Approximate Methods in Quantum Chemistry
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Lecture 40: Slowly Switched Constant Perturbation

Hello students! Welcome to this lecture. In the previous two lectures we have been discussing the time-dependent behavior of a quantum mechanical system. We first considered the systems where the Hamiltonian is time-independent and then considered the case where the Hamiltonian shows explicit time dependence. Before we proceed further in the present lecture, let us review some of the key results discussed so far.

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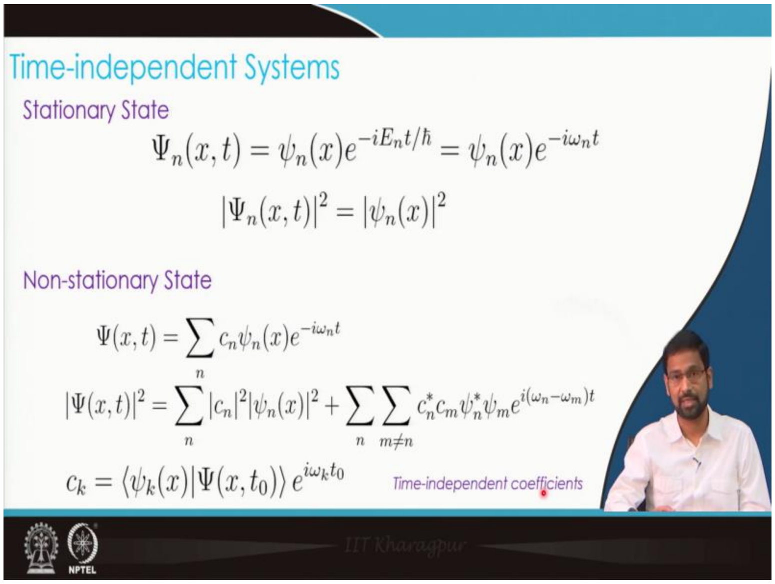

When the Hamiltonian is independent of time, a state with precise energy is known as a stationary state. The stationary state associated with an eigenstate ψ_n and energy E_n is given by,

$$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar} = \psi_n(x)e^{-i\omega_nt}$$

The above state is called stationary state since the probability density of the state is independent of time, i.e.,

$$|\Psi_n(x,t)|^2 = |\psi_n(x)|^2$$

The stationary states are obtained as long as the state of the system has a precise energy. When the state of the system is described as a linear combination of several eigenstates of the system, and hence an uncertainty in the corresponding energy, the corresponding probability density shows explicit time dependence.

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-i\omega_n t}$$

$$|\Psi(x,t)|^2 = \sum_n |c_n|^2 |\psi_n(x)|^2 + \sum_n \sum_{m \neq n} c_n^* c_m \psi_n^* \psi_m e^{i(\omega_n - \omega_m)t}$$

As can be seen, the second term in the above equation shows explicit time dependence. This results in the non-stationary state. Here the coefficients are given by the relation,

$$c_k = \langle \psi_k(x) | \Psi(x, t_0) \rangle \, e^{i\omega_k t_0}$$

Since the coefficients are determined from the initial value of the wave function (at time t_0), the coefficients do not evolve with time, rather their values do not change from the values obtained at $t = t_0$.

