Time dependent Perturbation Theory

In a large number of systems the Hamiltonian may depend on time resulting in the absence of stationary states. Again perturbation methods can be applied for those problems in which the Hamiltonian H may be written as the sum of two terms.

$$H(r,t) = H^0(r) + H'(r,t) \rightarrow (1)$$

Where $H^0(r)$ is the time independent and H'(r,t) is the time-dependent part. Our main interest is in problems for which $H' << H^0$. The time - dependent schrödinger equation to be solved is

$$i\hbar \frac{\partial \Psi}{\partial t} = H(r,t)\, \Psi(r,t) \rightarrow (2)$$

Where H(r,t) is of the form given in Equ (1). Let ${\Psi_n}^0$, n = 1, 2, 3, ... be the stationary state eigenfunctions of the unperturbed Hamiltonian H^0 forming a complete orthonormal set. The ${\Psi_n}^0$ are of the form.

$${\Psi_n}^0 = {\Psi_n}^0 \exp\left(-\frac{iE_n t}{\hbar}\right) \rightarrow (3) \qquad n = 1, 2, \ldots$$

And obey the equations

$$i\hbar \frac{\partial {\Psi_n}^0}{\partial t} = H^0 {\Psi_n}^0 \rightarrow (4)$$

In the presence of the perturbation H'(t), the states of the system may be expressed as a linear combination of ${\Psi_n}^0$ as

$$\Psi(r,t) = \sum_n c_n(t)\, {\Psi_n}^0 = \sum_n c_n(t)\, {\Psi_n}^0(r) \exp\left(-\frac{iE_n t}{\hbar}\right) \rightarrow (5)$$

Where c_n(t)'s are expansion coefficients. Substituting Equ (1) and (5) in Equ (2)

$$i\hbar \frac{\partial}{\partial t} \sum_n c_n(t)\, {\Psi_n}^0(r) \exp\left(-\frac{iE_n t}{\hbar}\right) = (H^0 + H') \sum_n c_n(t)\, {\Psi_n}^0(r) \exp\left(-\frac{iE_n t}{\hbar}\right) \rightarrow 6$$

Using eqs (4) and (3), Equ (6) reduces to

$$I\hbar \sum_n \frac{d}{dt} c_n(t)\, {\Psi_n}^0 \exp\left(-\frac{iE_n t}{\hbar}\right) = \sum_n c_n(t)\, H' {\Psi_n}^0 \exp\left(-\frac{iE_n t}{\hbar}\right) \rightarrow (7)$$

For convenience, we shall use the Dirac's notation for states. Multiplying Eq (7) from left by $\langle k|$ and using orthonormality of states.

$$i\hbar \frac{d\, c_k(t)}{dt} = \sum_n c_n(t)\, \langle k|\, H' |n\rangle \exp \frac{i(E_k - E_n)t}{\hbar}$$

$$i\hbar \frac{d\, c_k(t)}{dt} = \sum_n c_n(\mathrm{t})\, H_{kn}{}'\ \exp\,(\mathrm{i}\omega_{kn}\mathrm{t}) \quad \rightarrow (8)$$

Where

$$H_{kn}{}' = \langle \Psi_k{}^0 | H' \ | \Psi_n{}^0 \rangle = \langle k |\ H'\ | n \rangle \text{ and } \omega_k = \frac{(E_k - E_n)}{\hbar} \quad \longrightarrow (9)$$

The summation symbol in Equ (8) stands for summation over the discrete states and integration over the continuum states.

First - Order Perturbation

Replacing H' by $\lambda H'$ as in time - independent perturbation theory and expressing the coefficient $c_n(t)$ as a power series in λ

$c_n(t) = c_n{}^0(t) + \lambda^1 c_n{}^1(t) + \lambda^2 c_n{}^2(t) + \ldots \quad \rightarrow (10)$

Substituting the value of $c_n(t)$ in Equ (8) and replacing $H_{kn}{}'$ by $\lambda H_{kn}{}'$

$$i\hbar \left(\frac{dc^{(0)}{}_k}{dt} + \lambda^1 \frac{dc_k{}^1}{dt} + \lambda^2 \frac{dc^{(2)}{}_k}{dt} + \ldots \right)$$

$$= \sum_n \lambda\, H_{kn}{}'(\mathrm{r,t})\, (c_n{}^0(t) + \lambda^1 c_n{}^1(t) + \lambda^2 c_n{}^2(t) + \ldots)\ \exp\,(\mathrm{i}\omega_{kn}\mathrm{t}) \rightarrow$$

