution" to obtain the perturbed Hamiltonian

$$H = \frac{(\vec{p} + e\vec{A})^2}{2m} + V(r) \qquad \text{——— (41)}$$

upon expanding the first term, we obtain

$$H = \frac{p^2}{2m} + \frac{e}{2m}\vec{p}\cdot\vec{A} + \frac{e}{2m}\vec{A}\cdot\vec{p} + \frac{e^2A^2}{2m} + V(r)$$

or

$$H = H_0 + \frac{e}{2m}\vec{p}\cdot\vec{A} + \frac{e}{2m}\vec{A}\cdot\vec{p} + \frac{e^2A^2}{2m}$$

each term in the Hamiltonian is an operator, which will act on a wave function ψ (say). Let us check the action of the second term on ψ

$$\frac{e}{2m}(\vec{p}\cdot\vec{A})\psi = -\frac{ie\hbar}{2m}\sum_i \frac{\partial}{\partial x_i}(A_i\psi)$$

$$= -\frac{ie\hbar}{2m}(\vec{\nabla}\cdot\vec{A}) - \frac{ie\hbar}{2m}$$

$$= -\frac{ie\hbar}{2m}\left(\sum_i \frac{\partial A_i}{\partial x_i}\right)\psi - \frac{ie\hbar}{2m}\sum_i A_i\frac{\partial\psi}{\partial x_i}$$

$$= -\frac{ie\hbar}{2m}(\vec{\nabla}\cdot\vec{A})\psi - \frac{ie\hbar}{2m}\vec{A}\cdot\vec{\nabla}\psi$$

on using Eq. (40) for $\vec{A}$, we obtain

$$\vec{\nabla}\cdot\vec{A} = i\vec{k}\cdot\hat{e}\,A_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} - i\vec{k}\cdot\hat{e}\,A_0 e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$$

but $\vec{k}\cdot\hat{e} = 0$ because light is always transversely polarized

$$\Rightarrow \quad \vec{\nabla}\cdot\vec{A} = 0$$

$$\Rightarrow \quad \frac{e}{2m}(\vec{p}\cdot\vec{A})\psi = \frac{-ie\hbar}{2m}\vec{A}\cdot\vec{\nabla}\psi = \frac{e}{2m}\vec{A}\cdot\vec{p}\,\psi$$

$$\Rightarrow \quad \vec{A}\cdot\vec{p} = \vec{p}\cdot\vec{A}$$ for transversely polarized light.

Thus

$$H(t) = H_0 + \frac{e}{m}\vec{A}\cdot\vec{p} + \frac{e^2A^2}{2m}$$

if we ignore terms second order in $\vec{A}$, i.e., $\frac{e^2A^2}{2m}$, because they are smaller in magnitude than the first order term $\frac{e}{m}\vec{A}\cdot\vec{p}$, we have

$$\left.\begin{aligned} H(t) &= H_0 + V(t) \\ \text{where } V(t) &= \frac{e}{m}\vec{A}\cdot\vec{p} \end{aligned}\right\} \quad \text{—— (42)}$$

the expanded form of the time-dependent perturbation $V(t)$ is

$$V(t) = \frac{e}{m} A_0 e^{i\bar{k}\cdot\bar{r}} \hat{e}\cdot\bar{p}\, e^{-i\omega t} + \frac{eA_0}{m} e^{-i\bar{k}\cdot\bar{r}} (\hat{e}\cdot\bar{p})\, e^{i\omega t}$$

or

$$V(t) = V_1(r) e^{-i\omega t} + V_2(r) e^{i\omega t} \qquad \text{--- (43)}$$

where

$$V_1(\bar{r}) = \frac{e}{m} A_0 e^{i\bar{k}\cdot\bar{r}} \hat{e}\cdot\bar{p}$$

$$V_2(\bar{r}) = \frac{e}{m} A_0 e^{-i\bar{k}\cdot\bar{r}} \hat{e}\cdot\bar{p}$$

Note that the form of $V(t)$ is very similar to the form of the harmonic perturbation considered in the previous section. Thus, using those results, we can directly write the expression for transition rate

$$\Gamma_{n\to i} = \frac{2\pi}{\hbar} \left\{ |\langle i|V_1|n\rangle|^2 \delta(E_i - E_n - \hbar\omega) + |\langle i|V_2|n\rangle|^2 \delta(E_i - E_n + \hbar\omega) \right\}$$

$$= \frac{2\pi e^2 A_0^2}{\hbar m^2} \left\{ |\langle i|e^{i\bar{k}\cdot\bar{r}} \hat{e}\cdot\bar{p}|n\rangle|^2 \delta(E_i - E_n - \hbar\omega) + |\langle i|e^{-i\bar{k}\cdot\bar{r}} \hat{e}\cdot\bar{p}|n\rangle|^2 \delta(E_i - E_n + \hbar\omega) \right\}$$

--- (44)

assuming that $\omega \geq 0$, in the previous equation, the first delta function will be satisfied only if $E_i \geq E_n$, while in the second term the condition $E_i \leq E_n$ must be satisfied. This means that the first term will apply to the case of absorption of a photon of energy $\hbar\omega = E_i - E_n$, while the second term corresponds to emission of a photon of energy $\hbar\omega = E_n - E_i$. Next, we concentrate only on the absorption processes ($E_i > E_n$), and drop the second term. For handling emission processes, we will have to drop the first term. Thus,

$$\Gamma_{n\to i}^{(abs)} = \frac{2\pi e^2 A_0^2}{m^2\hbar^2} \left| \langle i | e^{i\bar{k}\cdot\bar{r}}\, \hat{e}\cdot\bar{p} | n \rangle \right|^2 \delta(\omega - \omega_{in}) \qquad (45)$$

where we have converted energy delta function into a frequency one, leading to an extra $\hbar$ term in the denominator

and $\omega_{in} = \frac{E_i - E_n}{\hbar}$.

