Time Dependent Quantum Chemistry
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Lecture 40
Geometric Phase and Dynamical Phase

Welcome back to module 6, we have presented so far the we have given the formal derivation of the quantum adiabatic theory, which assumes that the let us say taking an example of a particle in one dimensional box, the box is expanding very slowly, and if the box is expanding very slowly, then at the initial time before the expansion started, if it was in the nth, non-degenerate, discrete non-degenerate stationary state the particularly if it was there, then after the expansion, the particle will remain in the nth non degenerate stationary state of H(t) but the wave function accumulate two different phases.

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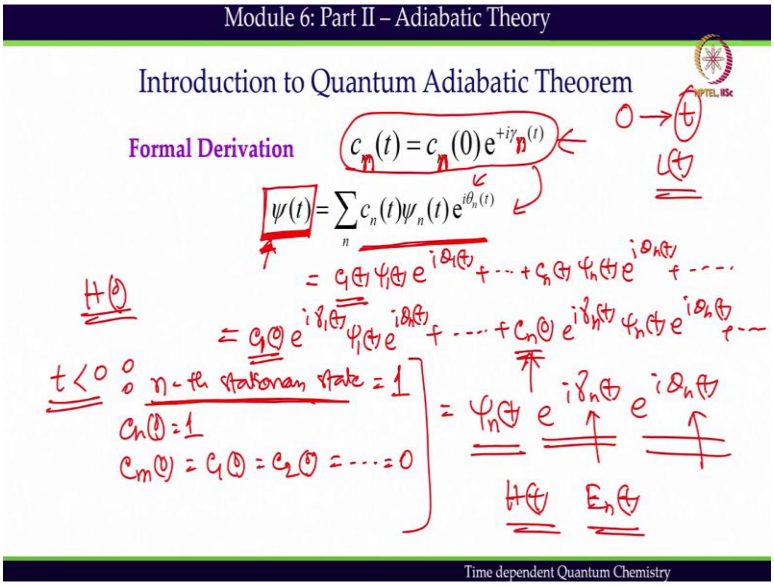

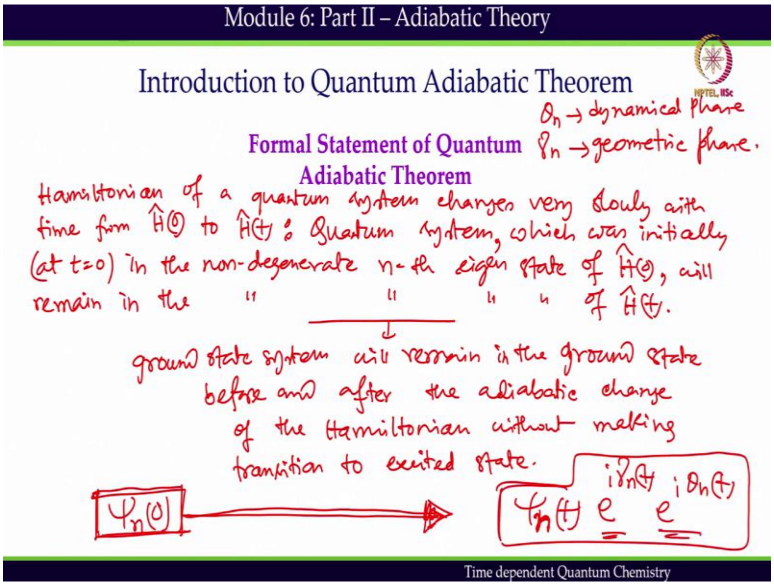

And these two phases are at a dynamical phase which has to be included in the wave function. So, the formal statement of quantum adiabatic theorem will write on the formal statement of the quantum adiabatic theorem under the quantum adiabatic theorem, the Hamiltonian of a quantum system the Hamiltonian of quantum system changes very slowly with time from an initial form which is H(0) to a final form H(t) during which this adiabatic process occurs.

