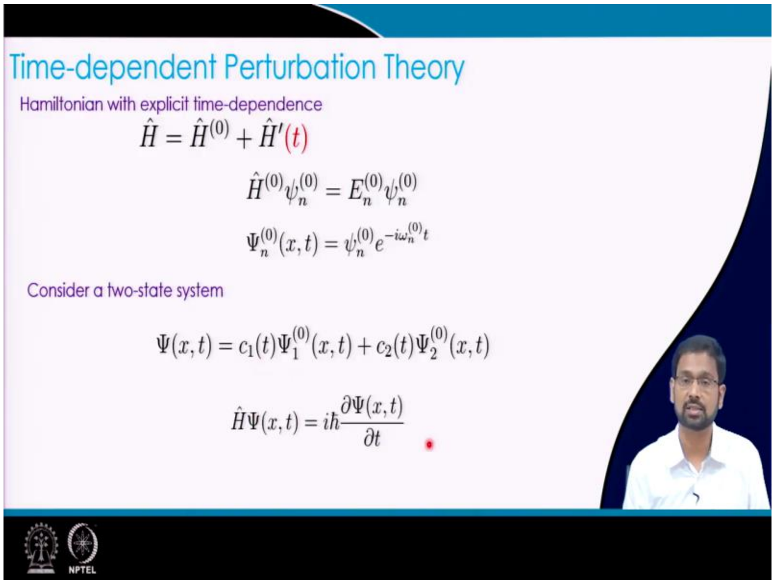
Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture 39: Time-Dependent Perturbation Theory - II

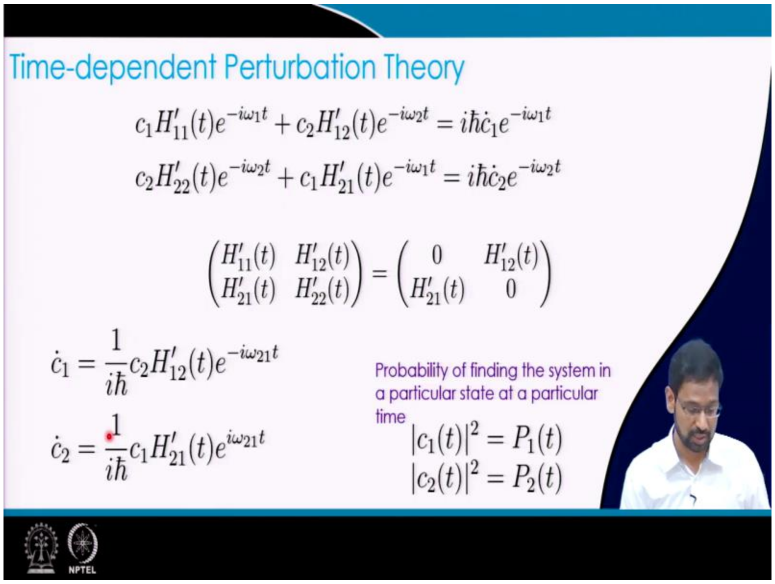
Hello students! Welcome to this lecture. In the last lecture we discussed about the time-dependent Schrodinger equation and time-dependent perturbation theory. We first discussed the stationary and non-stationary states when the system is defined by a time-independent Hamiltonian. We then considered the systems where the Hamiltonian shows explicit time dependence.

(Refer Slide Time: 01:20)



We considered the time-dependent part of the Hamiltonian as the perturbation added to the rest of the Hamiltonian, whose solutions we assume to know. We then considered a system with 2-states that are coupled via the time-dependent perturbation. From the corresponding time-dependent Schrodinger equation, we obtained a set of two equations.

(Refer Slide Time: 3:53)



$$c_1 H'_{11}(t)e^{-i\omega_1 t} + c_2 H'_{12}(t)e^{-i\omega_2 t} = i\hbar\dot{c}_1 e^{-i\omega_1 t}$$
$$c_2 H'_{22}(t)e^{-i\omega_2 t} + c_1 H'_{21}(t)e^{-i\omega_1 t} = i\hbar\dot{c}_2 e^{-i\omega_2 t}$$

The above two coupled equations show how the time evolution of the coefficients (that is the composition of the overall state) occurs due to the time-dependent perturbation. The perturbation matrix elements H'_{ij} (t) describe the coupling between the two states via the time-dependent Hamiltonian. In such a case, we can consider the diagonal elements of the perturbation Hamiltonian matrix as 0 and write down

$$\begin{pmatrix} H'_{11}(t) & H'_{12}(t) \\ H'_{21}(t) & H'_{22}(t) \end{pmatrix} = \begin{pmatrix} 0 & H'_{12}(t) \\ H'_{21}(t) & 0 \end{pmatrix}$$

