Time Dependent Perturbation Theory

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§ 1 Introduction

Not all problems can be solved exactly. Therefore, we need approximation methods. We have so far discussed approximation methods for energy eigen values and eigen functions. These methods give approximate solution of the eigenvalue problem

$$H\psi_n = E_n\psi_n. \tag{1}$$

The next class of problems, we are interested, require us to solve the time dependent Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi. \tag{2}$$

The exact solution of Eq.(2) can be written as

$$\psi = \exp\Big(\frac{-i\hat{H}(t-t_0)}{\hbar}\Big)\psi(x,t_0) \tag{3}$$

This is valid when $\hat{H}$ is independent of time. Eq.(3) is equivalent to

$$\psi(x,t) = \sum_n C_n \exp\Big(\frac{-iE_n(t-t_0)}{\hbar}\Big)\psi_n(x), \tag{4}$$

where ψ_n are eigenfunctions of the full Hamiltonian and C_n are the expansion coefficients which are computed from the knowledge of the wave function at an initial time $t = t_0$. Thus

$$\psi(x,t_0) = \sum_n C_n\psi_n(x) \tag{5}$$

$$C_n = \int \psi_n^*(x)\psi(x,t_0)dx. \tag{6}$$

This method, outlined above in Eq.(3)-Eq.(6) can be used only if $\hat{H}$ is independent of time and the solution of time independent Eq.(1) can be found. We need a different approach if the Hamiltonian $\hat{H}$ depends on time, or if $\hat{H}$ is time independent but the energy eigenvalues and eigenfunctions cannot be found exactly. There are three important methods to solve time dependent Schrodinger equation approximately.

- In the [*time dependent perturbation theory] we split the total Hamiltonain as*

$$H = H_0 + H' \tag{7}$$

where H_0, called unperturbed Hamiltonian, is independent of time and is such that the time dependent Schrodinger equation for H_0

$$i\hbar\frac{\partial\psi}{\partial t} = H_0\psi \tag{8}$$

can be solved exactly. The perturbing Hamiltonian H' may or may not depend on time. Both cases fall under time dependent perturbation theory when we need to solve the time dependent Schrodinger equation.

- *If the time dependence of the Hamiltonian is small, it varies slowly with time, the approximation scheme is known as adiabatic approximation. It is assumed that the instantaneous eigenvalues and eigenvectors of the Hamiltonian are known at ecah instant of time.*

- *In sudden approximation it is assumed that the time variation of the Hamiltonian is very fast and the Hamiltonian changes with time over only a very short interval of time. For example, consider a particle in a box of size L. If the walls of the box move and the size of the box is suddenly doubled, we may apply sudden approximation.*

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§ 2 Time Dependent Perturbation Theory

In the perturbation theory, one assumes that the total Hamiltonian can be spilt as

$$H = H_0 + H' \tag{9}$$

where H_0 is independent of time and is such that its eigenvalues and eigen functions, *i.e.,* the solutions of the equation

$$H_0 u_n = E_n u_n \tag{10}$$

are known exactly. H' is a perturbation and its matrix elements are assumed to be small compared to the matrix elements of H_0. H' may or may not, depend on time, but H_0 must be independent of time. We shall write

$$H = H_0 + \lambda H' \tag{11}$$

for intermediate steps and set $\lambda = 1$ in the end.

Note that the states represented by u_n are stationary states only when $H' = 0$. If the full Hamiltonian H is different from H_0, $(H' \neq 0)$, the states represented by u_n will not be stationary states. Thus if, at some initial time t_0, the system is in the state represented by one of the eigenfunctions u_i, it will not remain in the same state afterwards. We would like to compute the probability of system being found in a state of u_f at a later time.

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§ 3 Transition Amplitude

We shall at first derive an exact equation for amplitude for transition from an initial state u_i to a final state u_f.

We shall start with the expression

$$H = H_0 + \lambda H' \tag{12}$$

where λ to be set equal to 1 in final answer. The Schrodinger equation is

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \tag{13}$$

We assume that at time $t = t_0$ the wave function of the system is given to be $\phi_0(\vec{r})$ and we want to compute (approx) wave function at time t.

It is assumed that the eigenfunction and corresponding eigenvalues of H_0 are known exactly and will be denoted as u_n and E_n:

$$H_0 u_0 = E_n u_n. \tag{14}$$

To solve Eq.(13) we expand $\psi(x,t)$ as a sum in terms of the stationary states of H_0

$$\psi(x,t) = \sum C_n(t) e^{-i\frac{E_n(t-t_0)}{\hbar}} u_n(x), \tag{15}$$

where C_n, in general, depends on time, because the total Hamiltonian H is different from H_0. At time $t = t_0$ the wave function is given to be $\phi_0(\vec{r})$. Therefore, setting $t = t_0$, in Eq.(15) we get

$$\phi_0(\vec{r}) = \sum_n C_n(t_0) u_n(\vec{r}). \tag{16}$$

Therefore assuming $u_n(\vec{r})$ to be normalized, $C_n(t_0)$ are computed using

