Time Dependent Quantum Chemistry
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Module 08 Lecture 44
Quantum Dissipative Dynamics

Welcome back, to module 7, and we have presented Fermi's Golden rule for Nonradiative Transition. And we have seen that the rate of transition how quickly population can transfer can be transferred through this Nonradiative Transition depends on the coupling strength and the density of states, if it is a State to Continuum Transition.

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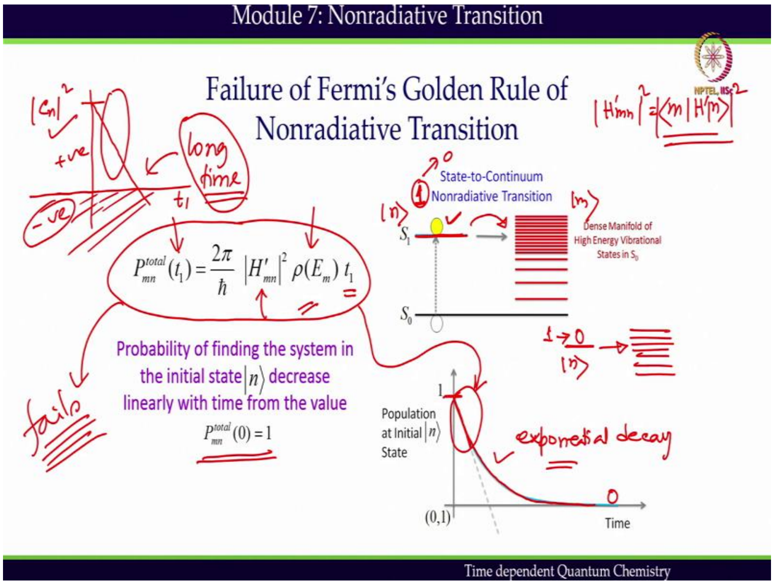

Now, after having understood this Nonradiative Transition, we will try to compare the theoretical findings with the possible experimental outcome. So, already we have understood that the total non radiative transition probability from initial state |n>, let us say I have an initial state |n> to a group of closely spaced final states |m>, |m> is representing the Continuum due to weak Perturbation is given by this Fermis Golden rule.

So, this is the Fermi's Golden rule we get for the transition probability. And here we remind that this is density of states for the final states density of states. And this term is the coupling term which is coupling between two states which is written as

$$H'_{mn}{}^{2} = | < \Psi_m^0 \| H' \| \Psi_n^0 > |^2$$

So, this integration is the coupling between two states, which are transferring the population. And we also assume that this t_1, this time is coming because we assumed that the interaction was started at t equals 0, and it was turned off at t equals t_1 time. And that is why we are checking the total probability of transition or in other words total population in the final state at t_1 time.

$$P_{mn}{}^{total} = \frac{4\pi^2 {H'_{mn}}^2}{h} 2\pi t_1 \, \rho(E_m)$$

Now, this equation, this Fermi's Golden rule for the State to Continuum Transition states that the probability of finding the system in the continuum of final states increases linearly with interaction time, as you can see, I have this time t_1. So, consequently, probability of finding the system in the initial state must decrease linearly with time from the value

$$P_{mn}^{total}(0) = 1$$

So, we can consider that I had a population 1 in the initial state and according to this equation, that population initial state population should linearly decrease as a function of time. So, this is the population in the n th's state, initial state. This is the time t_1 as I increase the time of interaction, it will just linearly decay.

Now, this Linear Decay Law, which is derived from Fermi's Golden rule, suggests that extrapolation of a linear decay or probability of finding the system at the initial state, so, this is the probability of finding the initial state for a long time would result in a negative value. So, this value this is a positive value and this is negative value.

So, I will have if I wait for longer time, if I allow the system to interact more and more, So, t_1 time is increasing, there will be a time when population in that state is going to be negative or in other words probability of finding the system in the initial state is going to be negative and negative population is meaningless. This part this is a consequence in this regime there is a consequence we are getting in the negative population consequence, this is meaningless.