And as a result, the quantum system the quantum system which was initially at t = 0 or before the beginning of the process in the non-degenerate nth eigenstate of H(0). So, the quantum system which was present in the nth eigenstate of H(0) will remain will remain in the non-degenerate nth eigenstate of H(t). Because the final Hamiltonian is now H(t) this simply means that the ground state what does it mean?

It means that the ground state system will remain in the ground state before and after the adiabatic change of the Hamiltonian without making transition to the excited state so, ground state will remain in the ground state but the wave function which was before $\boldsymbol{\Psi}_n(0)$ in this case ground state. So, we consider ground state to be if it was $\boldsymbol{\Psi}_n(0)$, now the wave function would be $\boldsymbol{\Psi}_n(t)$ that is the wave function, but it has now additional phase.

The phase is $e^{i\gamma_n(t)}\, e^{i\theta_n(t)}$ that is the difference. So, a wave function which was staying here now, the wave function is this one, after the adiabatic process has is over immediately after the adiabatic process is over. Here this θ_n is called dynamical phase and γ_n is called geometric phase. So, this is the kind of summary of quantum adiabatic theory the at time t equals 0 it was the wave function of the particle represented by $\boldsymbol{\Psi}_n(0)$ at t equals t time after immediately after the process is turned off.

Now, the wave function would be $\mathbf{\Psi}_n(t)$ that is the stationary state wave function obtained from H(T). But, in addition to that wave function, I have now additional phase that this phase factor now accumulated due to this adiabatic change the broad change of the process.

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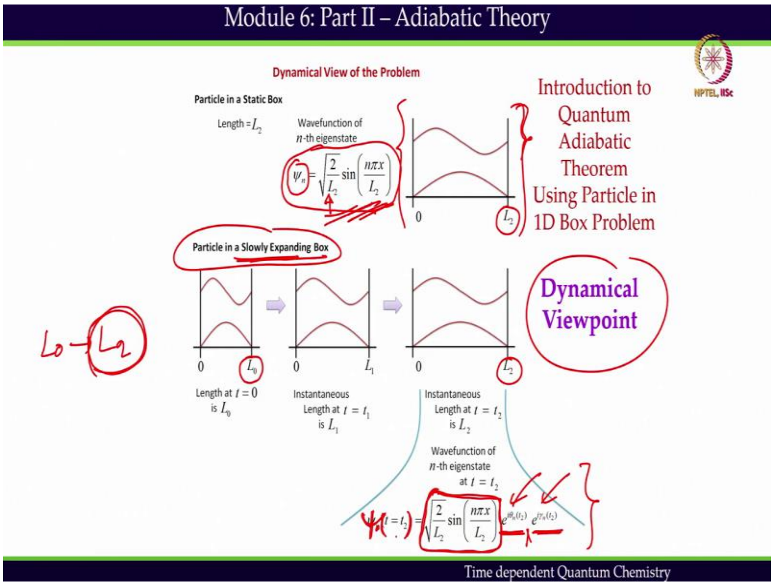

So, the entire pictorial viewpoint is following let us assume that I have one box of length L_2. So, if I have a box of length L_2 I know what is the wave function of that particle, particle wave function will be given by psi n which is given by this it depends on L_2 distance. Now, I will consider a box which is starting from an expanding box starting from L_0 to L_2 this L_2 this is the static box the box is not expanding, but here the in this expanding box problem it is slowly expanding from L_0 to L_2 finally, I have achieved this dimension L_2 which was present in the static box.

So, then in that case, the wave function immediately after the expansion for this expanding box will be this wave function which is coming from the static box function multiplied by two different phase factor these two phase factors are coming just due to the dynamical evolution of the box if it was not dynamically evolving to reach that dimension, we should have this static wave function the static wave function is given already the particle in the box.

But because it is dynamically evolving due to that dynamical evolution the wave function the static wave function will come and it will be augmented or multiplied by two different phase factor one phase factor is called dynamical phase factor another one is called geometric phase factor these two-phase factors will be added to the wave function because of the dynamical evolution this is known as adiabatic change of box.

So, this is the dynamical viewpoint of the entire theory which we have presented and the entire derivation is to get this expression final expression for the wave function final function and this there is no end here. This is this is actually the state at time at this time.

