Chapter 3: Time Dependent Perturbation Theory

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Introduction

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

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

- 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 Eq.(1), requiring the use of approximations.
- One such approach is based on perturbation theory, which is what we discuss next.

- For the purpose, we assume that the Hamiltonian $H(t)$ is of the form

$$H = H_0 + V(t) \tag{2}$$

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

$$H_0 \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle \tag{3}$$

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

$$H_0 \left|n\right\rangle = E_n \left|n\right\rangle \tag{4}$$

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

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

$$|\tilde{\psi}(t)\rangle = e^{i\frac{H_0 t}{\hbar}}|\psi(t)\rangle \tag{5}$$

$$\Rightarrow |\psi(t)\rangle = e^{-\frac{iH_0 t}{\hbar}}|\tilde{\psi}(t)\rangle \tag{6}$$

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

$$i\hbar\frac{d}{dt}\left(e^{-\frac{iH_0 t}{\hbar}}|\tilde{\psi}(t)\rangle\right) = (H_0 + V(t))\, e^{-\frac{iH_0 t}{\hbar}}|\tilde{\psi}(t)\rangle$$

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

Interaction Picture (contd.)

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

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

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

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

where

$$\boxed{\tilde{V}(t) = e^{\frac{iH_0 t}{\hbar}} V(t) e^{-\frac{iH_0 t}{\hbar}}} \tag{8}$$

- 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.

Interaction Picture (contd.)

- 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 (to some initial time) and t to obtain

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

- Because this equation has the unknown solution $|\tilde{\psi}(t)\rangle$ 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 R.H.S

$$\begin{aligned} |\tilde{\psi}(t)\rangle &= |\tilde{\psi}(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt' \tilde{V}(t')|\tilde{\psi}(t_0)\rangle \\ &= \left(1 + \frac{1}{i\hbar}\int_{t_0}^{t} dt' \tilde{V}(t')\right)|\tilde{\psi}(t_0)\rangle \end{aligned} \tag{10}$$

Interaction Picture (contd.)

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

$$|\tilde{\psi}(t)\rangle = |\tilde{\psi}(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt' \tilde{V}(t')|\tilde{\psi}(t_0)\rangle + \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \tilde{V}(t')\tilde{V}(t'')|\tilde{\psi}(t_0)\rangle \tag{11}$$

- If we define a time ordered product as

$$\begin{aligned} T\left[\tilde{V}(t')\tilde{V}(t'')\right] &= \tilde{V}(t')\tilde{V}(t'') \text{ if } t' \geqslant t'' \\ &= \tilde{V}(t'')\tilde{V}(t') \text{ if } t' \leqslant t'' \end{aligned} \tag{12}$$

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

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \tilde{V}(t')\tilde{V}(t'') = \frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' T\left[\tilde{V}(t')\tilde{V}(t'')\right] \tag{13}$$

Interaction Picture (contd.)

- So that to the second order

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

- By iterating the procedure infinite number of times, we obtain

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

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

$$\tilde{U}(t, t_0) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!}\left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} \ldots \int_{t_0}^{t} dt_1' \ldots dt_n' \times T\left[\tilde{V}(t_1')\tilde{V}(t_2')\ldots\tilde{V}(t_n')\right]$$

Interaction Picture (contd.)

leading to the final expression

$$\boxed{\tilde{U}(t, t_0) = T e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' \tilde{V}(t')}} \tag{15}$$

- In case we want to do k-th order perturbation theory, we can expand Eq.(15) upto k-th order, and perform various calculations. Eq.(13) and Eq.(15) form the Dyson series solution of the time dependent perturbation theory.

Linear Combination of Eigenfunctions Approach

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

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

- Note that $e^{-\frac{iE_j t}{\hbar}}$ 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 Eq.(16) in Eq.(1), with $H(t)$ given by Eq.(2), we have

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

$$= \sum_j \left(H_0 a_j(t) + V(t) a_j(t) \right) e^{-\frac{iE_j t}{\hbar}} |j\rangle$$

- Using

$$\begin{aligned} H_0 a_j(t)|j\rangle &= a_j(t) H_0 |j\rangle \\ &= E_j a_j(t) |j\rangle \end{aligned}$$

Linear Combination of Eigenfunctions Approach(contd.)

- we have

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

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

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

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

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

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

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

Linear Combination of Eigenfunctions Approach(contd.)