If I_0 is the flux (# of photons per unit area per unit time, then the intensity of the radiation field will be

$$\mathcal{I} = \hbar\omega \cdot I_0 = \frac{1}{2}\varepsilon_0 c E^2$$

$$\text{or} \quad \hbar\omega I_0 = \frac{1}{2} 2\varepsilon_0 c \omega^2 A_0^2 \quad \text{--- (46)}$$

and if the corresponding absorption cross section is $\sigma^{(ab)}_{n\to i}(\omega)$, then

$$\Gamma_{n\to i} = I_0 \sigma_{n\to i}(\omega)$$

$$\Rightarrow \sigma^{(ab)}_{n\to i}(\omega) = \frac{\Gamma_{n\to i}}{I_0} = \frac{\pi e^2}{m^2 \hbar \varepsilon_0 c} |\langle i| e^{i\vec{k}\cdot\vec{r}} \hat{e}\cdot\vec{p} |n\rangle|^2 \, \delta(\omega - \omega_{in})$$

using the definition of the fine structure constant α

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$$

$$\Rightarrow \sigma^{(ab)}_{n\to i} = \frac{4\pi^2 \alpha}{m^2 \omega_{in}} |\langle i| e^{i\vec{k}\cdot\vec{r}} \hat{e}\cdot\vec{p} |n\rangle|^2 \delta(\omega - \omega_{in})$$

— (47)

Let us simplify the matrix element $\langle i|e^{i\bar{k}\cdot\bar{r}}\hat{e}\cdot\bar{p}|n\rangle$. We approximate

$$e^{i\bar{k}\cdot\bar{r}} \simeq 1 + i\bar{k}\cdot\bar{r} + \cdots$$

$$\simeq 1 \qquad \text{——— (48)}$$

This approximation is good whenever

$\bar{k}\cdot\bar{r} = \frac{2\pi\hat{n}\cdot\bar{r}}{\lambda} << 1$. This is valid whenever $|r| << \lambda$, i.e. size of the system is much smaller than wavelengths. For microscopic systems

$|r| \sim A^0$

$\lambda \sim 10^3 A^0$ for visible ~~rays~~ and beyond (infrared, microwave, ...)

for such cases

$$\Rightarrow \frac{|r|}{\lambda} << 1$$

and approximation (48) will be good. Now

$M_{in} = \langle i|e^{i\bar{k}\cdot\bar{r}}\hat{e}\cdot\bar{p}|n\rangle \simeq \langle i|\hat{e}\cdot\bar{p}|n\rangle$

But for any H_0 of the form

of Eq (39) we have

$$\frac{\bar{p}}{m} = \frac{1}{i\hbar}[\bar{r}, H_0] = \frac{1}{i\hbar}[\bar{r}, p^2/2m] + \frac{1}{i\hbar}[\bar{r}, V(x)]$$

$$= \frac{1}{i\hbar\, 2m}[\bar{r}, p^2] + 0$$

$$\bar{p} = \frac{2i\hbar\,\bar{p}}{2mi\hbar} = \frac{\bar{p}}{m}$$

$$\Rightarrow \quad \bar{p} = \frac{m}{i\hbar}[\bar{r}, H_0]$$

$$\Rightarrow \langle i|\bar{p}\cdot\hat{e}|n\rangle = \frac{m}{i\hbar}\langle i|[\bar{r}\cdot\hat{e}, H_0]|n\rangle$$

$$= \frac{m}{i\hbar}\{\langle i|\bar{r}\cdot\hat{e}\,H_0|n\rangle - \langle i|H_0\,\bar{r}\cdot\hat{n}|n\rangle\}$$

Using $H_0|i\rangle = E_i|i\rangle$

$H_0|n\rangle = E_n|n\rangle$

$$\Rightarrow \langle i|\bar{p}\cdot\hat{e}|n\rangle = \frac{m(E_i - E_n)}{i\hbar}\langle i|\bar{r}\cdot\hat{e}|n\rangle$$

$$= \frac{m\omega_{in}}{i}\langle i|\bar{r}\cdot\hat{e}|n\rangle$$

under this approximation

$$\sigma_{n\to i}^{(ab)} = 4\pi^2\alpha\,\omega_{in}|\langle i|\bar{r}\cdot\hat{e}|n\rangle|^2\delta(\omega-\omega_{in})$$

note that dipole moment for the electrons

$$\vec{d} = -e\vec{r}$$

$$\Rightarrow \sigma_{n\to i}^{(ab)} = \frac{4\pi^2 \alpha \omega_{in}}{e^2} |\langle i|\vec{d}\cdot\hat{e}|n\rangle|^2 \delta(\omega-\omega_{in})$$

Thus the cross-section depends on the the transition matrix elements of the electric dipole operator, therefore, approximation (48) is called electric dipole approximation. Because $\vec{d}$ is an odd-parity operator, for inversion symmetric systems, states $|i\rangle$ and $|n\rangle$ should have opposite parities for the dipole matrix element $d_{in} \neq 0$.

For example, in atoms optical transitions are possible only between states whose angular momenta differ by one unit ($\Delta l = 1$), because those states will have opposite parities $(-1)^l$. Total absorption cross section for state $|n\rangle$ is defined as

$$\sigma_n^{(ab)}(\omega) = \sum_i \sigma_{ni}^{(ab)}(\omega).$$

[to plot $\sigma_n(\omega)$ we can use line broadening