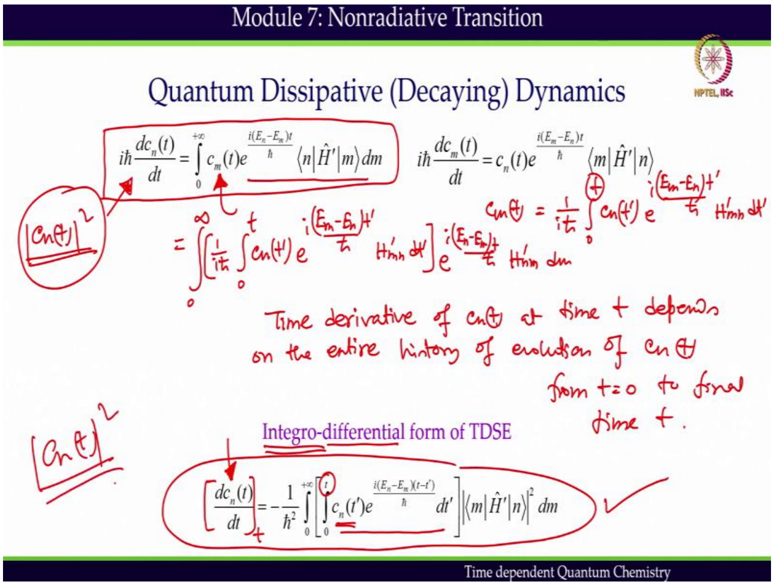
Time Dependent Quantum Chemistry
Professor Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Module 08 Lecture 45
Formal Derivation of Dissipative Quantum Dynamics

Welcome back to module seven, we are discussing Nonradiative Transition. Due to non adiabatic coupling, we have not shown the exact form of the coupling yet, but we have shown that this is going to be a constant coupling, Time Independent coupling rather. And that is why we have considered a constant interaction potential, which is coupling two states that is a discrete state and a Continuum state. And we have shown the integro differential form of the TDSE, which we get in the derivation of Quantum Dissipative Dynamics.

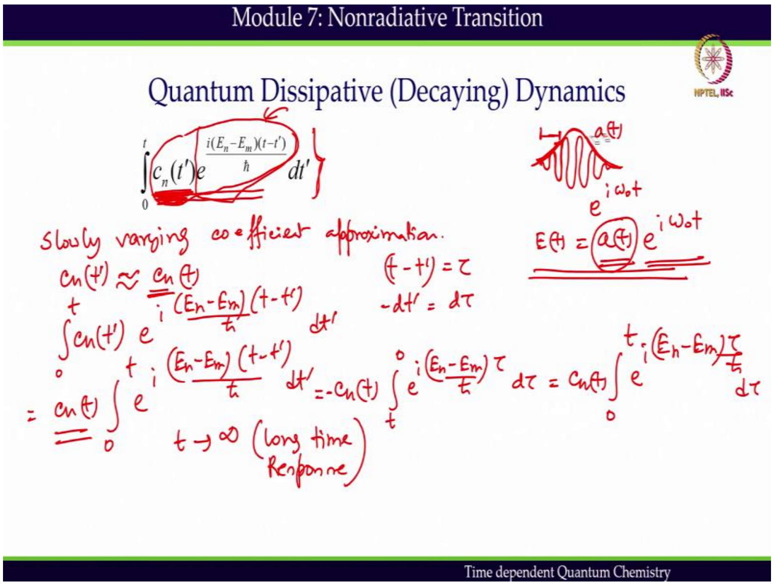
(Refer Slide Time: 01:03)

