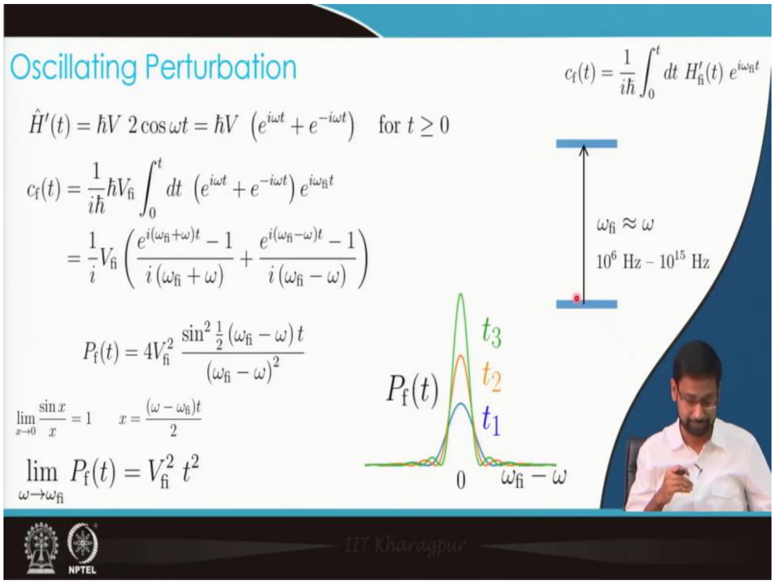
Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture 41: Oscillating Perturbation

Hello students! Welcome to this lecture. In the last few lectures we have been discussing the time dependent perturbation theory. In the last lecture we looked at a special case of perturbation where the time dependent-perturbation was a slowly switched constant perturbation. In that case, we saw that when we apply a slowly switched constant perturbation and wait for a long time, the time-dependent perturbation theory gives us the same results as obtained by the time-independent perturbation theory. However, in the present lecture we will look at a slightly more complicated problem, that relates to an oscillating perturbation. This occurs, for example, when molecular systems interact with electromagnetic radiation, in a spectroscopic experiment. Throughout the spectroscopic experiment, the radiation continuously interacts with the matter.

(Refer Slide Time: 01:58)



Oscillating Perturbation

$$c_f(t) = \frac{1}{i\hbar}\int_0^t dt\ H'_{fi}(t)\ e^{i\omega_{fi}t}$$

$$\hat{H}'(t) = \hbar V\ 2\cos\omega t = \hbar V\ \left(e^{i\omega t} + e^{-i\omega t}\right) \quad \text{for } t \geq 0$$

$$c_f(t) = \frac{1}{i\hbar}\hbar V_{fi}\int_0^t dt\ \left(e^{i\omega t} + e^{-i\omega t}\right) e^{i\omega_{fi}t}$$

$$= \frac{1}{i}V_{fi}\left(\frac{e^{i(\omega_{fi}+\omega)t} - 1}{i\,(\omega_{fi}+\omega)} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i\,(\omega_{fi}-\omega)}\right)$$

$$P_f(t) = 4V_{fi}^2\,\frac{\sin^2\frac{1}{2}(\omega_{fi}-\omega)\,t}{(\omega_{fi}-\omega)^2}$$

$$\lim_{x\to 0}\frac{\sin x}{x} = 1 \qquad x = \frac{(\omega-\omega_{fi})t}{2}$$

$$\lim_{\omega\to\omega_{fi}} P_f(t) = V_{fi}^2\ t^2$$

From the previous lecture, we derived the following relation for the coefficient of the final state due to a time-dependent perturbation ($H'(t)$) as,

$$c_f(t) = \frac{1}{i\hbar}\int_0^t dt\ H'_{fi}(t)\ e^{i\omega_{fi}t}$$

When we have an oscillating perturbation, i.e.,

$$\hat{H}'(t) = \hbar V \; 2\cos\omega t = \hbar V \;\; \left(e^{i\omega t} + e^{-i\omega t}\right) \quad \text{for } t \geq 0$$

we can obtain $c_f(t)$ as,

$$\begin{aligned} c_{\text{f}}(t) &= \frac{1}{i\hbar}\hbar V_{\text{fi}} \int_0^t dt \;\; \left(e^{i\omega t} + e^{-i\omega t}\right) e^{i\omega_{\text{fi}} t} \\ &= \frac{1}{i} V_{\text{fi}} \left(\frac{e^{i(\omega_{\text{fi}}+\omega)t} - 1}{i\left(\omega_{\text{fi}} + \omega\right)} + \frac{e^{i(\omega_{\text{fi}}-\omega)t} - 1}{i\left(\omega_{\text{fi}} - \omega\right)} \right) \end{aligned}$$