(11)

Equating the coefficients of $\lambda^0, \lambda^1, \lambda^2$

$$\frac{dc^{(0)}{}_k}{dt} = 0 \rightarrow (12)$$

$$i\hbar \frac{dc_k{}^1}{dt} = \sum_n c^{(0)}{}_n\, H_{kn}{}'\ \exp\,(\mathrm{i}\omega_{kn}\mathrm{t}) \quad \rightarrow (13)$$

$$i\hbar \frac{dc_k{}^{(2)}}{dt} = \sum_n c^{(1)}{}_n\, H_{kn}{}'\ \exp\,(\mathrm{i}\omega_{kn}\mathrm{t}) \rightarrow (14)$$

Equation (12) implies that the coefficient $c_k{}^0$ is constant in time which is understandable as the Zero - order Hamiltonian is time - independent. From (13) first order contribution to c_n is

$$c_n{}^1(t) = \frac{1}{i\hbar} \int \sum_n c^{(0)}{}_n\ H_{kn}{}'(\mathrm{r,t})\ \exp\,(\mathrm{i}\omega_{kn}\mathrm{t})\ \mathrm{dt} \ \rightarrow (15)$$

For times after t , $H' = 0$ and $c_k = c_k$ (t) for time greater than t. Equation (15) reduces to

$$c_n{}^1(t) = \frac{1}{i\hbar} \int_0^t \int\ H_{kn}{}'(\mathrm{r,t'})\ \exp\,(\mathrm{i}\omega_{kn}\mathrm{t'})\ \ \mathrm{dt'} \ \rightarrow (16)$$

The perturbation H' has induced transition to other states and after time t the probability that a transition to state k has occurred is given by $|c_k{}^1(t)|^2$. Instead , if the system is in a more complicated initial state, one can study its behaviour by a superposition process.

Fermi's Golden Rule

Consider the transition from a discrete state n to a continuum of states around E_k, where the density of the state is ρ(E_k). The number of states in the energy range E_k to (E_k+dE_k) is ρ(E_k) dE_k and total probability for transition into range dE_k is

$$P(t) = \frac{4}{\hbar^2}\int_{dE_k} |H_{kn}'|^2 \frac{\sin^2(\omega_{kn}-\omega)t/2}{(\omega_{kn}-\omega)^2} \rho(E_k)dE_k \rightarrow (17)$$

When t is large, the width of the main peak becomes small and only limited number of final states contribute to the above integral. Consequently, we can regard H_{kn}' and ρ(E_k) as constants over this range .

To evaluate the integral, the variable of integration may be changed from E_k to x by defining

$$X = \frac{(\omega_{kn}-\omega)}{2} = \left(\frac{(E_k-E_n)}{\hbar} - \omega\right)\frac{t}{2}; \qquad dx = \frac{t}{2\hbar} dE_k \rightarrow (18)$$

Equ (17) changes to

$$P(t) = \frac{2t}{\hbar} |H_{kn}'|^2 \rho(E_k) \int \frac{\sin^2 x}{x^2} dx \rightarrow (19)$$

The transition from the state E_n into a state E_k can be on either side of E_n. Though the integral is over a small range $(\omega_{kn} - \omega)$, the limits on x can be extended to $\pm\infty$ as the integrand is very small outside the actual range. The integral is a standard one and is given by

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi \rightarrow (20)$$

Equ (19) take the very simple form

$$P(t) = \frac{2\pi}{\hbar} t\ |H_{kn}'|^2 \rho(E_k) \rightarrow (21)$$

The number of transitions per unit time called transition probability, is usually denoted by the letter ω

$$\omega = \frac{2\pi}{\hbar} |H_{kn}'|^2 \rho(E_k) \rightarrow (22)$$

Equation (22) is called Fermi's Golden Rule. The transition probability is proportional to the square of the matrix element of the amplitude of the Harmonic perturbing term between states n and k to the density of final states. The intensities of spectral lines are proportional to these transition probabilities as they depend on the rate of transfer of energy between the electromagnetic field of the system.