$$C_n(t_0) = (u_n, \phi_0). \tag{17}$$

Substituting Eq.(15) in Eq.(13) we shall derive an equation for $C_n(t)$ which will solved by perturbation theory. Therefore Eq.(15) used in Eq.(13) gives

$$\sum_n i\hbar \frac{dC_n(t)}{dt} e^{\frac{-iE_n(t-t_0)}{\hbar}} u_n(x) + \sum_n C_n(t) E_n e^{\left(\frac{-iE_n(t-t_0)}{\hbar}\right)} u_n(x) \tag{18}$$

$$= \quad (H_0 + H') \sum_n C_n(t) e^{-iE_n(t-t_0)/\hbar} u_n(x) \tag{19}$$

$$= \sum_n C_n(t) E_n e^{-iE_n(t-t_0)/\hbar} u_n(x) + \sum_n C_n(t) e^{-iE_n(t-t_0)/\hbar} H' u_n(x) \tag{20}$$

Therefore,

$$\sum_n i\hbar \Big(\frac{dC_n(t)}{dt}\Big) e^{-iE_n(t-t_0)/\hbar} u_n(x) = \sum_n C_n(t) e^{-iE_n(t-t_0)/\hbar} H' u_n(x) \tag{21}$$

Take the scalar product with $u_m(x)$ and use the orthogonality property of u's to get,

$$i\hbar \Big(\frac{dC_m}{dt}\Big) e^{-iE_m(t-t_0)/\hbar} = \sum_n e^{-iE_n(t-t_0)/\hbar} (u_m, H' u_n) \tag{22}$$

or

$$i\hbar \frac{dC_m}{dt} = \sum_n e^{i(E_m - E_n)(t-t_0)/\hbar}(u_m, H' u_n) \tag{23}$$

define $\omega_{mn} = \frac{(E_m - E_n)}{\hbar}$ and write Eq.(23) in the form

$$\boxed{i\hbar\Big(\frac{dC_m}{dt}\Big) = \sum_n e^{i\omega_{mn}(t-t_0)}(u_m, H' u_n) C_n} \tag{24}$$

This is an exact equation. The value of $C_n(t)$ at $t = t_0$ is given by Eq.(17).

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§ 4 Perturbation Theory

We recall some of the equations from the previous section.

$$\begin{aligned} H &= H_0 + H' && (25)\\ H_0 u_n &= E_n u_n && (26)\\ \psi(x,t)\Big|_{t=t_0} &= \phi_0(x) && (27)\\ \psi(x,t) &= \sum_n C_n(t) \exp(-iE_n(t-t_0)/\hbar) u_n(x) && (28) \end{aligned}$$

where the coefficients C_n are functions of time and satisfy an exact equation given by

$$i\hbar \frac{d}{dt} C_n(t) = \sum_n \exp(i\omega_{mn}(t-t_0)) \langle m|H'|n\rangle C_n(t) \tag{29}$$

and the initial condition Eq.(27) on $\psi(x,t)$ implies

$$C_n(0) = (u_n, \phi_0). \tag{30}$$

It should be noted that the time dependence of the coefficients C_n is controlled by the interaction term H' only. In absence any perturbation, *i.e.*, , $H' = 0$ the coefficients C_n become constants independent of time. This is because C_n are the expansion coefficients in the expansion of the wave function in terms of the solutions $\exp(-iE_n(t-t_0)/\hbar)u_n(x)$ of the time dependent equation for the unperturbed Hamiltonian H_0. To obtain the perturbative solution of Eq.(29) we replace H' with $\lambda H'$ and expand C_n in powers of λ. These steps are similar to the steps leading to the Born approximation.

$$C_m(t) = C_m^{(0)}(t) + \lambda C_m^{(1)}(t) + \lambda^2 C_m^{(2)}(t) + \cdots \tag{31}$$

Substituting (31) in Eq.(29) and comparing the coefficients of different powers of λ

we successively get

$$
\begin{aligned}
i\hbar\frac{dC_m^{(0)}}{dt} &= 0 && (32)\\
i\hbar\frac{dC_m^{(1)}}{dt} &= \sum_n \exp(i\omega_{mn}(t-t_0))\langle m|H'|n\rangle C_n^{(0)}(t) && (33)\\
i\hbar\frac{dC_m^{(2)}}{dt} &= \sum_n \exp(i\omega_{mn}(t-t_0))\langle m|H'|n\rangle C_n^{(1)}(t) && (34)
\end{aligned}
$$

In many problems one is interested in computing the transition probability from an initial state u_i to a final state u_f under the action of the perturbation term H'. For such a problem we have

$$
\begin{aligned}
\phi_0(\vec{r}) &= u_i(\vec{r}), && (35)\\
C_m(0) &= (u_m, \phi_i) = (u_m, u_i) = \delta_{im}, && (36)\\
C_m(0) &= \begin{cases} 1 & m = i \\ 0 & m \neq i. \end{cases} && (37)
\end{aligned}
$$