Here, V_{fi} is the coupling strength between the stationary states *i* and *f* via the perturbation, ω_{fi} is the energy difference between the two stationary states, and ω is the frequency of oscillation of the perturbation (in case of electromagnetic radition, this is the frequency of the radiation). The terms in the round brackets in the last expression, have oscillatory functions in the numerator. The ω in the denominator can have very large values (10^6-10^{15} Hz for radio-wave to UV radiation), thus making the first term negligible. On the other hand, the second term can have small or large values depending on the value of ω_{fi}. Hence, ignoring the first term in the barckets, from the above value of the coefficient, we can obtain the population of the final state as,

$$P_{\text{f}}(t) = 4V_{\text{fi}}^2 \; \frac{\sin^2 \frac{1}{2}\left(\omega_{\text{fi}} - \omega\right) t}{\left(\omega_{\text{fi}} - \omega\right)^2}$$

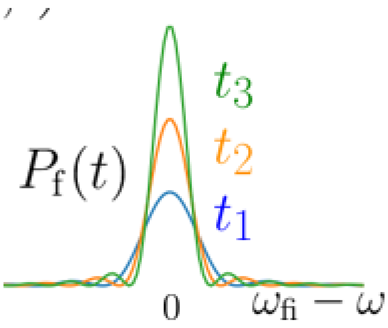
When, $\omega_{\text{fi}} \sim \omega$, the above expression can be evaluated as

$$\lim_{\omega \to \omega_{\text{fi}}} P_{\text{f}}(t) = V_{\text{fi}}^2 \; t^2$$

where, the following relation is used:

$$\lim_{x \to 0} \frac{\sin x}{x} = 1 \qquad x = \frac{(\omega - \omega_{\text{fi}})t}{2}$$

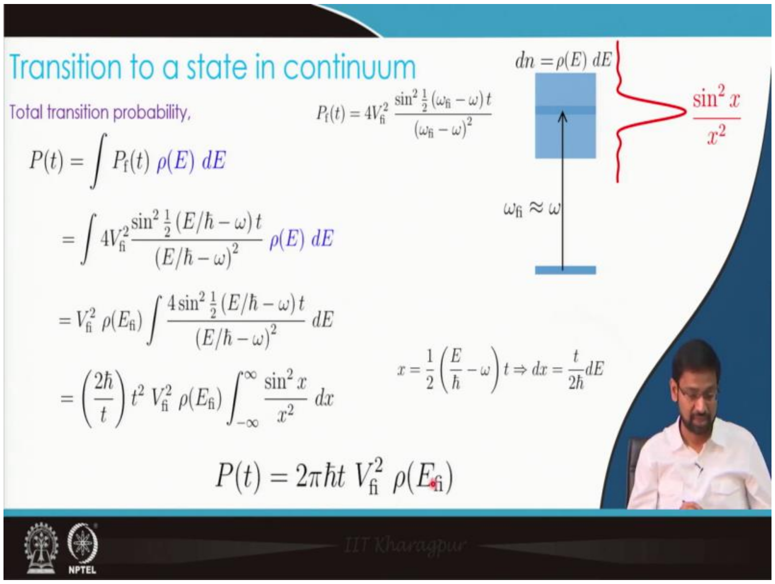
If we plot the population of the final state against $\omega_{\text{fi}} - \omega$, we see that the population peaks at $\omega_{\text{fi}} = \omega$ and it decays quickly when this resonance condition is not met. The other interesting feature observed here is that the population increases as t^2 at the resonance condition.



At the resonating condition ($\omega_{\mathrm{fi}} = \omega$), the rapid population transfer is reminiscent of the special case of Rabi oscillation for a degenerate 2-state system. When the two states are degenerate, even a minor perturbation was sufficient for a complete population transfer from state 1 to state 2. In the case of oscillating perturbation, when the resonance condition is met, the energy of the state *i* added with the radiation energy matches exactly to the energy of the final state. Here, as if the radiation (under resonating condition) introduces a degeneracy between the initial and final state. This causes a rapid population transfer.

In the above figure, you would notice that as time progresses, the peak height increases quadratically with *t*, while the peak width decreases with *t*. As a result, the overall population transfer occurs as a function of *t*.

(Refer Slide Time: 18:03)



Transition to a state in continuum

Total transition probability,

$$P_{\mathrm{f}}(t) = 4V_{\mathrm{fi}}^2 \frac{\sin^2 \frac{1}{2}(\omega_{\mathrm{fi}} - \omega)t}{(\omega_{\mathrm{fi}} - \omega)^2}$$

$$P(t) = \int P_{\mathrm{f}}(t)\ \rho(E)\ dE$$

$$= \int 4V_{\mathrm{fi}}^2 \frac{\sin^2 \frac{1}{2}(E/\hbar - \omega)t}{(E/\hbar - \omega)^2}\ \rho(E)\ dE$$

$$= V_{\mathrm{fi}}^2\ \rho(E_{\mathrm{fi}}) \int \frac{4\sin^2 \frac{1}{2}(E/\hbar - \omega)t}{(E/\hbar - \omega)^2}\ dE$$

$$x = \frac{1}{2}\left(\frac{E}{\hbar} - \omega\right)t \Rightarrow dx = \frac{t}{2\hbar} dE$$

$$= \left(\frac{2\hbar}{t}\right) t^2\ V_{\mathrm{fi}}^2\ \rho(E_{\mathrm{fi}}) \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\ dx$$