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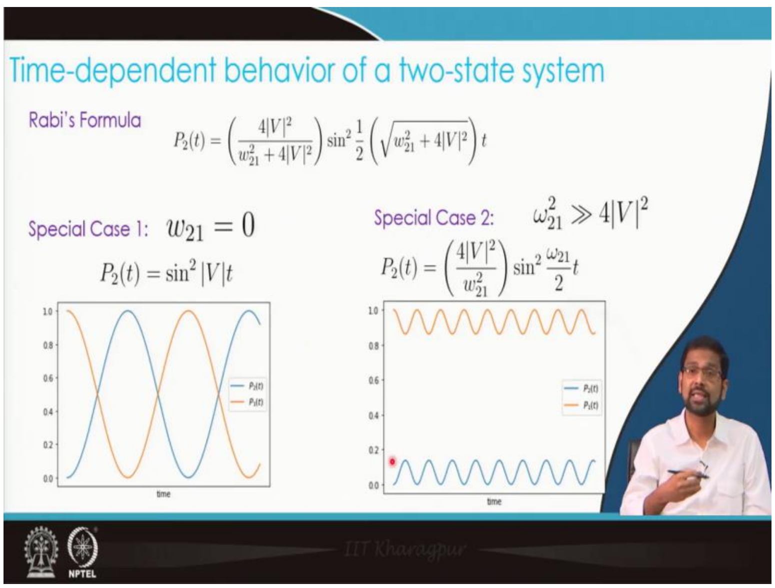

Now let us consider a case where the Hamiltonian has explicit time dependence. In that case, we considered the time dependent part of the Hamiltonian as a perturbation to the time independent part of the Hamiltonian, which was considered as the unperturbed system. We used this perturbation theory for a 2-state problem and obtained the Rabi formula.

$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2 + 4|V|^2}\right) \sin^2 \frac{1}{2} \left(\sqrt{w_{21}^2 + 4|V|^2}\right) t$$

The above relation shows the time-evolution of the population of the initially empty state (state 2). As can be seen, the population depends on the strength of the perturbation $|V|$ and the energy difference between the two stationary states ($\hbar\omega_{12}$). We then considered two special cases. In the first case, we took the two stationary states as degenerate and obtained,

$$P_2(t) = \sin^2 |V|t$$

which shows that the population of state 2 oscillates between 0 and 1, no matter how weak the perturbation is. We can select a particular configuration of the two states, by switching off the perturbation at a certain value of t. In the second special case, we considered the opposite scenario, i.e., the energy difference between the two stationary states is very large (as compared to the perturbation strength), i.e., $\omega_{21}^2 \gg 4|V|^2$. For this case, we obtained,

$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2}\right) \sin^2 \frac{\omega_{21}}{2} t$$

which shows that the population of state 2 oscillates between 0 and the pre-factor in the above relation. Maximum population of state 2 now depends on the strength of the perturbation as well as on the energy difference between the two states. It shows that a weak perturbation will lead to a marginal transfer of population from state 1 to state 2.

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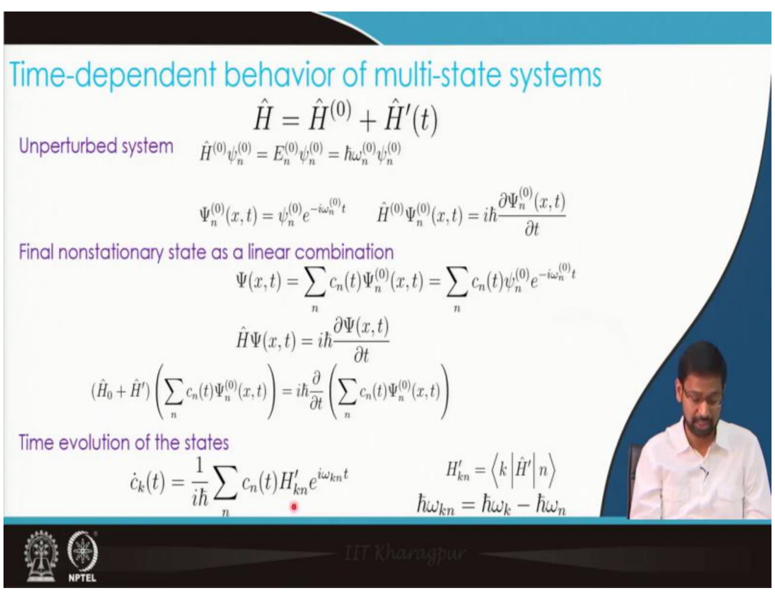