These equations can be solved successively to obtain the coefficients C_m to a desired order of perturbation theory. The first order result is easily found to be

$$\boxed{C_f(t) = \frac{1}{i\hbar}\int_{t_0}^{t}\langle f|H'|i\rangle \exp(i\omega_{fi}(t'-t_0))dt'} \qquad (38)$$

The above result is the basic result from which can be applied to actual problem of interest. Further progress can be made if time variation of H' is known. A simple and commonly encountered situation is the case of periodic perturbation with a single frequency. Assuming that H' varies periodically with time with a single frequency ω we write

$$H' = Fe^{i\omega t} + F^* e^{-i\omega t} \qquad (39)$$

where F is an operator which does not depend on t explicitly. Let us substitute Eq.(39) in Eq.(38) and integrate to get

$$C_f^{(1)}(t) = \langle f|F|i\rangle\left[\frac{e^{i(\omega_{fi}-\omega)t}-1}{-\hbar(\omega_{fi}-\omega)}\right] + \langle f|F^\dagger|i\rangle\left[\frac{e^{-i(\omega_{fi}+\omega)t}-1}{-\hbar(\omega_{fi}+\omega)}\right] \qquad (40)$$

The above results have been derived assuming that the final state corresponds to a discrete energy level. If the final state f corresponds to asome discrete energy level a state in continuum quantity of interest is the transition rate, or the transition probability per unit time. Further discussion and a derivation of the result for the transition probability per unit time, the Fermi Golden rule, will be presented in § 5. Note that when $\omega_{fi} = \pm\omega$ the coefficient C_f diverges signalling breakdown of the perturbation theory due a resonance. This case will be dicsussed in detail in § 6

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§ 5 Fermi Golden Rule

In this section we assume that the perturbation is either independent of time, or varies periodically with a single frequency and that the energy of the final states lies in continuum. In this case the quantity of interest is the transition probability per unit time and we will derive the Fermi Golden rule for this transition probability per unit time.

We shall start from Eq.(40) with $\omega = 0$ and a similar treatment can be for the case $\omega \neq 0$.

When the perturbation term is independent of time the probability amplitude, upto first order,(setting $t_0 = 0$) is given by

$$C_f^{(1)}(t) = \langle f|H'|i\rangle \left(\frac{\exp(i\omega_{fi}t) - 1}{-\hbar\omega_{fi}}\right) \tag{41}$$

and the hence one has

$$|C_f^{(1)}(t)|^2 = \frac{4\sin^2(\omega_{fi}t/2)}{\hbar^2\omega_{fi}^2}\,|\langle f|H'|i\rangle|^2. \tag{42}$$

We plot $|C_f^{(1)}(t)|^2$ in the figure below. Note that $|C_f^{(1)}(t)|^2$ is large for $\omega_{fi} \approx 0$,*i.e.*, , for $E_i \approx E_f$. Only a small range of energy ΔE values

$$\Delta E \approx 2\pi(\hbar/t) \tag{43}$$

have an appreciable transition probability. As $t \to \infty, \Delta E \to 0$ and one recovers conservation of energy. The Eq.(43) suggests that if a measurement is made after time Δt, the accuracy in E will be of the order of $\Delta E \approx h/\Delta t$ which a form of statement of time energy uncertainty relation.

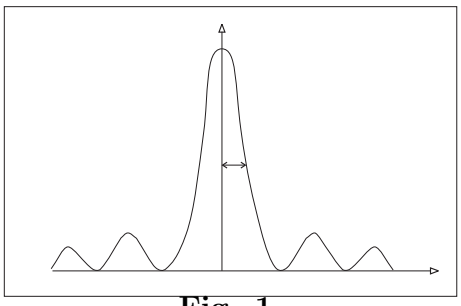

Fig. 1.
*QM-24-F02;*Golden-Rule

Note that the area under the peak increases as t. Thus if we compute the *transition probability* at time t, given by

$$\int_{E-\Delta E}^{E+\Delta E} |C_f^{(1)}(t)|^2 |dE, \tag{44}$$

to a set of states in the energy range E and $E \pm \Delta E$, the answer will be proportional to *time*. In the case of transitions to a state in continuum, the quantity of interest

is the *rate of transitions* to a group of final states having the energy in the range $E \pm \Delta E$, and hence one needs to compute the transition probability per unit time. So we compute

$$\frac{d}{dt}|C_f^{(1)}(t)|^2 = \frac{2}{\hbar}|\langle f|H'|i\rangle|^2\Big(\frac{\sin\omega_{fi}t}{\omega_{fi}}\Big) \tag{45}$$

and for large t this expression tend to

$$\frac{2\pi}{\hbar^2}|\langle f|H'|i\rangle|^2\delta(\omega_{fi}) = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\delta(E_f - E_i) \tag{46}$$

where use has been made of the standard results

$$\lim_{x\to\infty}\frac{\sin kx}{x} = \pi\delta(x) \tag{47}$$

$$\delta(ax) = \frac{1}{|a|}\delta(x) \tag{48}$$

for the Dirac δ function. Hence the required transition probability per unit time to the group of final states, obtained by differentiating Eq.(44) w.r.t. t and denoted by w_{fi}, is given by

$$w_{fi} = \frac{2\pi}{\hbar}\sum_{\text{final states}}|\langle f|H'|i\rangle|^2\,\delta(E_f - E_i) \tag{49}$$