$$P(t) = 2\pi\hbar t\ V_{\mathrm{fi}}^2\ \rho(E_{\mathrm{fi}})$$

So far, we have discussed the population transfer from one initial state to one final state. Often, the final state (an excited state) lies closely spaced with many other excited states. Here, we will discus the case where the final state is part of a continuum, i.e., there are many closely spaced states, with density of states (i.e., number of states per unit energy), given by $\rho(E)$. The number of states present in an energy range dE is given by $dn = \rho(E)dE$. The total transition probability from the initial state *i* to this continuum of dn states is given by,

$$P(t) = \int P_{\mathrm{f}}(t)\ \rho(E)\ dE$$

From previous slide, we have obtained

$$P_{\mathrm{f}}(t) = 4V_{\mathrm{fi}}^2 \, \frac{\sin^2 \frac{1}{2}\left(\omega_{\mathrm{fi}} - \omega\right) t}{\left(\omega_{\mathrm{fi}} - \omega\right)^2}$$

Hence the total transition probability $P(t)$ becomes,

$$= \int 4V_{\mathrm{fi}}^2 \frac{\sin^2 \frac{1}{2}\left(E/\hbar - \omega\right) t}{\left(E/\hbar - \omega\right)^2} \; \rho(E) \; dE$$

where, ω_{fi} is replaced by $E/\hbar$, where E is the energy difference between the initial state and the continuum. The above integral contains a $\sin^2 x/x^2$ term which peaks at the resonance condition, hence we can write the above expression for $P(t)$ as,

$$= \left(\frac{2\hbar}{t}\right) t^2 \; V_{\mathrm{fi}}^2 \; \rho(E_{\mathrm{fi}}) \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} \; dx$$

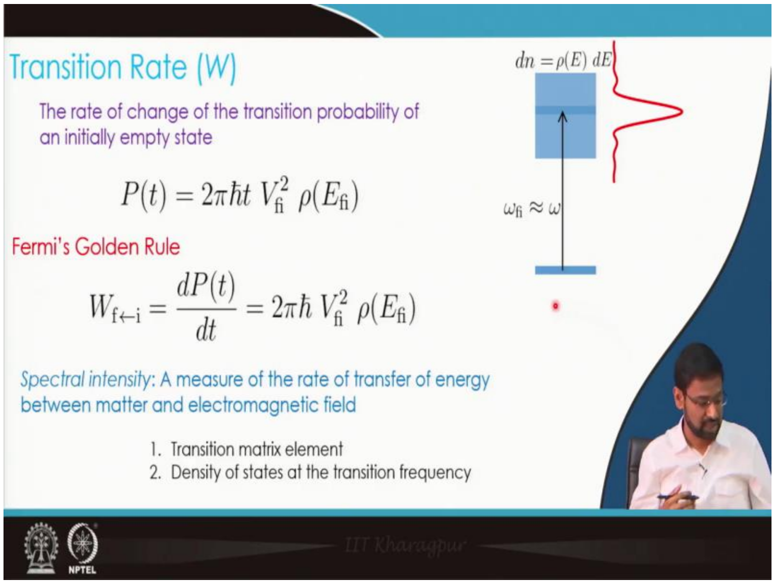
where,

$$x = \frac{1}{2}\left(\frac{E}{\hbar} - \omega\right) t \Rightarrow dx = \frac{t}{2\hbar} dE$$

Note, since the function under the integral is zero beyond a narrow range of x, hence the change in the integration limit from $-\infty$ to $+\infty$, is acceptable. The above expression for $P(t)$ can be further simplified to

$$P(t) = 2\pi\hbar t \; V_{\mathrm{fi}}^2 \; \rho(E_{\mathrm{fi}})$$

(Refer Slide Time: 26:44)



Transition Rate (W)

The rate of change of the transition probability of an initially empty state

$$P(t) = 2\pi\hbar t \; V_{\mathrm{fi}}^2 \; \rho(E_{\mathrm{fi}})$$

Fermi's Golden Rule

$$W_{\mathrm{f}\leftarrow\mathrm{i}} = \frac{dP(t)}{dt} = 2\pi\hbar \; V_{\mathrm{fi}}^2 \; \rho(E_{\mathrm{fi}})$$

Spectral intensity: A measure of the rate of transfer of energy between matter and electromagnetic field

1. Transition matrix element
2. Density of states at the transition frequency

Starting from the above expression of the total transition probability, we can obtain the rate of change of the transition probability or the transition rate as,

$$W_{\mathrm{f}\leftarrow\mathrm{i}} = \frac{dP(t)}{dt} = 2\pi\hbar\ V_{\mathrm{fi}}^{2}\ \rho(E_{\mathrm{fi}})$$

The above expression is known as the Fermi's golden rule. The transition rate from an initially occupied state i to an initially empty state f, depends on two quantities, the transition matrix element V_{fi} and the density of states at the transition frequency$\rho(E_{\mathrm{fi}})$. This equation has a great practical application, because transition rate can be used to estimate the spectral intensity observed in a spectroscopic experiment.

Thank you for your attention.