With the above form of the perturbation Hamiltonian matrix, we can rewrite the set of coupled equations as

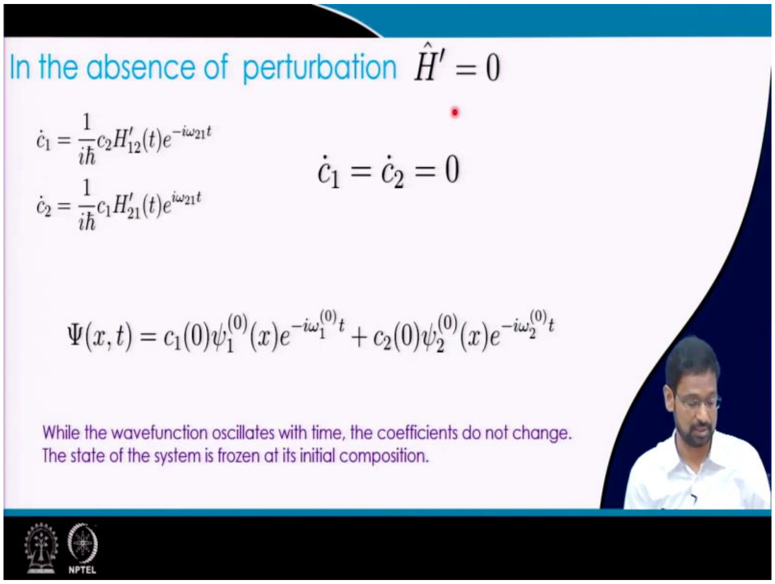
$$\dot{c}_1 = \frac{1}{i\hbar} c_2 H'_{12}(t) e^{-i\omega_{21} t}$$
$$\dot{c}_2 = \frac{1}{i\hbar} c_1 H'_{21}(t) e^{i\omega_{21} t}$$

The left side of the equations show the time evolution of the two coefficients, which depend on the strength of the coupling and the energy difference between the two states. The coefficients can be used to describe the probability of finding the system in a particular state by the following relation,

$$|c_1(t)|^2 = P_1(t)$$
$$|c_2(t)|^2 = P_2(t)$$

$P_1(t)$ and $P_2(t)$ provide the time-dependent population of the states. If the initial state was in state 1, then $P_1(0) = 1$ and $P_2(0) = 0$. With increasing time, due to the time-dependent perturbation, the two states mix and their population changes from their initial values.

(Refer Slide Time: 09:43)

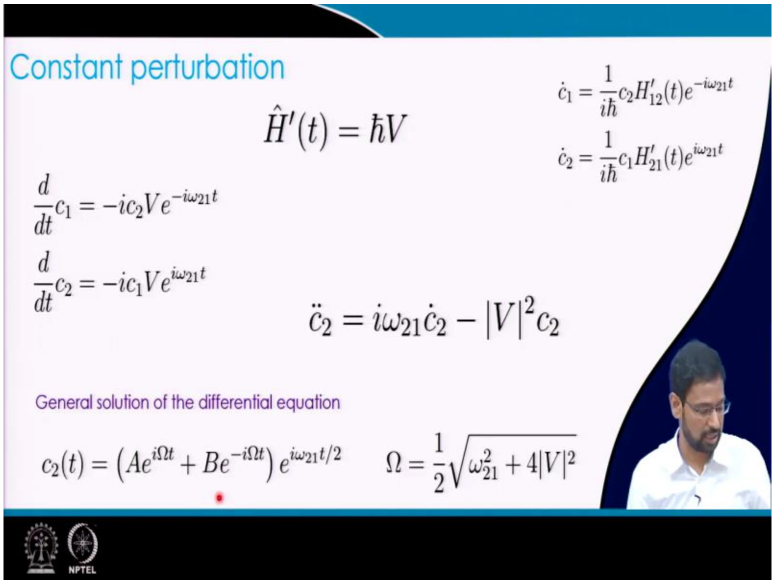


Let us first consider a special case, where there is no time-dependent part in the Hamiltonian. Hence, $\hat{H}' = 0$. In such a case, the $H'_{12} = H'_{21} = 0$. The coupled equations of the coefficient become,

$$\dot{c}_1 = \frac{1}{i\hbar} c_2 H'_{12}(t) e^{-i\omega_{21}t} \qquad \dot{c}_1 = \dot{c}_2 = 0$$
$$\dot{c}_2 = \frac{1}{i\hbar} c_1 H'_{21}(t) e^{i\omega_{21}t}$$

Since the time derivative of c_1 and c_2 is zero, the coefficients do not change with time. Hence, the composition does not change from its initial value. This is for the special case where the Hamiltonian is time-independent.