Next, let us extend our discussion to a multi-state system. The total Hamiltonian is divided into two parts: time-independent part (the unperturbed system) and the time-dependent part (the perturbation). The solution of the unperturbed system results in n number of stationary states. The final state is expressed as a superposition of these stationary states,

$$\Psi(x,t) = \sum_n c_n(t)\Psi_n^{(0)}(x,t) = \sum_n c_n(t)\psi_n^{(0)} e^{-i\omega_n^{(0)} t}$$

which follows the following time-dependent Schrodinger equation, $\hat{H}\Psi(x,t) = i\hbar \dfrac{\partial \Psi(x,t)}{\partial t}$

By following the strategy similar to the 2-state problem, we obtain the time-evolution of the coefficient of the state k as

$$\dot{c}_k(t) = \frac{1}{i\hbar}\sum_n c_n(t) H'_{kn} e^{i\omega_{kn} t}$$

where, $H'_{kn} = \left\langle k \left| \hat{H}' \right| n \right\rangle$ represents the perturbation Hamiltonian matrix element between the stationary state k and n, whose energy difference is given by, $\hbar\omega_{kn} = \hbar\omega_k - \hbar\omega_n$

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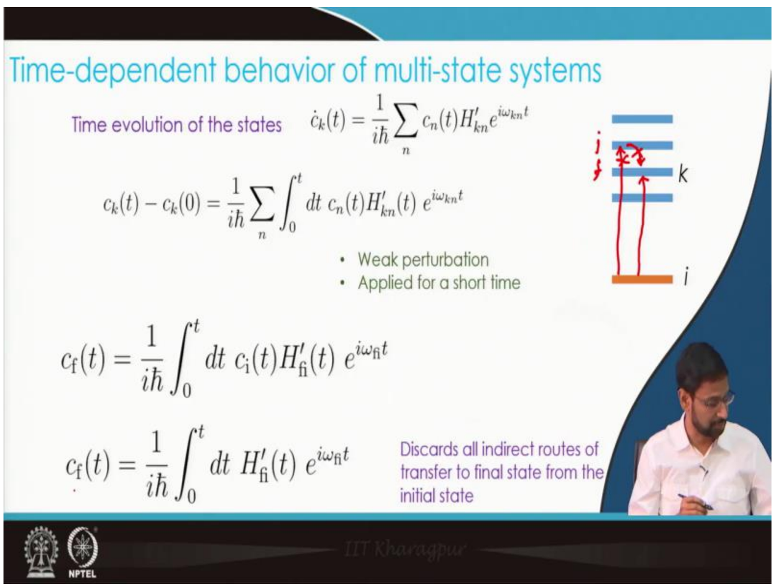

The above equation shows that the time evolution of the state k depends on all stationary states of the system. To solve this particular equation, we can integrate both LHS and RHS time t = 0 to t,

$$c_k(t) - c_k(0) = \frac{1}{i\hbar}\sum_n \int_0^t dt\ c_n(t) H'_{kn}(t)\ e^{i\omega_{kn} t}$$

Before attempting to proceed with the above equation, let us make two approximations, i.e., let us assume the perturbation is weak and is applied for a short duration. This restricts our discussion to the first-order time dependent perturbation. When the perturbation is weak and is applied for a short period of time, the coefficients are not going to change drastically from their initial values. If at the start of the experiment, the system is in a state i, the coefficient $c_i = 1$ while $c_{j\neq i} = 0$.

This simplifies the summation to a single term,

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

where, c_{f} is the coefficient of the final state (initially empty) and c_{i} is that of the initially occupied state. Furthermore, if the perturbation is weak and short, $c_{\mathrm{i}} \sim 1$,

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

The above relation shows that the population of the final state can only arise from the initial state, but that we discard any indirect transition, say from *i* to *j* followed by *j* to *f*.