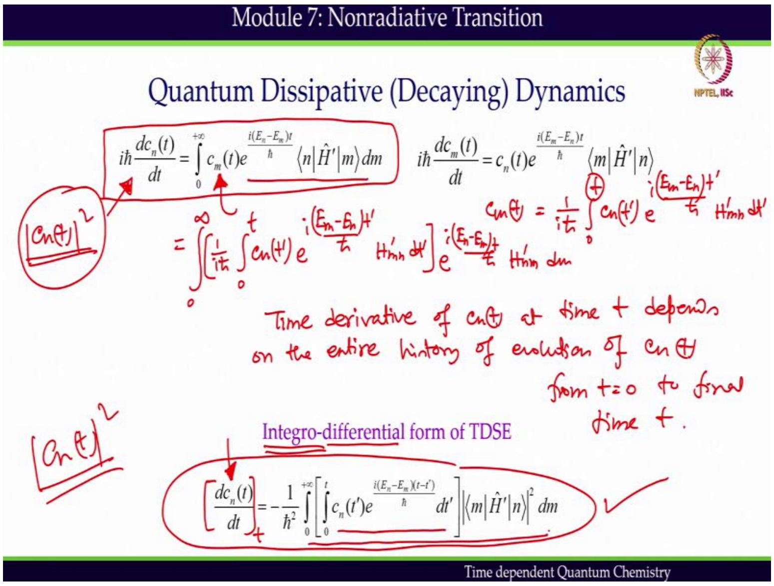


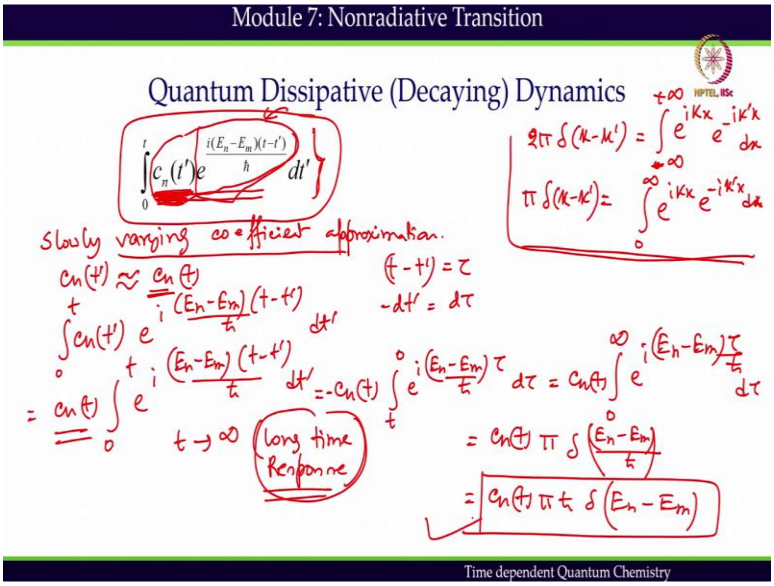
$$\frac{dc_n}{dt} = -\frac{4\pi^2}{h^2}\int_0^{\infty}\left[\int_0^t c_n(t')e^{\frac{i2\pi(E_m-E_n)(t-t')}{h}}dt'\right]|<m|H'|n>|^2 dm$$

And so far, what we have shown is that, this is the form we get, and we have to get a solution, we have to reduce this equation, this equation looks very complicated, but if we use a few more assumptions, this equation can be reduced to a very simple form. And our target so far is to find out how this cn t population in the initial state is varying, and it should vary like an exponential decay.

(Refer Slide Time: 01:32)







So, we will move forward as in the integro-differential form, we had this integration. So, we will look at the first-time integration part. We will, we will go part by part. So, in the integro-differential equation, we had this time integration. And then so this is the time integral part. And then this is the state integral part. So, two integrals we will look at it separately. So first, we will look at the time integral part.

If we look at the time integral part, we see that this is an interesting and very familiar form, we have used a pulse we have introduced in the module one we have introduced a pulse the pulse looks like this an optical pulse particularly, and then also we have introduced wave packet is the same concept, similar concept wave packet is localized particle wave in space and optical pulse is the localized electromagnetic wave in time, but both having similar idea it has an envelope function and a very fast varying carrier wave which is represented by $\cos\omega_0 t$.

But generally trigonometric functions are difficult to deal with that is why we have always represented by $e^{i\omega_0 t}$. That is the usual representation in the time domain the pulse and so, finally, the electric field is represented as

$$E(t) = a(t)\, e^{i\omega_0 t}$$

That is how we have represented this is the slowly varying component this is the fast-varying component and the concept of slowly varying and fast varying we have already demonstrated those concepts in module one.

So, it is it will be much easier to understand now, and because it is a very slowly varying component, just check the know just note the similarity between this mathematical function and this integrand here we have this is also just like a slowly varying component and then e to the power something is the fast-varying component. And this similarity shows that we will be able to further reduce following the slowly varying envelope approximation.

So, we will consider a slowly varying envelope, slowly varying coefficient approximation. In this approximation we are saying that $c_n(t')$ this is time varying part $c_n(t')$ is very slowly varying as compared to this part and if it is slowly varying, then one can say that

$$c_n'(t') \approx c_n(t)$$

And if it is, so, then one can take this

$$\int_0^t c_n(t')e^{\frac{i2\pi(E_m-E_n)(t-t')}{h}}dt' = c_n(t)\int_0^t e^{\frac{i2\pi(E_m-E_n)(t-t')}{h}}dt'$$

we have this.