(Refer Slide Time: 12:24)



Next, let us consider a constant perturbation, applied during a particular time window.

$$\hat{H}'(t) = \hbar V$$

The time-evolution of the coefficients become,

$$\frac{d}{dt} c_1 = -i c_2 V e^{-i\omega_{21} t}$$
$$\frac{d}{dt} c_2 = -i c_1 V e^{i\omega_{21} t}$$

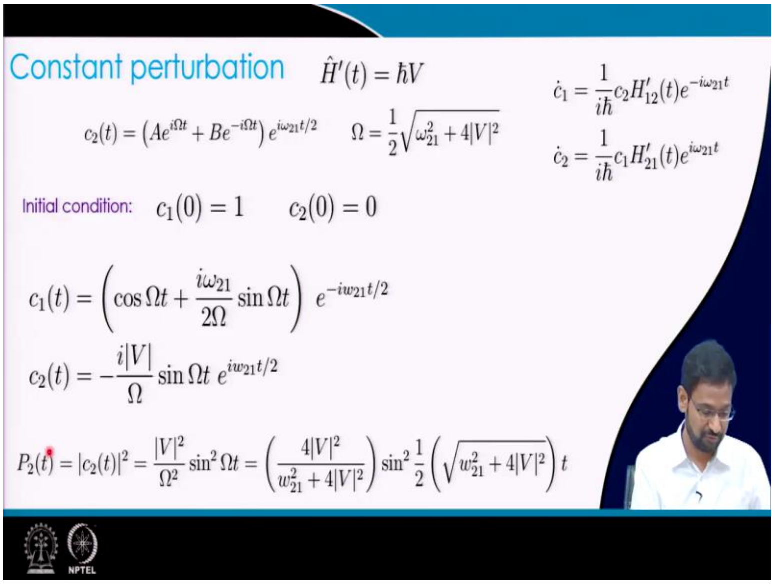
The above two equations are coupled. Using a variable substitution, we can rewrite them as the following 2nd order differential equation

$$\ddot{c}_2 = i\omega_{21}\dot{c}_2 - |V|^2 c_2$$

The general solution of the 2nd order differential equation given above is,

$$c_2(t) = \left(A e^{i\Omega t} + B e^{-i\Omega t}\right) e^{i\omega_{21} t/2} \qquad \Omega = \frac{1}{2}\sqrt{\omega_{21}^2 + 4|V|^2}$$

(Refer Slide Time: 16:19)



The above equation provides the time evolution of the coefficient c_2' with the unknown constants A and B. We can solve this as an initial value problem. If we consider the system to be initially in state 1, we have

$$c_1(0) = 1 \qquad c_2(0) = 0$$

By using the above relations in the expression for $c_2(t)$, we obtain

$$c_1(t) = \left(\cos\Omega t + \frac{i\omega_{21}}{2\Omega}\sin\Omega t\right) \; e^{-iw_{21}t/2}$$

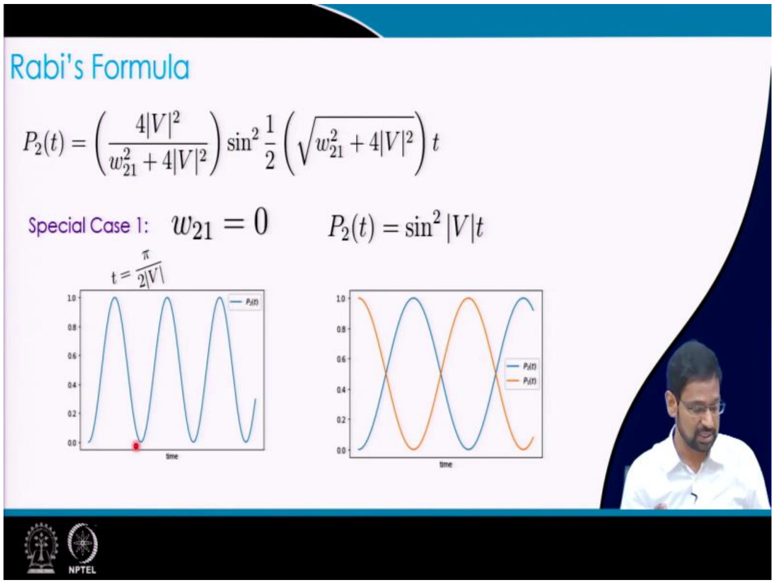
$$c_2(t) = -\frac{i|V|}{\Omega}\sin\Omega t \; e^{iw_{21}t/2}$$