Writing

$$\sum_{\text{final states}}(\cdot) = \int dE_f\rho(E_f)(\cdot) \tag{50}$$

where $\rho(E_f)$ is the density of final states. Using Eq.(50) in Eq.(49) give

$$\boxed{w_{fi} = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\,\rho(E)} \tag{51}$$

where we have set $E_f = E_i = E$. This result, derived by Dirac, was named Golden Rule by Fermi.

When the perturbation varies harmonically with time, we must analyse Eq.(40) and the result is

$$\boxed{w_{fi} = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\,\rho(E_f)} \tag{52}$$

The analysis proceeds by keeping only one of the two terms in Eq.(40) and showing that the other term is not important. The final energy E_f can have only one of the two values $E_i + \hbar\omega$ or $E_i - \hbar\omega$ only.

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Application to scattering

The Fermi Golden rule can be applied to scattering and gives the first Born approximation result for the scattering amplitude. Let the incident beam be described

by plane waves of momentum $\hbar\vec{k}_i$. We wish compute the differential cross section $\sigma(\theta, \phi)$.

We therefore seek the rate of transtion into solid angle $d\Omega$ in the direction of $\vec{k}_f$. The Fermi Golden rule gives the transition probabilty per unit time w to be

$$w_{i\to f} = \frac{2\pi}{\hbar}\rho(k_f)|\langle\vec{k_f}|H'|\vec{k_i}\rangle|^2, \tag{53}$$

where the potential energy is taken to be the perturbation Hamiltonian $H' = V(\vec{(}r))$. We now need to compute the density of states $\rho(\vec{k})$ for the final states. For the initial and final states, we will work with the plane wave solutions with periodic boundary conditions given by

$$u_i(\vec{r}) = \frac{1}{L^{3/2}}\exp(i\vec{k}_i\cdot\vec{r}), \qquad u_f(\vec{r}) = \frac{1}{L^{3/2}}\exp(i\vec{k}_f\cdot\vec{r}). \tag{54}$$

The allowed values of $\vec{k}$ in a box are $k_x = 2\pi n_x/L, k_y = 2\pi n_y/L, k_z = 2\pi n_z/L$ etc. where n_x, n_y, n_z are positive integers. There will be $(L/2\pi)^3 dk_x dk_y dk_z$ states for the propagation vector in the range $\vec{k}$ and $\vec{k} + d\vec{k}$. The range dk is related to the range dE of energy given by

$$E = \frac{\hbar^2k^2}{2\mu} \Rightarrow \frac{dE}{dk} = \frac{\hbar^2 k}{\mu}. \tag{55}$$

and the number of states is

$$\rho(E)dE = \frac{L^3}{(2\pi)^3}dk_x dk_y dk_z \tag{56}$$

where $\rho(E)$ is the density of states. For differential cross section we need to compute the transtion probability to states with final propagation vector in a small range of angles θ, ϕ. The number of states with the direction $\vec{k}$ in the solid angle $d\Omega = \sin\theta\, d\theta\, d\phi$ and magnitude in a small range dk is given by $k^2 d\Omega$. Using Eq.(55), we get

$$\rho(E)dE = \frac{L^3}{(2\pi)^3}k^2\, dk\, d\Omega \Rightarrow \rho(k) = \frac{L^3}{8\pi^3}\frac{\mu\, k}{\hbar^2}d\Omega. \tag{57}$$

Using the density of states (56), wave functions (54), the Golden rule gives the transition probability w

$$w = \frac{2\pi}{\hbar}\rho(E)|\langle\vec{k_f}|H'|\vec{k_i}\rangle|^2 \tag{58}$$

$$= \frac{\mu L^3 k}{(4\pi^2\hbar^3)}|\langle\vec{k_f}|H'|\vec{k_i}\rangle|^2\, d\Omega. \tag{59}$$

Let us now recall the definition of differential cross section. Let a scattering experiment be performed with a total of N particles. The number of particles scattered into solid angle $d\Omega$ per unit time is proportional to the solid angle and to the incident flux. The constant of proportionality is just the differential cross section. The number of particles scattered into the solid angle is just the transition probability w times N. The incident flux is N times the probability current for the

initial state and equals $\frac{N\hbar k}{\mu}$. . Therefore, using (59 for w, and (54) for the wave functions

$$\begin{aligned} N \times w &= \sigma(\theta,\phi) \times d\Omega \times N \times \text{Flux} && (60)\\ N \times \frac{\mu k L^3}{(4\pi^2\hbar^3)} d\Omega &= |\langle \vec{k_f}|H'|\vec{k_i}\rangle|^2\, d\Omega = \sigma(\theta,\phi) \times d\Omega \times \frac{\hbar k}{\mu} && (61)\\ \therefore \sigma(\theta,\phi) &= \frac{\mu^2 l^3}{4\pi^2\hbar^4} |\langle \vec{k_f}|H'|\vec{k_i}\rangle|^2. && (62) \end{aligned}$$