This strange consequence clearly shows the failure of the Fermi's Golden rule to determine the decay behaviour of an excited Quantum system due to non radiative transition after a long time.

So, what is going on for after a long time, this equation fails to represent the real-life problem, because it is not possible the population if it is starting from 1, it can go to 0, it cannot be negative in this state negative population does not mean anything, or negative probability of finding the particle in that state does not mean anything. It can be 0, which means that all the population has been transferred to the final state, there is no population anymore in this state.

So, it can be 0, but less than 0 it is not possible. So, what is going on for a shorter time is perfectly fine, we can accept that, but for longer time behaviour of the system it is failing to it fails to represent the long-time behaviour of a Quantum decay dynamics.

We know that from a very simple kinetic model, if we consider the simplest kinetics, which can be one can imagine, for any chemical kinetics problem is that a system if it is starting from population 1, it decays exponentially. That is something which we have experience in real life, and because it decays exponentially, there will be a time when the population will be 0. And that is exactly what we expect.

If I start from an initial state ׀n> and if it is transferring the population to a very closely lying space, states, then there will be a time when for a long time, there will be a at a particular long time, there will be a population where population is 0. So, it is starting from 1 and going to 0 population. And that is somehow depicted within this Exponential Decay, Decay law.

So, an Exponential Decay law is, well accepted law for any Quantum Decay. But Fermi's Golden rule, showing that it is going to be Linear Decay. And that is why it fails to represent long term behaviour of a Quantum Dynamics or Quantum Decay Dynamics.

So, all we need to do is that we have to find out some rigorous treatment of so that we can get this exponential decay from TDSE. In having said that, we can also note that for a long time, sorry, for a short time, this regime, one can say that, for a short time, even an Exponential Decay can behave like a Linear Decay. So, Fermi's golden rule is actually representing this short time behaviour of a real system, it is not representing the long-term behaviour of a Quantum Decay or Quantum Dissipative Dynamics.

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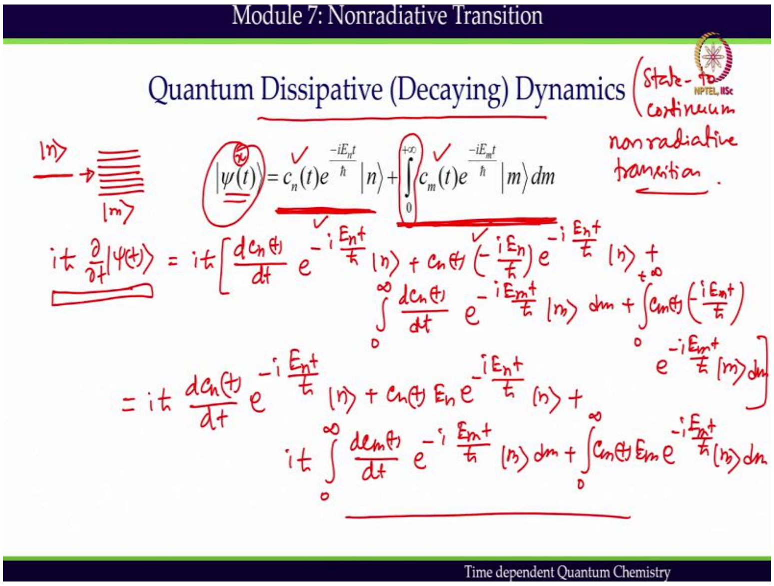

So, for rigorous treatment of the Quantum Dissipative Dynamics or Quantum Decaying Dynamics, which will lead to State to Continuum Nonradiative Transition, we are actually working on this State to Continuum Nonradiative Transition. What we need to do is that, we have to express the total wave function in a following way I have this initial state to be ׀n> and then we have continue of final states ׀m>.