And this can be taken out within this approximation that $c_n(t)$ is very slowly varying. That is why within this integration, it is slowly varying and is adopting the final value. So, it is almost constant within this integration time interval, we can say and the constant value is nothing but the $c_n(t)$ value. That is the way we are saying.

So, and the slowly varying and envelope approximation, one can say that, because, you see, if you look at this variation, the fast variation. So, if I am integrating between let us set this time interval or this time interval, one can see that how much variation I have in the fast-varying component, whereas slowly varying component did not change much will say that this is almost similar, and that is the approximation we are making.

So, within this approximation, one can take it out and after taking it out one can assume that

$$-t' = \tau$$

new variable definition I am giving and in that case

$$-dt' = d\tau$$

So, this integral part can be written as

$$-c_n(t\ )\int_t^0 \ e^{\frac{i2\pi(E_n-E_m)\tau}{h}} d\tau'$$

And so, which is nothing but

$$c_n(t\ )\int_0^t \ e^{\frac{i2\pi(E_n-E_m)\tau}{h}} d\tau'$$

As

$$\int_a^b f(x)dx = -\int_b^a f(x)dx$$

that is the integration we have and this integration can be evaluated if I considered that t is tends to infinite which means that the integral the limit of the integral is considered to be infinite which means we are looking at the long-time response.

If we use the long-time response then this integral becomes infinite and the moment I take it infinite then I have one definition of Dirac delta function Dirac delta function has many definitions. In this module we have shown Dirac delta function as a definition in terms of cardinal sin function.

Now, here the definition which I am going to give right now, that definition we have used already in that translational motion Quantum dynamics of translational motion that is the

$$2\pi\delta(k-k') = \int_{-\infty}^{\infty} e^{ikx}e^{-ik'x}dx = 2\int_{0}^{\infty} e^{ikx}e^{-ik'x}dx$$

So, this is the definition of Dirac Delta function and this definition we can use to so,

$$\int_{0}^{\infty} e^{ikx}e^{-ik'x}dx = \pi\delta(k-k')$$

and one can use this Dirac delta function definition to reduce this equation because, as we are taking long time response this is t, this is going to be my infinity and for long-time response, this part is going to be now

$$c_n(t \quad)\frac{h}{2}\delta(E_n - E_m)$$

So, the entire within the approximations which we have made slowly varying coefficient approximation as well as using this Dirac delta function and also long time response if we consider then this entire time integral becomes like this.

$$c_n(t \quad)\frac{h}{2}\delta(E_n - E_m)$$

(Refer Slide Time: 11:51)

Quantum Dissipative (Decaying) Dynamics

NPTEL, IISc

$$\int_0^{+\infty} dm \left|\langle m|H'|n\rangle\right|^2 \Rightarrow \int_0^{\infty} dE_m$$

over all states

↑ over energy levels.

E_m — m_1 — m_2 — m_3 — m_4

$E_{m'}$ — — —

$E_{m''}$ — —

$\rho(E_m)\, dE_m$ = total state in dE_m range

Probability of transition to each energy level $|\langle E_m|H'|n\rangle|^2$

$$\int_0^{\infty} dm |\langle m|H'|n\rangle|^2 = \int_0^{\infty} dE_m\, \rho(E_m) |\langle E_m|H'|n\rangle|^2$$

in term of states — in term of energy levels.

Quantum Dissipative (Decaying) Dynamics

NPTEL, IISc

$$\int_0^{+\infty} dm \left|\langle m|H'|n\rangle\right|^2 \Rightarrow \int_0^{\infty} dE_m$$

over all states

↑ over energy levels.

E_m — m_1 — m_2 — m_3 — m_4

$E_{m'}$ — — —

$E_{m''}$ — —

$\rho(E_m)\, dE_m$ = total state in dE_m range

Probability of transition to each energy level $|\langle E_m|H'|n\rangle|^2$

$$\int_0^{\infty} dm |\langle m|H'|n\rangle|^2 = \int_0^{\infty} dE_m\, \rho(E_m) |\langle E_m|H'|n\rangle|^2$$

in term of states

$$= \int_0^{\infty} dE_m\, K(E_m)$$

$$K(E_m) = \rho(E_m) |\langle E_m|H'|n\rangle|^2$$

On the other hand, we have this integration the spatial integration like this, where we are integrating over all states and we have to remember that, I can have the same energy at the same energy level I can have many states available. So, this is m_1, this is m_2 states, this is m_3 states, this is m_4 state, like this.