Hence the differential cross section is given by the Born approximation result

$$\boxed{\sigma(\theta,\phi) = \left(\frac{\mu}{2\pi\hbar^2}\right)^2 \left| \int e^{i\vec{q}\cdot\vec{r}} V(\vec{r})\, d^3r \right|^2}, \qquad (63)$$

and $\vec{q} = (\vec{k_i} - \vec{k_f})$ is the momentum transfer.

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§ 6 Probability for Resonance Transitions

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The case of periodic perturbation with a single frequency is an important one for many physical situations including the interaction of radiation with matter. Assuming that H' varies periodically with time with a single frequency ω we write

$$H' = Fe^{i\omega t} + F^* e^{-i\omega t} \qquad (64)$$

where F is an operator which does not depend on t explicitly. Let us substitute Eq.(64) in Eq.(38) and integrate to get

$$C_f^{(1)}(t) = \langle f|F|i\rangle \left[\frac{e^{i(\omega_{fi}-\omega)t} - 1}{-\hbar(\omega_{fi} - \omega)}\right] + \langle f|F^\dagger|i\rangle \left[\frac{e^{-i(\omega_{fi}+\omega)t} - 1}{-\hbar(\omega_{fi} + \omega)}\right]. \qquad (65)$$

In this section we discuss the case of resonance transition from an initial discrete level i to a final discrete level f when the applied perturbation varies harmonically in time. Here the term level refers to an energy level of H_0. The first order perturbation result for a transitions between two discrete levels is given by Eq..(65). When the frequency $\hbar\omega$ is close to one of the two differences $E_i - E_f$, or $E_f - E_i$, the above result blows up and the perturbation theory breaks down. In this case we must get back to the exact equations and analyze them again making a different kind of approximation. We will do so and *solve the resulting approximate equations exactly.*

We start with Eq..(24) after substituting

$$H' = Fe^{i\omega t} + F_1 e^{-i\omega t} \qquad (66)$$

we get

$$\begin{aligned} i\hbar \frac{dC_m(t)}{dt} &= \sum_n \exp\big(i(\omega_{mn} + \omega)t\big)\langle m|F|n\rangle C_n(t) \\ &\quad + \sum_n \exp\big(i(\omega_{mn} - \omega)t\big)\langle m|F^\dagger|n\rangle C_n(t). \qquad (67) \end{aligned}$$

In the perturbation approximation after integration, the large coefficients came from those terms which were multiplied with an exponential with a small argument. For a given ω when there are two energy levels i and f such that $|E_f - E - i|$ matches with $\hbar\omega$, we need to retain *all* the terms involving the two coefficients C_i and C_f in the summation in the right hand side of Eq..(67). Thus the resulting approximate equations to be solved assume the form

$$\begin{aligned} i\hbar\frac{dC_f(t)}{dt} &= \exp\big(i(\omega_{fi}+\omega)t\big)\langle f|F|i\rangle C_i(t) \\ &\quad + \exp\big(i(\omega_{fi}-\omega)t\big)\langle f|F^\dagger|i\rangle C_i(t). \end{aligned} \tag{68}$$

and

$$\begin{aligned} i\hbar\frac{dC_i(t)}{dt} &= \sum_n \exp\big(i(\omega_{if}+\omega)t\big)\langle i|F|f\rangle C_f(t) \\ &\quad + \exp\big(i(\omega_{if}-\omega)t\big)\langle i|F^\dagger|f\rangle C_f(t). \end{aligned} \tag{69}$$

. In these equations we retain only those exponentials which have small arguments. Taking $\hbar\omega \approx (E_f - E_i)$, using the notation $\nu \equiv \omega_{fi} - \omega$, and therefore writing $\omega_{if} + \omega = -\nu$, we get

$$i\hbar\frac{dC_f(t)}{dt} = \langle f|F^\dagger|i\rangle e^{i\nu t}C_i(t) \tag{70}$$

$$i\hbar\frac{dC_i(t)}{dt} = \langle i|F|f\rangle e^{-i\nu t}C_f(t) \tag{71}$$

Next we solve these equations exactly with the initial conditions $C_i(0) = 1, C_f(0) = 0$. The probability of transition from the initial level E_i to the final level E_f at time t is then given by

$$\boxed{P_{i\to f}(t) = \frac{2|\langle f|F|i\rangle|^2}{\hbar^2\Omega^2}|\,\{1-\cos\Omega t\}}, \tag{72}$$

where

$$\Omega^2 = \frac{\hbar^2\nu^2 + 4|\langle f|F|i\rangle|^2}{\hbar^2}. \tag{73}$$