So, at any instant of time, during the interaction, the total wave function will be represented as a linear combination of the initial state and all final states when I say all final states I am considering 0 to infinite states, all final states we are including.

$$\Psi(t)>= c_n(t)e^{-\frac{i2\pi E_n t}{h}}|n>+\int_0^{\infty} c_m(t)e^{-i\frac{2\pi E_m t}{h}}|m>dm$$

This kind of limit considering this kind of limit is very useful for the mathematical derivation, but in practical reality one can imagine that it is going to a very large number of states and when they are coupled, we are considering this, this coupled the time dependent wave function, which will be representing the system during the interaction time is a coupling between the initial state and all Continuum states.

Here, we note that the total wave function depends both on position space and time we know that **Ψ** has to be dependent on position and time. However, here we are just showing **Ψ**(t) for notational simplicity, we just remove this x part, we know that it depends on x but for the time being, we will just remove this notation. So, that we can we do not have many notations to write down simultaneal, but we remember that it is having this x part also.

The first term represents the initial state and the second term represents the continuum of the final states. So, if this is the wave function instantaneous wave function during the interaction time, then we have to solve it we have to get the final expression for this or in other words, we have to get the expression for c_n and c_m from Time Dependent Schrodinger equation and Time Dependent Schrodinger equation we have to write down like this way,

$$\frac{ih}{2\pi}\frac{\partial}{\partial t}\Psi(t) = H\Psi(t)$$

So, left hand side, we have to take the derivative of the left hand side. So, we will consider the first time derivative first for this. So, if we take the time derivative of this equation, we get

$$\frac{ih}{2\pi}\frac{\partial}{\partial t}\Psi(t) = \frac{ih}{2\pi}\Big[\frac{dc_n}{dt}e^{-\frac{i2\pi E_n t}{h}}|n> + c_n(t)\Big(\frac{-i2\pi E_n}{h}\Big)e^{-\frac{i2\pi E_n t}{h}}|n> + \int_0^\infty \left\{\frac{d}{dt}c_m(t)\right\}e^{-i\frac{2\pi E_m t}{h}}|m> dm + \int_0^\infty c_m(t)\left(\frac{-i2\pi E_m}{h}\right)e^{-i\frac{2\pi E_m t}{h}}|m> dm\Big]$$

So, this is the entire time derivative one can explicitly do that and finally, what I get from this time derivative if I simplify it, then what I get here is

$$\frac{ih}{2\pi}\frac{\partial}{\partial t}\Psi(t) = \frac{ih}{2\pi}\frac{dc_n}{dt}e^{-\frac{i2\pi E_n t}{h}}|n> + c_n(t)E_n e^{-\frac{i2\pi E_n t}{h}}|n> + \frac{ih}{2\pi}\int_0^\infty \left\{\frac{d}{dt}c_m(t)\right\}e^{-i\frac{2\pi E_m t}{h}}|m> dm + \int_0^\infty c_m(t)E_m e^{-i\frac{2\pi E_m t}{h}}|m> dm]$$

one can explicitly do that and one can very easily get this the time derivative. So left hand part is done, we will use this time derivative later.

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Quantum Dissipative (Decaying) Dynamics

$|n\rangle$, $|m\rangle$ — E_m continuously varying. $(0, \infty)$

$$i\hbar \frac{\partial|\psi(t)\rangle}{\partial t} = i\hbar \frac{dc_n(t)}{dt} e^{\frac{-iE_n t}{\hbar}}|n\rangle + c_n(t)E_n e^{\frac{-iE_n t}{\hbar}}|n\rangle + i\hbar\int_0^{+\infty} \frac{dc_m(t)}{dt} e^{\frac{-iE_m t}{\hbar}}|m\rangle dm + \int_0^{+\infty} c_m(t) E_m e^{\frac{-iE_m t}{\hbar}}|m\rangle dm$$

$$\hat{H}|\psi(t)\rangle = \left(\hat{H}_0 + \hat{H}'\right)|\psi(t)\rangle = \hat{H}_0|\psi(t)\rangle + \hat{H}'|\psi(t)\rangle$$

(a) $|n\rangle$: $\hat{H}_0|n\rangle = E_n|n\rangle$

(b) $|m\rangle$: $\hat{H}_0|m\rangle = E_m|m\rangle$

(c) $\langle n|n\rangle = 1$, $\langle n|m\rangle = 0$

$\langle m|m'\rangle = \delta(m-m')$
$= 0 \quad m \neq m'$
$= 1 \quad (m = m')$

m and m′ are two states in continuum.