So, this integration is over all states not energy states. So, this is over all states what I need to do is that, because here I have found an expression in terms of energy level, this is E_n and E_m are energy levels. So, this is the energy level for this, this is another energy level m' , this is another energy level m'' .

So, for a same energy level I may have different states and this integration is over all states, all we need to do is that I have to convert this integration to over energy levels. So, this is going to be then over energy levels and in order to do that, what I will do I will consider the density of states. So, if we assume that $\rho(E_m)$ is the density of states, which means that $\rho(E_m)dE_m$ gives me total states in dE_m range.

So, one can write down and this is the total states in the dm range and probability of transition, probability of transition to each state, each energy level is given by $|<E_m|H'|n>|^2$. So, in that case, I will be able to write down

$$\int_0^\infty dm\,|<m|H'|n>|^2 = \int_0^\infty dE_m \rho(E_m)|<E_m|H'|n>|^2$$

.

So, this part, this integration we are doing in terms of states and this integration we are doing in terms of energy levels, we are just changing the representation. And if we do that, then things will be very easy to deal with, because now I will do one thing, I will just consider this part to be a function of some energy.

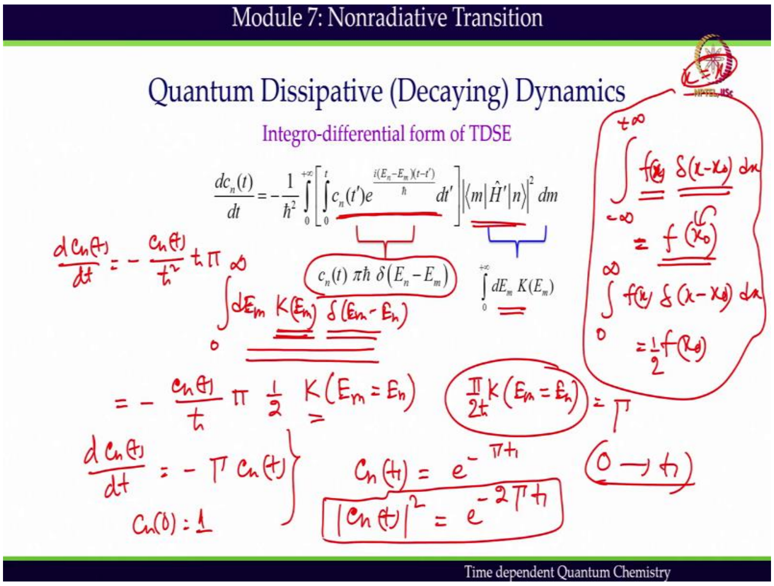
So, I will be able to write down as

$$\int_0^\infty dE_m k(E_m)$$

$$k(E_m) = \rho(E_m)$$

So, this K (E_m) is a function of energy levels, which is given by rho E_m density of states at that state at that point at that energy level, and the probability of transition to that energy level. This is just a function of energy.

(Refer Slide Time: 16:54)



So, now we will go back these two representations will be used and we see that this portion can be written as this delta function multiplied by these parts, and this integration can be converted to over the states, over the energy levels. So, if we do that, then we get following

$$\frac{dc_n}{dt} = -c_n(t \quad)h\pi\frac{4\pi^2}{h^2}\int_0^{\infty} dE_m k(E_m)\delta(E_m - E_n)$$

That is the integration we get.

And this part is familiar integration, because we use similar kind of integration in the translational motion, when we have described translational motion in module 3, what we have used there, if I have, let us say, smooth function f(x), if I have a smooth function f(x), and I am integrating

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0) = f(x_0)$$

So, if the integration limit is considered to be 0 to infinity,

$$\int_0^{\infty} f(x)\delta(x - x_0) = \frac{1}{2}f(x_0)$$

This is something which is a property of the delta function if a smooth function is multiplied by a delta function, then the value of the integration is going to be the value of the function at the position of the delta function, where the delta function exist and delta function exists when x equals x_0.