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

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

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

- Defining

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

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

Linear Combination of Eigenfunctions Approach(contd.)

- where

$$V_{ij}(t) = \langle i \mid V(t) \mid j \rangle \tag{21}$$

- We obtain the matrix form of time dependent Schrödinger equation

$$\boxed{i\hbar \frac{d\tilde{a}_i}{dt} = \tilde{V}(t)\tilde{a}(t)} \tag{22}$$

- Note that so far we have not employed any approximations, as a result of which Eq. 22 is an exact representation of the time-dependent Schrödinger equation.

Time-Dependent Perturbation Theory...

- But, this equation is impossible to solve in most cases.
- Therefore, next we formulate time-dependent perturbation theory (TDPT), which allows us to solve Eq. 22, approximately.
- For the purpose, we introduce a perturbation parameter λ, similar to the case of time-independent perturbation theory, to write

$$\begin{aligned} H_0 + V(t) &\longrightarrow H_0 + \lambda V(t) \\ \tilde{a}(t) &\rightarrow \tilde{a}^{(0)}(t) + \lambda \tilde{a}^{(1)}(t) + \lambda^2 \tilde{a}^{(2)}(t) + \cdots \end{aligned} \tag{23}$$

Linear Combination of Eigenfunctions Approach(contd.)

- Eventually, we will set $\lambda = 1$.
- Substituting Eqs.(22) in Eq.(21), we have

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

- On comparing terms order by order in powers of λ, we have

$$i\hbar \frac{d\tilde{a}^{(0)}}{dt} = 0 \tag{24}$$

$$i\hbar \frac{d\tilde{a}^{(1)}}{dt} = \tilde{V}(t)\tilde{a}^{(0)}(t) \tag{25}$$

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

- or, in general

$$i\hbar \frac{d\tilde{a}^{(k)}}{dt} = \tilde{V}(t)\tilde{a}^{(k-1)}(t) \tag{26}$$

Linear Combination of Eigenfunctions Approach(contd.)

- Clearly, Eq.(26) represents a hierarchy of equations which can be solved iteratively.
- Eq.(24) can be integrated right away

$$\Rightarrow \tilde{a}^{(0)} = \tilde{c} \equiv constant$$

$$where\ \tilde{c} = \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} \tag{27}$$

- Substituting Eq.(27) in Eq.(25), we have

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

Linear Combination of Eigenfunctions Approach(contd.)

- or

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

$$\boxed{\tilde{a}_i^{(1)}(t) = \frac{1}{i\hbar} \sum_j \int_{t_0}^{t} dt' V_{ij}(t') c_j e^{-i\omega_{ji} t'}} \tag{28}$$

- By substituting this expression for $\tilde{a}_i^{(1)}(t)$ in the equation for $\tilde{a}_i^{(2)}(t)$, we can obtain an expression for $\tilde{a}_i^{(2)}(t)$, which will surely be more complicated.
- By employing this iterative procedure, successive higher-order equations can also be solved. Note that as the order becomes higher, the complexity of the underlying equations will increase tremendously.
- Next, we apply TDPT to some specific cases

Example(I): Constant Perturbation- Fermi's Golden Rule

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

$$V(t) = \begin{cases} 0 & for\ t < 0 \\ V & for\ t \geq 0 \end{cases} \tag{29}$$

- 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 p, 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.,

$$a_j(0) = c_j = \delta_{nj} \tag{30}$$

- Using Eq.(29) and Eq.(30) in Eq.(28), we have

$$\tilde{a}_i^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} dt' e^{i\omega_{in}t'} \langle i \mid V \mid n \rangle$$

or

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

Example(I): Constant Perturbation(contd.)

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

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

or

$$\begin{aligned} P_{n\to i}(t) &= \frac{(2 - e^{i\omega_{in}t} - e^{-i\omega_{in}t})}{\hbar^2\omega_{in}^2}|\langle i \mid V \mid n\rangle|^2 \\ &= \frac{2(1 - \cos\omega_{in}t)}{\hbar^2\omega_{in}^2}|\langle i \mid V \mid n\rangle|^2 \\ &= \frac{4\sin^2(\omega_{in}t/2)}{\hbar^2\omega_{in}^2}|\langle i \mid V \mid n\rangle|^2 \end{aligned}$$

or

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

Example(I): Constant Perturbation(contd.)