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H' turned on at $t=0$
turned off at $t=t_1$
} → TDSE / $\psi(t)$

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$= 0 \quad m \neq m'$
$= 1 \quad (m = m')$

H'
(a) $\langle m|H'|m'\rangle = 0$
(b) $\langle m|H'|m\rangle = \langle n|H'|n\rangle = 0$
(c) $\langle n|H'|m\rangle$ constant
$0 - \infty \; |m\rangle$
(d) $t=0, |c_n(0)|^2 = 1 \quad |c_m(0)|^2 = 0$

Contd...

First we will look at the, the next part. So, this is the time derivative we have and right hand side of the TDSE if we look at this, that is going to be this one is the right hand side TDSE. So, here the Unperturbed Hamiltonian gives the stationary state energy.

$$H\Psi(t) = (H_0 + H')\boldsymbol{\Psi}(\boldsymbol{t}) = \boldsymbol{H_0}\boldsymbol{\Psi}(\boldsymbol{t}) + \boldsymbol{H'}\boldsymbol{\Psi}(\boldsymbol{t})$$

So, we know that this Unperturbed Hamiltonian gives the stationary state energy all stationary state information before the interaction process started, we get all the stationary state information from this unperturbed Hamiltonian and from that, only we get to know what are the states available and which states should be coupled to each other for this population transfer.

So, following consequences we can write down immediately first of all, for the initial state, we said that initial state here is going to the all-final states. So, for initial state |n>, we can write down $H_0|n> = E_n|n>$ that is coming directly from the Time Independent Schrodinger equation for all final states, one can write down

$$H_0|m> = E_n|m>$$

And we have said that E_m is continuously varying, because it is Continuum and we are saying that this is not a discrete state anymore, E_m is continuously varying. So, E_m continuously varying, continuous from 0 to infinity, from 0 to infinity. And because they are the Eigen states of the Hamiltonian H_0, one can use the orthogonality relation for the Eigen states which is

$$<n|n>= 1\,, <n|m>= 0, \qquad <m|m'>= \delta(m-m')$$

basically m and m dash are two states in Continuum.

So, this is going to be 1 when you have m equals m'. So, these are the orthogonality relations we have already. In addition to this, we will assume few more conditions, which will help us reduce the equation very easily. We said that the Hamiltonian interaction Hamiltonian H' is actually responsible for the interaction.

So, this H' is turned on at t equals 0 time and it is turned off at t equals t_1 time. So, this is something which we again assume just like what we did in the when we have used Perturbation theory to formulate this Fermi's Golden rule for this Nonradiative transition. So, TDSE when I, when I am using TDSE, TDSE is actually giving me wave function during this time interval when the interaction is going on. And we need to find out then final state population for that.

So, for the coupling particularly for this coupling part, we will make assumptions following assumptions we will make for this coupling associated with this coupling part, the first assumption is that this coupling does not allow interaction between states of the Continuum, which means that $< m|H|m' >= 0$, it is not coupling between the states in the continuum where m and m' are representing two states in the Continuum any two states in the Continuum.

The coupling does not allow interaction of any state with itself that is also another assumption we are making $< n|H|n >= 0$, which this coupling is not coupling the states with itself both states n and m states which they are not coupling each other, they are not coupling the state with itself.

C another condition we assume that for all states coupling is constant $< n|H|m >= 0$. We have 0 to infinite states, m states. For all states, this part is constant. And finally, we will assume that at t equals 0, I had population in the initial state 1 and c m all population in the final state was 0. So, in the final state there was no population. So, this is another initial condition we have defined.

$$|c_n(0)|^2 = 1, |c_m(0)|^2 = 0$$