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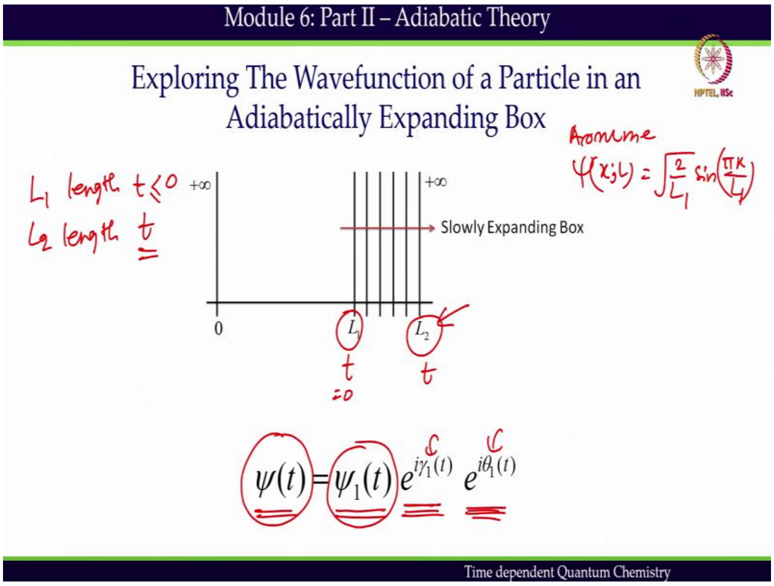

So, we will go back to our problem one-dimensional problem and we have seen that the wave function will be represented by this entire wave function $\Psi(t) = \Psi_1(t) e^{i\gamma_1(t)} e^{i\theta_1(t)}$

at time t will be represented by this. And now we will explicitly calculate what would be the expression for our values for this dynamical phase and the geometric phase for the given problem. The problem is that boxes expanding from L_1 bond is the length 2 L_2 length and at this is t equals 0 and this is at time t, it has up to time t it has expanded.

And we will say that we will assume that assume that my particle before the expansion it was in the ground state, so, the ground state wave function will be written like this way,

$\Psi(x; L) = \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L}$. And it was ground state, that is why it should be L_1. So, this was the wave function of the particle before the expansion, but the particle the box has expanded from L_1 to L_2 and L_1 is the box length less than equals 0 just before the expansion started and L_2 is the length when it has expanded completely and immediately after the expansion, this is the box length L_2. So, according to adiabatic theory, the wave function at time t immediately after the length has expanded to L_2 what is the wave function of the particle that is represented by $\boldsymbol{\Psi}_1$(t), that is the ground state wave function at time t. And then it is phase factors will be multiplied.

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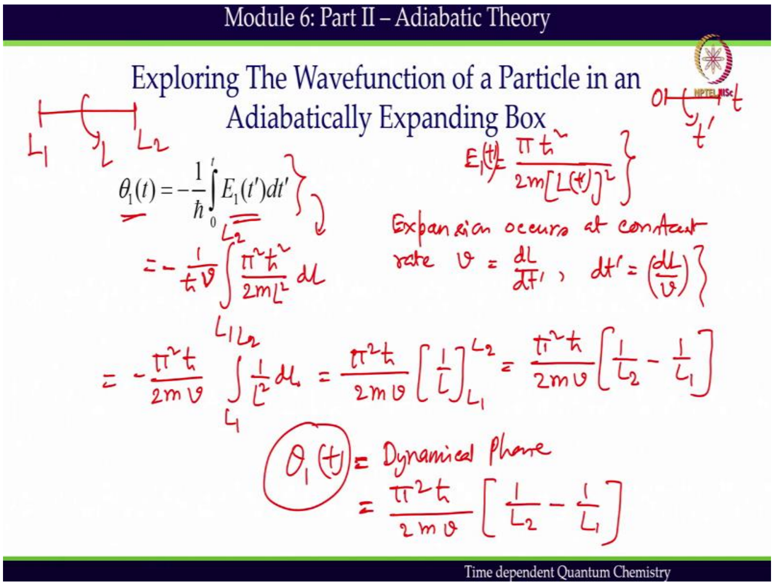

So, we will explicitly see how to get that first we will look at this $\theta_1(t)$ how much is going to be theta 1 t will depend on this integration that we have seen an E_1 the energy we know that it is going to be $\frac{\pi^2 h^2}{8m\pi^2[L(t')]^2}$. So, anytime so 0 to t this is the time interval we have the expansion time interval at any time is given within this interval is going to be t', and that is the integration we have taken.