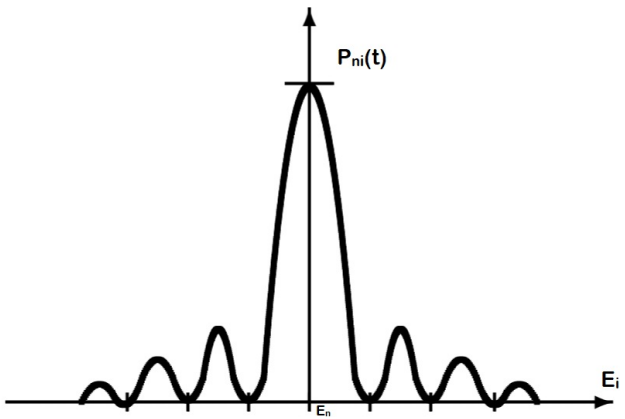
- Using the fact that

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

we can write

$$\boxed{P_{n\to i}(t) = \left(\frac{\sin\frac{E_{in}t}{2\hbar}}{\frac{E_{in}}{2}}\right)^2 |\langle i \mid V \mid n\rangle|^2} \tag{31}$$

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



Example(I): Constant Perturbation(contd.)

- from this curve it is obvious that:
  1. Most of the probability at a given time t is contained within the central maximum

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

  2. The height of central peaks grows as t^2 because $E_n \to E_i$ for $E_{in} \to 0 \Rightarrow \sin^2 \frac{E_{in}t}{2\hbar} \sim \frac{E_{in}^2 t^2}{4\hbar^2}$
  If we take $\Delta E = E_{in}$, then from point (1), it is obvious that the transition probability dominates for the 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 point (1) above it is also obvious that in the large time limit ($t \to \infty$) transition will happen only to those states with the energies $E_i = E_n$, i.e., for which final energy is same as initial energy.

Example(I): Constant Perturbation(contd.)

- If the final energies E_i form a continuum, the total transition probability to all allowed final states is

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

- where $\rho(E_i)$ ≡density of states, i.e., the number of states per unit energy range
- Assuming that the matrix elements $\langle i \mid V \mid n \rangle$ do not vary much with respect to E_i, we have

$$P_n(t) = |\langle i \mid V \mid n \rangle|^2 \int dE_i \rho(E_i) \left(\frac{\sin \frac{E_{in} t}{2\hbar}}{\frac{E_{in}}{2}} \right)^2 \qquad (32)$$

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

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

Example(I): Constant Perturbation(contd.)

we obtain

$$lim_{t\to\infty}\left(\frac{\sin\frac{E_{in}t}{2\hbar}}{E_{in}}\right)^2 \longrightarrow \frac{\pi t}{2\hbar}\delta(E_{in}) \tag{33}$$

- on Eq.(33)$\longrightarrow$Eq.(32) we have

$$\Rightarrow P_n(t) = \frac{2\pi t}{\hbar}|\langle i \mid V \mid n\rangle|^2\rho(E_i)\Big|_{E_i=E_n} \tag{34}$$

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

$$\boxed{\Gamma_n = lim_{t\to\infty}\frac{dP_n(t)}{dt} = \frac{2\pi}{\hbar}|\langle i \mid V \mid n\rangle|^2\rho(E_i = E_n)} \tag{35}$$

Example(I): Constant Perturbation(contd.)

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

$$\boxed{\Gamma_{n\to i} = \frac{2\pi}{\hbar}|\langle i \mid V \mid n\rangle|^2 \delta(E_i - E_n)} \tag{36}$$

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 initial state.

Example(II): Harmonically Varying Perturbation

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

$$V(t) = \begin{cases} 0 & for\ t < 0 \\ V\cos\omega t & for\ t \geq 0 \end{cases} \tag{37}$$

- 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 Eq.(28)

$$\begin{aligned} \tilde{a}_i^{(1)}(t) &= \frac{\langle i \mid V \mid n\rangle}{2i\hbar}\int_0^t dt' \left[e^{i(\omega_{in}+\omega)t'} + e^{i(\omega_{in}-\omega)t'}\right] \\ &= \frac{\langle i \mid V \mid n\rangle}{2i\hbar}\left[\frac{e^{i(\omega_{in}+\omega)t}}{i(\omega_{in}+\omega)} + \frac{e^{i(\omega_{in}-\omega)t}}{i(\omega_{in}-\omega)}\right] \end{aligned} \tag{38}$$