It is to noted that the transition probability is periodic in time with the period $2\pi/\Omega$ and it varies from 0 to a maximum value

$$\frac{2|\langle f|F|i\rangle|^2}{\hbar^2\nu^2 + 4|\langle f|F|i\rangle|^2} \tag{74}$$

For the exact resonance $\nu = \frac{E_f - E_i - \hbar\omega}{\hbar} = 0$ and we get the transition probability to be

$$\boxed{P_{i\to f}(t) = \frac{1}{2}\big(1-\cos 2|\langle f|F|i\rangle|t/\hbar\big)}, \tag{75}$$

and the system makes periodic transitions between the levels i and f with the period $\pi\hbar/|\langle f|F|i\rangle|$.

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Details of Solution

For the resonance transitions the equations satisfied by the coefficients C_i and C_f, Eq..(70) and Eq..(71), are

$$i\hbar\frac{dC_f(t)}{dt} = \langle f|F^\dagger|i\rangle e^{i\nu t}C_i(t) \tag{76}$$

$$i\hbar\frac{dC_i(t)}{dt} = \langle i|F|f\rangle e^{-i\nu t}C_f(t) \tag{77}$$

In this section we solve these equations exactly and obtain expressions for $C_i(t)$ and $C_f(t)$. To solve we define

$$b_f = C_f \exp(-i\epsilon t) \tag{78}$$

so that

$$\frac{d}{dt}C_f(t) = \frac{d}{dt}\Big(b_f e^{i\epsilon t}\Big) \tag{79}$$

$$= \Big(\frac{d}{dt}b_f + i\epsilon b_f\Big)e^{i\epsilon t} \tag{80}$$

Eliminating C_f Eq..(76) and Eq..(77), using Eq..(78) and Eq..(79), we get

$$\dot{C}_i = \frac{1}{i\hbar}\langle i|F|f\rangle b_f \tag{81}$$

and

$$\dot{b}_f + i\epsilon b_f = \frac{1}{i\hbar}\langle f|F^\dagger|i\rangle C_i$$

$$= \frac{1}{i\hbar}\langle f|F|i\rangle^* C_i \tag{82}$$

Eliminating C_i from Eq..(80) and Eq..(82) we get

$$\ddot{b}_f + i\epsilon\dot{b}_f = \frac{1}{i\hbar}\langle f|F^\dagger|i\rangle\dot{C}_i$$

$$= -\frac{|F_{fi}|^2}{\hbar^2}b_f \tag{83}$$

Therefore, we have

$$\ddot{b}_f + i\epsilon\dot{b}_f + \frac{|F_{if}|^2}{\hbar^2}\dot{b}_f = 0 \tag{84}$$

This is a linear differential equation with constant coefficient and can be solved exactly. The solutions of Eq..(84) have the form

$$b_f(t) = \exp(i\alpha t) \tag{85}$$

where α satisfies the equation

$$\alpha^2 + \epsilon\alpha - \frac{|F_{if}|^2}{\hbar^2} \tag{86}$$

The two roots of this equation are $\alpha_\pm$ where

$$\alpha_\pm = -\frac{\epsilon}{2} \pm \Delta \tag{87}$$

where Δ is given by

$$\Delta^2 = \frac{\epsilon^2}{4} + \frac{|F_{if}|^2}{\hbar^2} \tag{88}$$

Substituting back in Eq..(85) the general solution for b_f becomes

$$b_f(t) = A\exp(i\alpha_+ t) + B\exp(i\alpha_- t) \tag{89}$$

and hence

$$C_f(t) = \Big[A\exp(i\alpha_+ t) + B\exp(i\alpha_- t)\Big]\exp(i\epsilon t) \tag{90}$$

We then get, from Eq..(77),

$$\begin{aligned} C_i(t) &= \left(\frac{i\hbar}{F_{if}^*}\right)\big[iA\alpha_+\exp(i\alpha_+ t) + i\alpha_- B\exp(i\alpha_- t) \\ &\quad + i\epsilon A\exp(i\alpha_+ t) + i\epsilon B\exp(i\alpha_- t)\big] \end{aligned} \tag{91}$$

At time $t = 0$, the initial conditions are $C_i(0) = 1$ and $C_f(0) = 0$ giving

$$iA\alpha_+ + iB\alpha_- + i\epsilon(A+B) = F_{if}^*/\hbar \tag{92}$$

$$A + B = 0 \tag{93}$$

Using Eq..(91) and Eq..(92) we get

$$A(\epsilon/2 + \Delta) + B(\epsilon/2 - \Delta) = -\frac{F_{if}^*}{\hbar} \tag{94}$$

or

$$2A\Delta = -\frac{F_{if}}{\hbar} \tag{95}$$

$$A = -\frac{F_{if}}{2\Delta\hbar} \tag{96}$$

$$B = \frac{F_{if}^*}{2\hbar\Delta} \tag{97}$$

Rearranging Eq..(91) and using $B = -A$ we get

$$C_i(t) = \left(\frac{i\hbar}{F_{if}^*}\right)\big[iA(\epsilon+\alpha_+)\exp(i\alpha_+ t) + iB(\epsilon+\alpha_-)\exp(i\alpha_- t)\big] \tag{98}$$

$$= \left(\frac{i\hbar}{F_{if}^*}\right)(iA)\big[(\epsilon+\alpha_+)\exp(i\alpha_+ t) - (\epsilon+\alpha_-)\exp(i\alpha_- t)\big] \tag{99}$$