Finally, we obtained the time evolution of the two coefficients in terms of the known quantities (the energy difference between the unperturbed states and the strength of the coupling). Since the population of the state is related to the coefficients, we can write the population of the state 2 (initially empty state) as,

$$P_2(t) = |c_2(t)|^2 = \frac{|V|^2}{\Omega^2}\sin^2\Omega t = \left(\frac{4|V|^2}{w_{21}^2 + 4|V|^2}\right)\sin^2\frac{1}{2}\left(\sqrt{w_{21}^2 + 4|V|^2}\right)t$$

At any time t, we can obtain $P_1(t)$ as $1 - P_2(t)$.

(Refer Slide Time: 19:28)



The relation

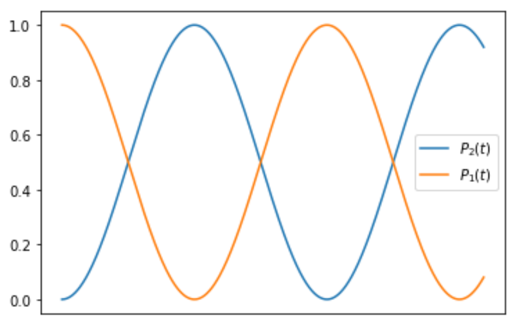
$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2 + 4|V|^2}\right) \sin^2 \frac{1}{2} \left(\sqrt{w_{21}^2 + 4|V|^2}\right) t$$

is popularly known as the Rabi formula. Let us discuss this for a few special cases.

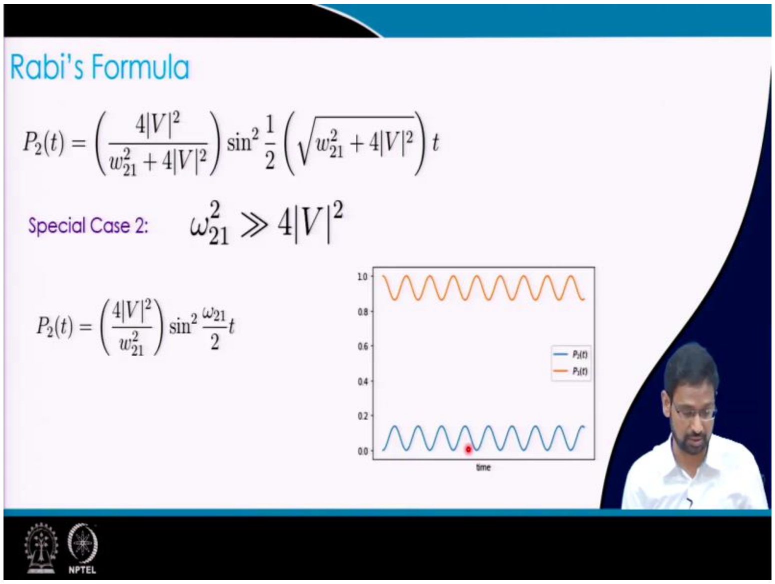
Special case – I: Lets consider when the two states in question are degenerate ($\omega_{21} = 0$). The Rabi's formula becomes,

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

which is the square of a sine function. Since the sine function fluctuates between -1 to +1, the population of the 2nd state would vary between 0 (empty) and 1 (full populated) as a function of time *t*. We can prepare state of any composition by removing the perturbation at a time that can be easily calculated from the above relation. For example, at $t = 2\pi/V$, the system exclusively exists in the 2nd state. It is interesting to note that for even very weak perturbation, we can expect a complete population transfer to the 2nd state, we just need to wait longer. The oscillatory nature of the population of the two states is shown in the diagram in the figure below.