- As before, the transition probability will be $P_{n\to i}(t) = |a_i^{(1)}(t)|^2$

Example(II): Harmonically Varying Perturbation

- When we calculate this probability using Eq.(38), in addition to mod squared terms for the two terms, we will also have cross terms which will be oscillatory in the limit $t \longrightarrow \infty$, and will average out to zero. Thus the transition rate will be just the sum of mod squared of the individual terms which will give rise to delta functions in the limit $t \longrightarrow \infty$, as before, leading to

$$\Gamma_{n\to i} = \frac{2\pi}{\hbar}\frac{|\langle i \mid V \mid n\rangle|^2}{4}\left[\delta(E_i - E_n - \hbar\omega) + \delta(E_i - E_n + \hbar\omega)\right] \tag{39}$$

- 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.

Example(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 the 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

$$\boxed{H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) = \frac{p^2}{2m} + V(r)} \tag{40}$$

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

$$\mathrm{A}(\mathrm{r}, t) = A_0 \hat{e} e^{i(\mathrm{k}.\mathrm{r} - \omega t)} + c.c. \tag{41}$$

  above c.c. implies complex conjugate, while $\hat{e}$ is a unit vector in the the direction of polarization of the incident light.
- From Eq.(41) it is obvious that we are assuming linearly polarised (or plane polarised light).
- Note that this amounts to a semi classical theory in which the matter is treated quantum mechanically, while the radiation is treated classically.

Interaction of Radiation with Matter

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

$$H = \frac{(\mathrm{p} + e\mathrm{A})^2}{2m} + V(r) \tag{42}$$

- Upon expanding the first term, we obtain

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

or

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

- Each term in the Hamiltonian is an operator, which will act on a wave function ψ (say).

- Let us check the action of second term on ψ

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

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

$$= -\frac{ie\hbar}{2m}\left(\boldsymbol{\nabla}\cdot\mathrm{A}\right)\psi - \frac{ie\hbar}{2m}\left(\mathrm{A}\cdot\boldsymbol{\nabla}\right)\psi$$

- On using Eq.(41) for A, we obtain

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

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

$$\Rightarrow \boldsymbol{\nabla}\cdot\mathrm{A} = 0$$

$$\Rightarrow \frac{e}{2m}\mathrm{p}\cdot\mathrm{A}\psi = -\frac{ie\hbar}{2m}\left(\mathrm{A}\cdot\boldsymbol{\nabla}\right)\psi = \frac{e}{2m}\mathrm{A}\cdot\mathrm{p}\psi$$

$$\Rightarrow \mathrm{p}\cdot\mathrm{A} = \mathrm{A}\cdot\mathrm{p},\ \textit{for transversely polarized light}$$

- Thus

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

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

$$H(t) = H_0 + V(t)$$
$$where\ V(t) = \frac{e}{m}\mathrm{A}\cdot\mathrm{p} \tag{43}$$

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

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

or

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

where

$$V_1(\mathrm{r}) = \frac{e}{m}A_0 e^{i\mathrm{k}\cdot\mathrm{r}}\hat{e}\cdot\mathrm{p} \tag{44}$$
$$V_2(\mathrm{r}) = \frac{e}{m}A_0 e^{-i\mathrm{k}\cdot\mathrm{r}}\hat{e}\cdot\mathrm{p}$$

- 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

$$\begin{aligned}\Gamma_{n\to i} &= \frac{2\pi}{\hbar}\Big\{|\langle i \mid V_1 \mid n\rangle|^2\delta(E_i - E_n - \hbar\omega) \\ &\qquad + |\langle i \mid V_2 \mid n\rangle|^2\delta(E_i - E_n + \hbar\omega)\Big\} \\ &= \frac{2\pi e^2 A_0^2}{\hbar m^2}\Big\{|\langle i \mid e^{i\mathrm{k}.\mathrm{r}}\hat{e}.\mathrm{p} \mid n\rangle|^2\delta(E_i - E_n - \hbar\omega) \\ &\qquad + |\langle i \mid e^{-i\mathrm{k}.\mathrm{r}}\hat{e}.\mathrm{p} \mid n\rangle|^2\delta(E_i - E_n + \hbar\omega)\Big\}\end{aligned} \tag{45}$$