Substituting for $\alpha_\pm$ from Eq..(87) we get

$$\begin{aligned} C_i(t) &= \left(\frac{i\hbar}{F^*_{if}}\right)\left(\frac{-iF^*_{if}}{2\Delta\hbar}\right) \times \exp(-i\epsilon t/2) \\ &\qquad \times\Big[(\epsilon/2+\Delta)e^{i\alpha_+ t} - (\epsilon/2+\Delta)e^{i\alpha_- t}\Big] \qquad (100) \\ &= \frac{1}{2\Delta}\,\exp(-i\epsilon t/2)\Big[2\Delta\cos(\Delta t) + i\epsilon\sin(\Delta t)\Big] \qquad (101) \end{aligned}$$

and $C_i(t)$ is given by

$$C_i(t) = e^{-i\frac{\epsilon t}{2}}\left(\cos\Delta t + i\frac{\epsilon}{2\Delta}\sin\Delta t\right) \qquad (102)$$

Also Eq..(90) with $B=-A$ gives

$$\begin{aligned} C_f(t) &= A\exp(i\epsilon t)\big[\exp(i\alpha_+ t) - \exp(i\alpha_- t)\big] \qquad (103) \\ &= 2iA\exp(i\epsilon t/2)\sin\Delta t \qquad (104) \\ &= -\Big(\frac{iF^*_{if}}{\Delta\hbar}\Big)\sin\Delta t \qquad (105) \end{aligned}$$

Hence the probability o finding the system in the state f at time t is

$$\begin{aligned} |C_f(t)|^2 &= \frac{|F_{if}|^2}{\Delta^2\hbar^2}\sin^2\Delta t \qquad (106) \\ &= \frac{|F_{if}|^2}{\Delta^2\hbar^2}\sin^2\Big(\frac{\epsilon^2}{4}+\frac{|F_{if}|^2}{\hbar^2}\Big)^{1/2} t \qquad (107) \end{aligned}$$

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§ 7 Examples and Applications

Several important applications will now be taken up briefly where the results of time dependent perturbation are used.

QM-24-02-L2 ▷

I-Transition to a discrete level

We assume that under the action of perturbation the transition takes place to another state of system which corresponds to a discrete level. In this case Eq.(38) is the basic formula, and $|C_{fi}(t)|^2$ gives the probability of a transition at time t from the initial state i to the final state f. We list a few cases of interest.

Interaction switched on adiabatically

We assume that the interaction is switched on at some time and later switched off adiabatically. As an example consider a charged harmonic oscillator moving in a potential $\frac{1}{2}m\omega^2x^2$.

$$H_0 = \frac{P^2}{2m} + \frac{m\omega^2}{2}\,x^2 \qquad (108)$$

Suppose an electric field varying with with time is switched on. This would introduce an extra term in Hamiltonian given by

$$H\prime = -qE(t)x \tag{109}$$

corresponding to the situation when the electric field is independent of x but may change with time. For example, one may have

$$E = E_0(1 - e^{\frac{-t}{t_0}}) \qquad t > 0 \tag{110}$$

with the field being switched on at $t = 0$ and increasing to E_0. The energy levels $(n + \frac{1}{2})\hbar\omega$ of the harmonic oscillator are no longer stationarty states under the action of this electric field. If the system is in the state E_i at time $t = 0$, it has a non zero probability of being in some other state E_f at a later time. The method of time dependent perturbation allows us to compute this probability when the field is weak.

Harmonic Perturbation

Our next case of interest is when the perturbation varies with time with a single frequency. In this case the result Eq.(25) provides the perturbation theory answer for the transition amplitude. This case has application to interaction of electromagnetic radiation with matter. The single frequency case corresponds to a monochromatic radiation.

Resonance Case

An important application of the time dependent perturbation theory is when the perturbation Hamiltonian $H\prime$ varies with time as

$$H' = 2H'_0 \sin(\omega t) \tag{111}$$

when the frequency ω matches with a difference $\frac{E_f - E_i}{\hbar}$ for some final level the probability of transition to E_f becomes very large and is small for all other energy levels. In this case the basic perturbation theory result, Eq.(38), breaksdown. In this case the problem is simplified by working in two level approximation i.e. by neglecting effect of all other energy levels and the inifinite set of coupled equations reduce to two coupled linear equations which can be solved exactly.