So, if this is the expression for the ground state wave function, ground state particle, the energy of the particle is given by this, this is the instantaneous energy of the particle in the ground state. Then, we will say that, we will assume that the expansion occurs at a constant rate v that is $\frac{dl}{dt}$ is constant. And if $\frac{dl}{dt}$ is constant or $\frac{dl}{dt'}$ is constant, then one can write down $dt' = dl/v$ that we can do.

And what is L here L is the instantaneous length. So, L has changed from L_1 to L_2 and any instantaneous length in between is going to be L. So, that is the definition of this. So, what we can do is that this total time integration can be converted to spatial integration like this way,

$$\theta_1(t) = -\frac{2\pi}{hv}\int_{L_1}^{L_2}\frac{\pi^2 h^2}{8m\pi^2[L]^2}dL$$

L is an instantaneous length in the interval L_1 to L_2. So, I have been able to convert this integration to in terms of L and if we do that, then I will be able to integrate it very easily

$$\theta_1(t) = -\frac{2\pi \quad h^2}{8m}\int_{L_2}^{L_1}\frac{1}{[L]^2}dL = \frac{2\pi \quad h^2}{8m}[\frac{1}{L_2} - \frac{1}{L_1}]$$

So, we finally get this $\theta_1(t)$ this value is the dynamical phase which is accumulated by the wave function due to this dynamical evolution is going to be

$$\frac{2\pi}{8m}\frac{h^2}{}\int_{L_2}^{L_1}\frac{1}{[L]^2}\,dL = \frac{2\pi}{8m}\frac{h^2}{}\left[\frac{1}{L_2}-\frac{1}{L_1}\right]$$

. So, we have got one phase factor for the expanding one-dimensional box problem.

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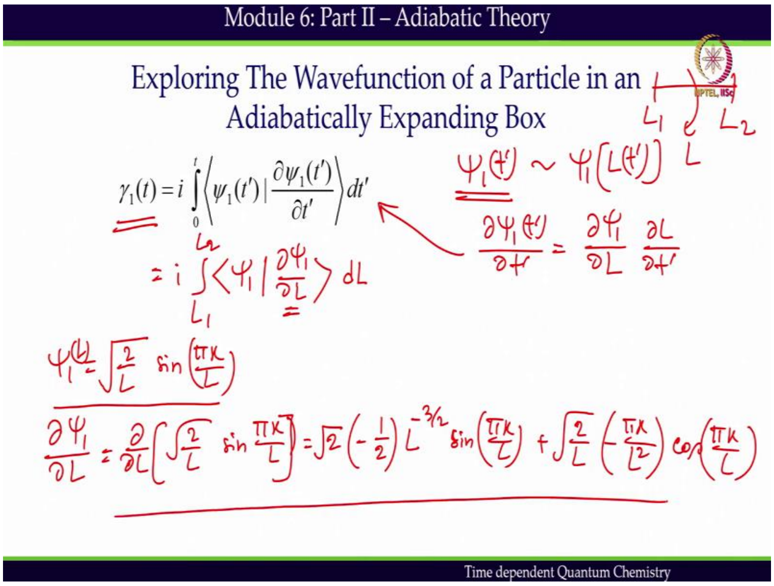

Next, we look at the geometric phase in the geometric phase we have this expression and here **$\Psi_1(t')$** **Ψ_1** time dependent because it is the **Ψ_1** L it is actually depends on L that is why an L is time dependent that is why psi is time dependent. So, one can write down this derivative as follows

$$\frac{\partial \Psi_1}{\partial t'} = \frac{\partial \Psi_1}{\partial L}\frac{\partial L}{\partial t'}$$

again we are converting this expression in terms of L. So, if we do that, then I will be able to write down

$$\gamma_1(t) = i\int_{L_1}^{L_2} < \Psi_1 \parallel \frac{\partial \Psi_1}{\partial L} > dL$$

We know that

$$\Psi_1(x; L) = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$$

So, L we said that this is L_1 this is L_2 at any instant of time the length of the box is given by L in between these two intervals so, that is given by this the wave function ground state function will be given by this.