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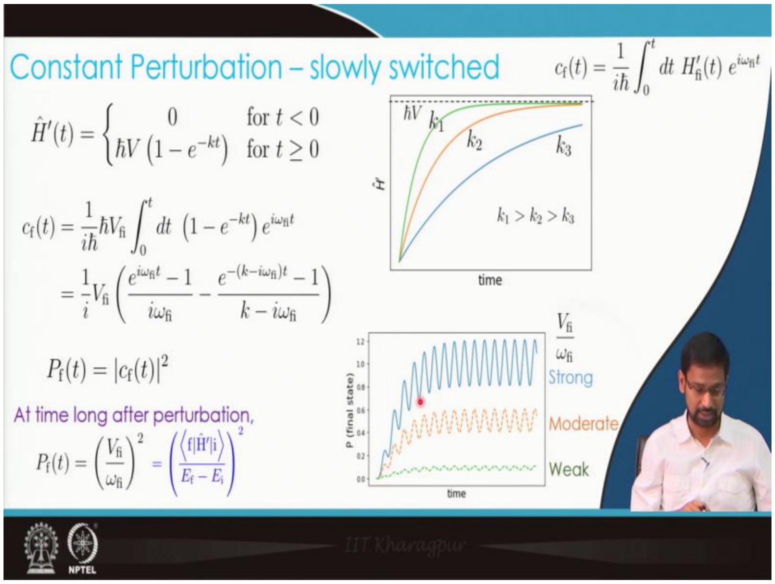


Now, let us apply this information to a model problem where we apply a constant perturbation that is slowly turned on. The perturbation for such a system is given by,

$$\hat{H}'(t) = \begin{cases} 0 & \text{for } t < 0 \\ \hbar V\left(1-e^{-kt}\right) & \text{for } t \geq 0 \end{cases}$$

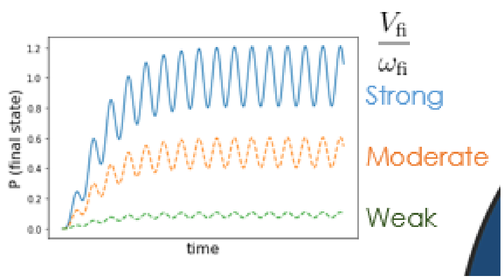
Here the perturbation is slowly switched on at time *t* and where *k* controls how fast the perturbation is switched on.

Applying the above perturbation on the results obtained in the previous slide, we have the coefficient of the final state,

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

The integration of the above exponential functions is rather trivial. The population of the final state can be obtained from the relation, $P_{\mathrm{f}}(t) = |c_{\mathrm{f}}(t)|^2$.

In the above equation, there are three independent parameters, V_{fi} (the coupling strength), ω_{fi} (the energy difference between the initial and final stationary states), and k (rate of switching on the perturbation). We would try to understand the effect of the strength and rate of perturbation as a function of the energy separation, or in other words, we shall consider the free parameters, $V_{\mathrm{fi}}/\omega_{\mathrm{fi}}$ and k/ω_{fi} and study their effect on population transfer by carrying out a few numerical exercises.



The above diagram shows the population of the final state for three cases, when V_{fi} (or more precisely, $V_{\mathrm{fi}}/\omega_{\mathrm{fi}}$) is strong, moderate and weak. At long time scale, we see in each of the cases a steady population appears, although the exact value of the population depends on the strength of the coupling. At large values of t,

$$P_{\mathrm{f}}(t) = \left(\frac{V_{\mathrm{fi}}}{\omega_{\mathrm{fi}}} \right)^2$$

where V_{fi} is essentially the matrix element between state f and state i coupled by the perturbation part of the Hamiltonian divided by ω_{fi}, which is simply the difference between the energy of final state and energy of the initial state. This is reminiscent of the time-independent perturbation theory,

$$= \left(\frac{\left\langle \mathrm{f} | \hat{\mathrm{H}}' | \mathrm{i} \right\rangle}{E_{\mathrm{f}} - E_{\mathrm{i}}} \right)^2$$

This simply tells that if you switch on your perturbation slowly and you wait long enough (t >>), the time dependent perturbation theory essentially goes back to the time-independent perturbation theory.