$H'(t)$ has a continuous range of frequencies

In this class of examples the perturbation is a superpostion of a continuous range of frequencies. For a pair of specified initial and final states, several frequencies close to the resonance freqeuncy, $(E_f - E_i)/\hbar$, will contribute appreciably and all such contributions must be added up. In this case the result is very similar to that given under Fermi Golden rule. An example of this case is interaction of atoms with white light.

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QM-24-02-L3

II-Transitions to a set of final states in continuum

The cases of interest are further grouped according to the time dependence of the perturbation Hamiltonian $H'(t)$

Interaction $H'(t)$ switched on adiabatically

In the previous case we have considered an example in which a charged harmonic oscillator is subjected to perturbation $\frac{1}{2}m\omega^2x^2$

$$H' = V_0 \exp(-t/t_0) \tag{112}$$

Suppose we place a hydrogen atom between the plates of charged capacitor which is subsequently discharged through a resistance. We may then again ask a question: what is the probability that if at time $t = 0$ H-atom is in an initial state n, after some time t, it will be found in some final, excited, state m. The question is similar to the above example of charged harmonic oscillator and falls under the class of problems mentioned in I.

However, the H- atom offers one more possibility. Under the action of external perturbation, the atom may get ionized and the final energy then does not correspond to a discrete energy level. The transition in this case takes place to a level in the continuum.

Perturbation $H'(t)$ is independent of time

This is, for example, the case for scattering; we are interested in knowing the probability per unit time that a particle gets scattered into solid and $d\Omega$. The differential scattering cross section, $\sigma(\theta, \phi)$ is related to such a probability.

$$\sigma(\theta,\phi) = \frac{\text{prob per unit time of particle getting scattered in solid angle } d\,\Omega}{\text{prob per unit time of a particle in incident beam crossing a unit area}} \tag{113}$$

In case of scattering

$$H = H_0 + V(r) \qquad H_0 = \frac{P^2}{2m} \tag{114}$$

and $V(r)$ is to be treated as perturbation ($H\prime \equiv V(r)$). Here the initial state corresponds to plane waves with momentum $\vec{p}_i$ and final states corresponds to momentum $\vec{p}_f$. The initial and final states are eigenstates of the *unperturbed Hamiltonian* H_0.

In the presence of the potential, the momentum is not conserved and hence the possibility of momentum changing to some final value $\vec{p}_f$ after some time. Note that here ($H\prime = V(r)$) is not dependent on time, but we are still using time dependent method because the question concerns, time evolution of eigen states of H_0 under the action of full Hamiltonian H.

$H'(t)$ varies harmonically with time

An example of interest here is ionization of an atom in presence of an external periodic electric field which varies with a single frequency.

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QM-24-02-L4

III-Periodic perturbation– resonant transition

An important application of the time dependent perturbation theory is when the perturbation Hamiltonian $H\prime$ varies with time as

$$H' = 2H'_0 \sin(\omega t) \tag{115}$$

when the frequency ω matches with a difference $\frac{E_f - E_i}{\hbar}$ for some final level the probability of transition to E_f becomes very large and is small for all other energy levels. In this case problem can be simplified by working in two level approximation i.e. by neglecting effect of all other energy levels.

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§ 8 Tutorial

[1] An arbitrary quantum mechanical system is initially in the state $|0>$. At time $t = 0$ a perturbation of the form $H' = H_0 \exp(-t/T)$ is swithced on. Show that at large times the probability of the system being in the state $|1>$ is given by

$$\frac{|\langle 0|H_0|1\rangle|^2}{(\hbar/T)^2 + (\Delta E)^2}$$

where ΔE is the energy difference betwen the states $|0\rangle$ and $|1\rangle$.

[2] A particle of charge e is confined to a cubical box of side $2b$. An electric field $\vec{E}$ given below is applied to the system.

$$\vec{E} = \begin{cases} (0 & t < 0 \\ \vec{E_0} \exp(-\alpha t) & t > 0) \end{cases}$$

where $\alpha > 0$, The vector E_0 is perpendicular to one of the surfaces of the box. To the lowest order in E_0 calculate the probability that the charged particle, in the ground state at time $t = 0$, is excited to the first state at time $t = \infty$.

[3] A particle of charge q moving in one dimension is initially bound to a delta function potential at the origin. From time $t = 0$ to $t = \tau$ it is exposed to a constant electric field $\mathcal{E}$ in the x direction.

(a) Assume that the continuous energy wave functions may be approximated by the free particle wave functions, find the density of states as $\rho(E)$ as function of energy E

(b) Assuming that the electric field may be treated as a perturbation find the probability that the particle will be found in a continuous energy state with energy in the range E and $E + dE$ if at time $t = 0$ it was known to be in the bound state.Sss

You may assume that the normalized bound state wave function for the delta function potential $V(x) = -\gamma\delta(x)$ is given by,

$$u(x) = \sqrt{\frac{m\gamma}{\hbar^2}} \exp(-\tfrac{m\gamma}{\hbar^2}|x|)$$