**Time Dependent Quantum Chemistry**
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**Lecture 42**
**Nonradiative Transition Part 2**

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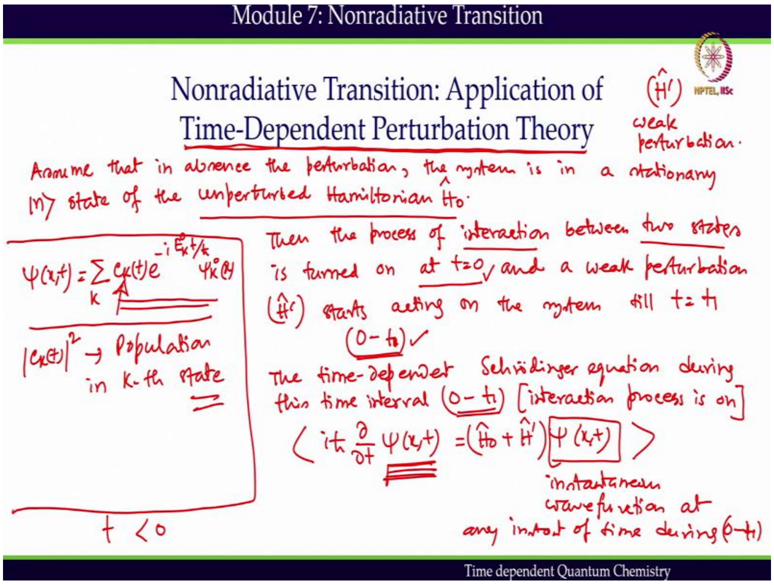


A generic approach to the exploration of Quantum Dynamics using Time Dependent Perturbation theory Time Dependent Perturbation theory, which we have already introduced in the earlier module 6 in module 6 we have introduced it and we will to use the final form, but before we use that, we will just remind the basic features, so that we can understand why and what are the context based on which this Perturbation theory was developed and how we are going to use that.

So, what assumption we make here in this in this entire problem is that this is a general generic approach I will just show any time when we use this Time Dependent Perturbation theory, this is the approach we should follow will assume that, first we assume that the Quantum system in absence of Perturbation, So, there is a Perturbation in this case this is constant interaction potential.

So, this H’ is the perturbation weak perturbation but, assume that in absence of Perturbation This is an important point to understand first, because this will enable you to quickly employ Time Dependent Perturbation theory if you if you have this idea very clear. So, first you assume that in absence of the perturbation that interaction process in absence of the perturbation the system is in a stationary, let us say ׀n> state of the Unperturbed Hamiltonian.

So, before the interaction process, I will assume that my system is in |n> state particular discrete state and this discrete state how do I get that discrete state? In fact, I can get all the discrete all the states which are available by all this states which are available in other words the spectrum of the system from the Hamiltonian Unperturbed Hamiltonian using the Time Independent Schrodinger equation.

So, all possible states can be explored using Time Independent Schrodinger equation which is $H_0\Psi_k^0 = E_k^0\Psi_k^0$. So, k is let us say k is starting from 0, 1, 2 like this way and one of the states is actually |n> state discrete |n> state. So, one can get these states from the Unperturbed Hamiltonian where perturbation has not been introduced and yet and we can get that.

So, this one is the Eigen state of the system and this is the Eigen energy the energy of the Eigen state corresponding Eigen state. So, this is something which is before t<0, which means it is I have not started the Perturbation, I have not introduced the interaction yet. So, all possible states can be optained from this unperturbed Hamiltonian.

Then the process of interaction the process of interaction between two states is turned on at t equals 0 and what are the two states there are two states which are available. Here, I have some states which are available. So, |n> state let us say i I will erase all the states I do not need all the states this is just for information. Now, I have all states can be obtain directly from Time Dependent Time Independence Schrodinger equation, but let us say I have |n> state and then there are other states also. I will call it let us say m state.

And here my intention is that this all the states can be obtained from Time Independent Schrodinger equation, but interaction between these states, how these two states are getting coupled interacting, they have to be coupled then only they can transfer the population. So, that coupling interaction process will start at t equals 0 time and a weak perturbation which is represented by this [H'] starts acting on the system until t equals $t_1$.

So, within this interval 0 to $t_1$ interval, this interaction process will be acting and during this time this 0 to $t_1$ time the system is time evolving as a function of time because they are coupled now. So, the Time Dependent, Time Dependent Schrodinger equation during this time interval 0 to $t_1$ when the interaction process is going on, during this time interval Time Independent Schrodinger equation during this interval and this is the interval when the interaction process is on during this time interval only the Time Dependent Schrodinger equation will give me instantaneous wave function instantaneous wave function

$$\frac{ih}{2\pi}\Psi(x,t) = (H_0 + H')\Psi(x,t)$$

So, this $\Psi(x,t)$ is the instantaneous wave function this is the instantaneous wave function wave function at any instant of time during 0 to $t_1$ time. So, during this time when the interaction processes is on during that time only, I need to find out the wave function and how do I get the wave function from this Time Dependent Schrodinger equation. And as we know that this particular wave function Time dependent Schrodinger wave function can be expressed in terms of its available stationary states.