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- 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 process ($E_i > E_n$), and drop the second term.
- For handling emission process, one will have to drop the first term. Thus,

$$\Gamma_{n\to i}^{(abs)} = \frac{2\pi e^2 A_0^2}{\hbar m^2} |\langle i \mid e^{i\mathbf{k}\cdot\mathbf{r}} \hat{e} \cdot \mathbf{p} \mid n \rangle|^2 \delta(\omega - \omega_{in}) \qquad (46)$$

- where we have converted energy delta function into a frequency one, leading to an extra term to the denominator and $\omega_{in} = \frac{E_i - E_n}{\hbar}$

- If I_0 is the photon flux (number of photons per unit area per unit time), then the intensity of the radiation will be (the right hand side of this equation is obtained using the concept of Poynting vector)

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

using $\mathrm{E} = -\frac{1}{c}\frac{\partial \mathrm{A}}{\partial t}$

$$\hbar\omega I_0 = 2\varepsilon_0 c\omega^2 A_0^2 \tag{47}$$

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

$$\Gamma_{n\to i} = I_0 \sigma^{(ab)}_{n\to i}(\omega)$$

using Eq. 47

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

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- Using the definition of the fine structure constant α

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

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

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

$$\begin{aligned} e^{i\mathrm{k}\cdot\mathrm{r}} &\approx 1 + i\mathrm{k}\cdot\mathrm{r} + \ldots \\ &\approx 1 \end{aligned} \tag{48}$$

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

$$|\mathrm{r}| \sim \text{Å}$$

$$\lambda \sim 10^3\,\text{Å}\ \textit{for visible range and}$$

$$\textit{beyond}(\textit{infrared}, \textit{microwave}, \ldots)$$

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- For such systems $\Rightarrow \frac{|\mathrm{r}|}{\lambda} << 1$ and approximation (48) will be good. Now

$$M_{in} = \langle i \mid e^{i\mathrm{k}\cdot\mathrm{r}}\hat{e}\cdot\mathrm{p} \mid n\rangle = \langle i \mid \hat{e}\cdot\mathrm{p} \mid n\rangle$$

- But for any H_0 of the form of Eq.(40), we have

$$\begin{aligned}\frac{1}{i\hbar}[\mathrm{r}, H_0] &= \frac{1}{i\hbar}\left[\mathrm{r}, \frac{p^2}{2m}\right] + \frac{1}{i\hbar}[\mathrm{r}, V(r)] \\ &= \frac{1}{i\hbar 2m}\left[\mathrm{r}, p^2\right] + 0 \\ &= \frac{2i\hbar\mathrm{p}}{i\hbar 2m} = \frac{\mathrm{p}}{m}\end{aligned}$$

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

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

- We have

$$\langle i \mid [\mathrm{r}\cdot\hat{\mathrm{e}}, H_0] \mid n\rangle = \langle i \mid \mathrm{r}\cdot\hat{\mathrm{e}}H_0 - H_0\mathrm{r}\cdot\hat{\mathrm{e}} \mid n\rangle$$

- using

$$\langle i|H_0 = E_i\langle i|$$
$$H_0|n\rangle = E_n|n\rangle$$

$$\Rightarrow \langle i \mid \mathrm{p}\cdot\hat{\mathrm{e}} \mid n\rangle = \frac{m(E_i - E_n)i}{\hbar}\langle i \mid \mathrm{r}\cdot\hat{\mathrm{e}} \mid n\rangle$$
$$= mi\omega_{in}\langle i \mid \mathrm{r}\cdot\hat{\mathrm{e}} \mid n\rangle$$

- Under this approximation

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

Note that the dipole moment for the electrons $\mathrm{d} = -\mathrm{er}$

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

- Thus the cross section depends on the transition matrix elements of the electric dipole operator, therefore, approximation (48) is called electric dipole approximation. Because d is an odd parity operator, for inversions symmetric systems, states $|i\rangle$ and $|n\rangle$ should have opposite parity for the dipole matrix element $d_{in} \neq 0$. For example in atoms optical transitions are possible only between states whose angular momentum differ by one unit($\Delta l = 1$), because these states will have opposite parities $(-1)^l$. Total absorption cross section for state $|n\rangle$ is defined as

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