(Refer Slide Time: 23:54)



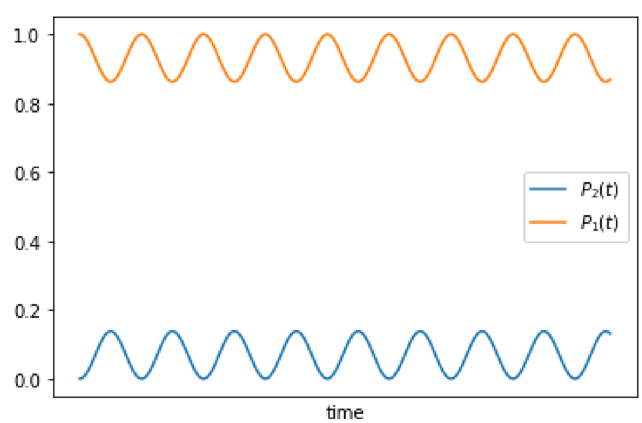
Now, let us look at the other extreme, i.e., the energy difference between the two states is much greater than the strength of the perturbation, i.e.,

$$\omega_{21}^2 \gg 4|V|^2$$

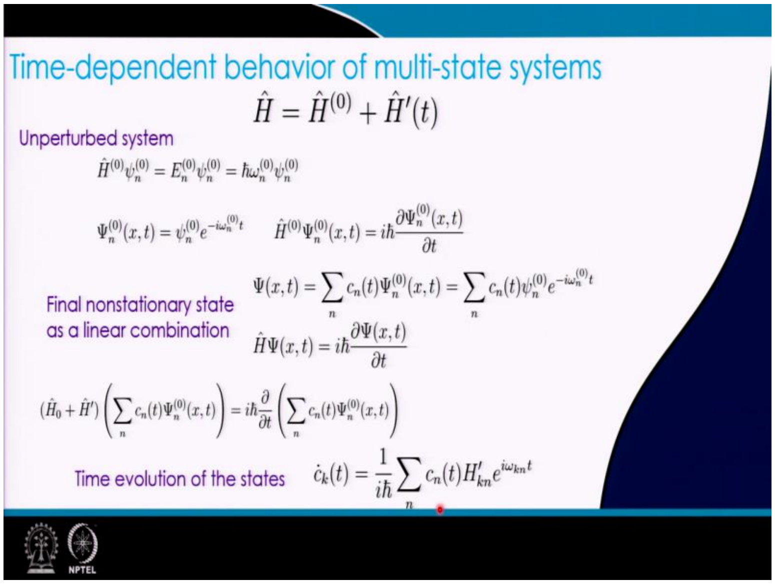
In this case, the Rabi's formula is simplified to,

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

This relation shows that the population of the 2nd state is again oscillatory, but here the maximum population of the state 2 is controlled by the factor that appears before the sine-squared function, i.e., $4|V|^2/\omega_{21}^2$. The following diagram shows the populations of state 1 and 2 for a weak-perturbation case. It can be seen that the population of state 1 remains close to 1 and the population of the 2nd state remains close to 0. In other words, with weak perturbation, the population transfer is minimal.



(Refer Slide Time: 26:12)



Now, we can generalize our discussion from the 2-state system to multistate system, where the time-dependent part of the Hamiltonian is treated as the perturbation. The unperturbed system has a complete set of eigenfunctions given by, $\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} = \hbar\omega_n^{(0)}\psi_n^{(0)}$

We can write down the corresponding stationary states as, $\Psi_n^{(0)}(x,t) = \psi_n^{(0)} e^{-i\omega_n^{(0)}t}$

which follows the TDSE $\hat{H}^{(0)}\Psi_n^{(0)}(x,t) = i\hbar\dfrac{\partial\Psi_n^{(0)}(x,t)}{\partial t}$

We can express our final state as a superposition of the stationary states with time-dependent coefficients in a similar way to what we did for the 2-state system, i.e.,

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

The above state follows the following TDSE (with the complete Hamiltonian),

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

By replacing the Hamiltonian and the wave function in terms of the unperturbed system, we obtain,

$$(\hat{H}_0 + \hat{H}')\left(\sum_n c_n(t)\Psi_n^{(0)}(x,t)\right) = i\hbar\frac{\partial}{\partial t}\left(\sum_n c_n(t)\Psi_n^{(0)}(x,t)\right)$$

You would recall a similar equation in the 2-state problem. Following the same strategy, we can obtain the following relation for the time evolution of the coefficient for the k^{th} state as,

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

The above equation shows that the time evolution of a state (k) depends on the strength of the coupling (H'_{kn})of this state with all other states (n) and also the difference in the energy (ω_{kn}) of this state with respect to the other stationary states of the system.

We will continue our discussion on the multi-state system in our next lecture.

Thank you for your attention.