So that concept can be used here. We will assume that K (E_m) is a smooth function which has been multiplied by delta function this that is why this value of this function is going to be then, this is going to be now

$$= -\frac{c_n(t)}{h} 2\pi^2 \frac{1}{2} K(E_m - E_n)$$

I have to find out these functions value. So, if we assume that this entire

$$\frac{\pi^2}{h} K(E_m - E_n) = \Gamma$$

So, in that case, I will be able to write down simplify this equation as

$$\frac{dc_n}{dt} = -\Gamma c_n(t)$$

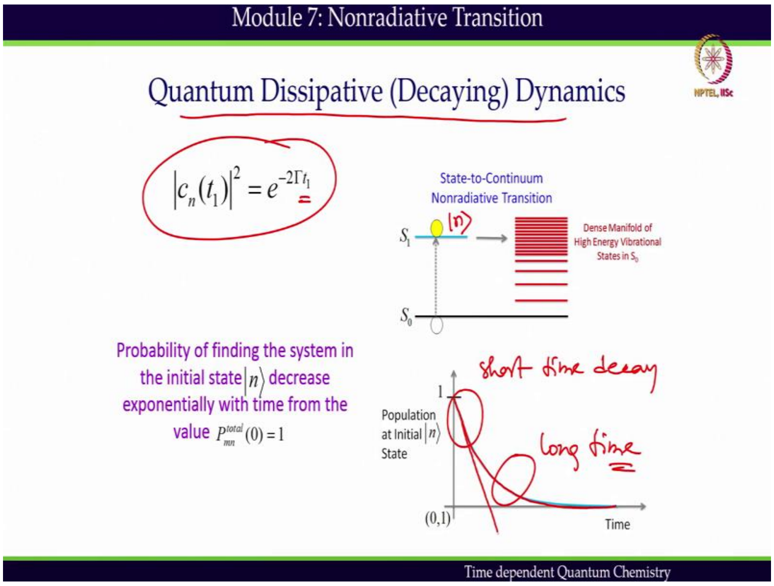
a simple equation we have got. And this equation can be integrated with assumptions that $c_n(0)$ was 1. So, if we do that, then I will be able to get this integration to be $c_n(t_1)$, to integration would be done from 0 to t_1 time, then I will be able to get

$$c_n(t_1) = e^{-\pi t_1}$$

or

$$|c_n(t_1)|^2 = e^{-2\Gamma t_1}$$

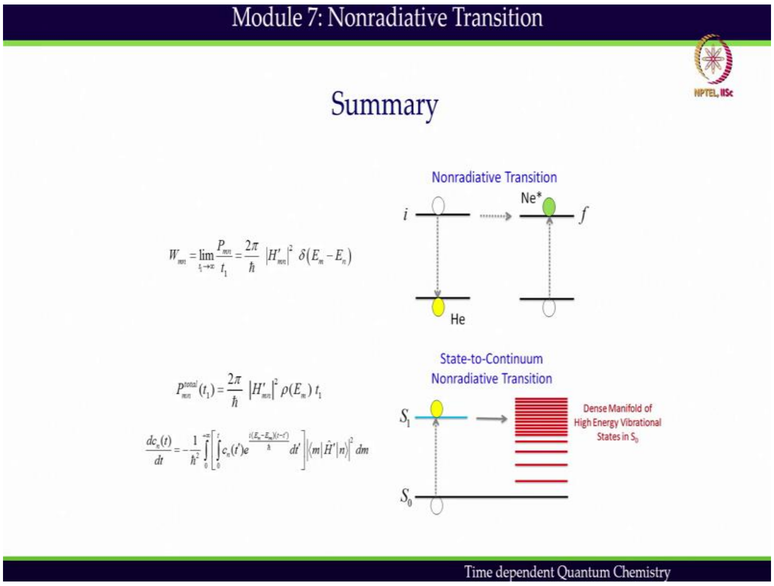
(Refer Slide Time: 21:59)



So, this is the expression, which is very useful, because now it is showing that it is showing that the population in the initial state that is the initial state, I started with n population in the initial state is decaying as a function of interaction time, exponentially. So, now I have been able to, I have been able to reproduce this exponential decay law that is the Quantum Dissipative dynamics where, whereas, a linear decay law was predicted by Fermi's golden rule.

So, which means that Fermi’s golden rule is applicable for short time decay. It cannot represent the long-time decay, long-time behaviour can be explained through these Quantum Dissipative dynamics where we are using integro-differential form of the TDSE.

(Refer Slide Time: 23:01)



So, we have come to the conclusion end of this module, where we have discussed Nonradiative transition from one discrete state to another discrete state and from one discrete state to a Continuum of states, we have seen that Fermi's Golden rule for the Nonradiative transition is controlling the transition probability for the short time of the process. If I have to represent it in the long term process, then I have to use this integro-differential form of the TDSE. So, we will stop here and we will continue the discussion of Time Dependent Quantum Chemistry in the next module.