So, $\Psi(x,t)$ is expressed as .

$$\Psi(x,t) = \sum_k \Psi_k(t) e^{-i\frac{2\pi E_k t}{h}} \Psi_k^0(x)$$

That is way that we will do that. So, instantaneous wave function is nothing but a superposition state and superposition state and we are taking a superposition of all available states and this $c_k$ there is a meaning of $c_k$ here what is the meaning of $c_k$, $c_k$ is the contribution of each state in the end it will it will infer the population.

So, $|c_k(t)|^2$ will give me the population in k th State. So, this is the general idea of any Time Dependent Perturbative approach, where we will first find out all the possible states available associated with unperturbed Hamiltonian that the spectrum of the system and before the interaction then interaction process will be turned on at zero time and it will be kept On for a particular certain time during this time interval the wave function will be time evolving and how can I get the wave function with function can be operated from this TDSE.

This is the instantaneous will function at the time when this interaction is going on. And this wave function is expressed as a linear combination of all stationary states where this expansion coefficient is related to the population final state population that is the population of a particular state.

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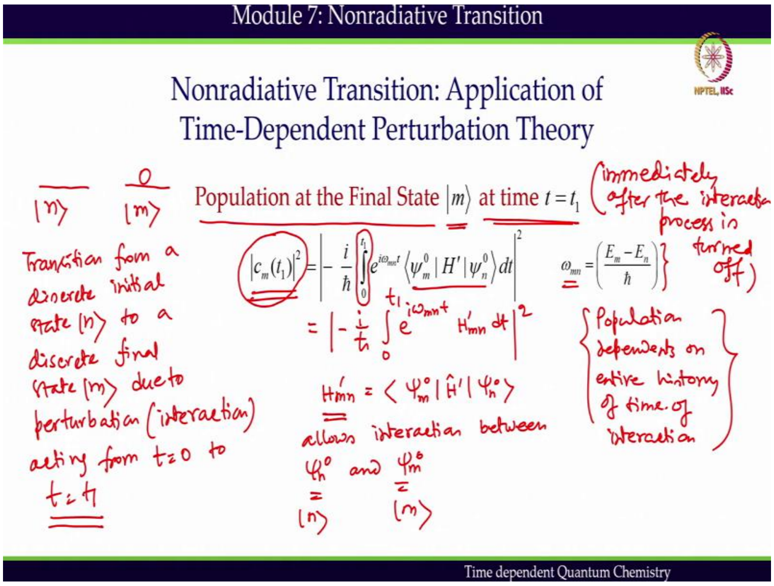


So, using that if we say that I had |n> initial discrete state and I had another state |m> and interaction process started. So, what we will do is that transition from a discrete initial state |n> to a discrete final state |m> due to perturbation which is the interaction acting from t equals 0 to t equals $t_1$ time until $t_1$ time it was acting and question is what is the final state population?

So, population at the final state |m> at time t equals $t_1$ just immediately after the interaction processes start off is turned off. At that time will check the population in the final state and population is given by this the magnitude square $|c_m(t)|^2$ this is the result of time dependent Schrodinger equation, first order Time Dependent Perturbation theory we will then and where we have this

$$\omega_{mn} = 2\pi\frac{E_m - E_n}{h}$$

So, this is something which we get directly from Time Dependent first order Perturbation theory or in other words, I will just simplify this one

$$|c_m(t)|^2 = \left| -\frac{2\pi i}{h}\int_0^t e^{i\omega_{mn}t} < \Psi_m^0 \| H' \| \Psi_n^0 > dt \right|^2$$

So, the population depends this population depends on entire history of time, that is why we have to integrate this time.

So, this is another point to be noted here the population depends entire history of time, time of interaction that is why you are integrating and so,

$$|c_m(t)|^2 = \left| -\frac{2\pi i}{h} \int_0^t e^{i\omega_{mn}t} H'_{mn} dt \right|^2$$

Where

$$H'_{mn} = < \Psi_m^0 \| H' \| \Psi_n^0 >$$

So, this is the term which allows the interaction between $\Psi_n^0$ and $\Psi_m^0$. These two states this is |n> state this is |m> state interaction between these two states.

So, because we said that we have only constant as we have pointed out before that this interaction occurs due to non-Adiabatic coupling. So, this H the form of H' is that it is a non-Adiabatic coupling. So, it is a constant it does not depend on time. So, because it does not depend on time we can easily integrate this expression and because the H' is a constant is not does not depend on time. So, we will integrate it will stop here and we will continue this session in the next meeting.