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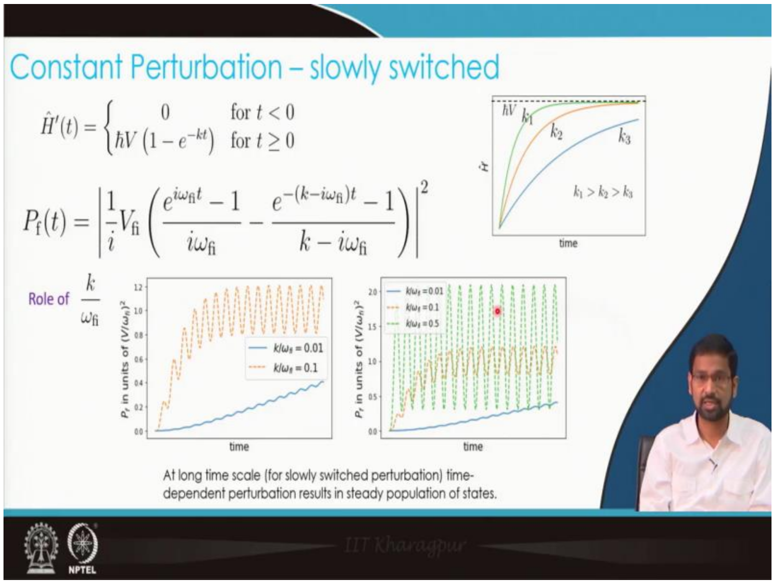
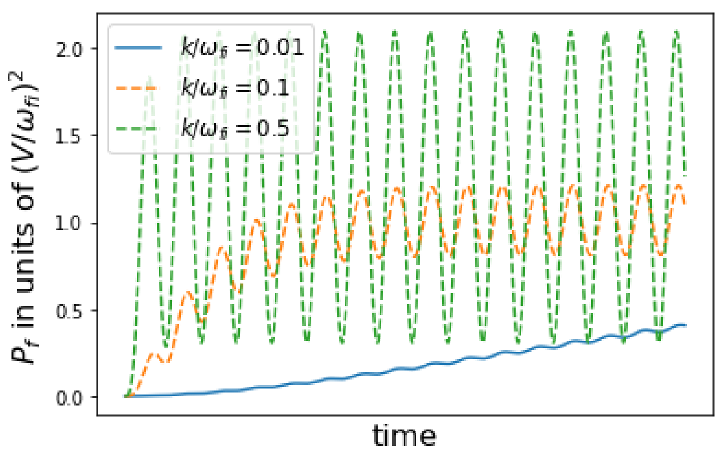


Next, we learn the effect of the rate of switching-on the perturbation on the population of the final state. For this, we keep a fixed value of V_{fi} and change k. From previous analysis, we know that at long time, the population becomes $\left(\frac{V_{\mathrm{fi}}}{\omega_{\mathrm{fi}}}\right)^2$. Hence, we express the population in the unit of $\left(\frac{V_{\mathrm{fi}}}{\omega_{\mathrm{fi}}}\right)^2$, such that at large values of t, the population approaches 1.

For small k value (k/ω_{fi} = 0.01), the population of the final state increases slowly but with very little oscillations or with very little transience. However, for k/ω_{fi} = 0.1, the rise of population is rapid and presence of transience is clearly noticed. The transience is prominent for even larger values of k/ω_{fi} = 0.5, as can be seen in the figure below.



In all the three cases, the strength of the perturbation is same. Hence, we observe the final population to be the same in all three cases. The only difference is that when we switch on the perturbation slowly, the population transfer occurs slowly with little transience. For a sudden change in the perturbation, the system behaves violently and the population gets quickly transferred, but in the presence of strong transience.

The two numerical exercises combinedly teach us that, most time-dependent perturbations if they are introduced slowly and if we measure the system long after the perturbation has been switched on, we get the same result as we have for the time-independent perturbation theory.

Thank you for your attention.