So, if I have this ground state wave function like this, then I will be able to get the derivative with respect to L because that is derivative what I need here, it is going to be now

$$\frac{\partial \Psi_1}{\partial L} = \frac{\partial}{\partial L}\left[\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\right] = \sqrt{2}(-\frac{1}{2})L^{-3/2}\sin\frac{\pi x}{L} + \sqrt{\frac{2}{L}}(-\frac{\pi x}{L^2})\cos\frac{\pi x}{L}$$

So, we get this first derivative with respect to L of this function

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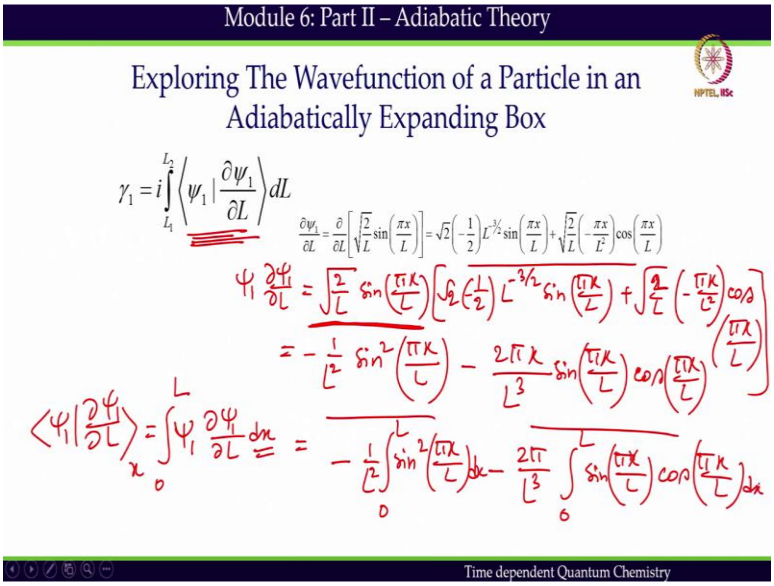

And once we get the first derivative, we will be able to because I have to multiply now Ψ_1. So, I if I want to find out Ψ_1

$$\Psi_1\frac{\partial \Psi_1}{\partial L} = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\,[\sqrt{2}(-\frac{1}{2})L^{-3/2}\sin\frac{\pi x}{L} + \sqrt{\frac{2}{L}}(-\frac{\pi x}{L^2})\cos\frac{\pi x}{L}]$$

So, if I multiply then finally, what I get is going to

$$\Psi_1\frac{\partial \Psi_1}{\partial L} = -\frac{1}{L^2}sin^2\left(\frac{\pi x}{L}\right) - \frac{2\pi x}{L^3}\sin\frac{\pi x}{L}\cos\frac{\pi x}{L}$$

And in the end, we have to get the integration.

$$< \Psi_1 \| \frac{\partial \Psi_1}{\partial L} > = \int_0^L \Psi_1^* \frac{\partial \Psi_1}{\partial L}\, dx$$

because this ground state wave function is a real function. So, psi 1 star and psi 1 are equivalent.

They do not have the complex conjugate because they are real. So, what I get have to do now, this entire thing has to be integrated

$$< \Psi_1 \parallel \frac{\partial \Psi_1}{\partial L} >= -\frac{1}{L^2}\int_0^L sin^2\left(\frac{\pi x}{L}\right)dx - \frac{2\pi}{L^3}\int_0^L x\sin\frac{\pi x}{L}\cos\frac{\pi x}{L}\,dx$$

So, this is the integration we which we need to perform.

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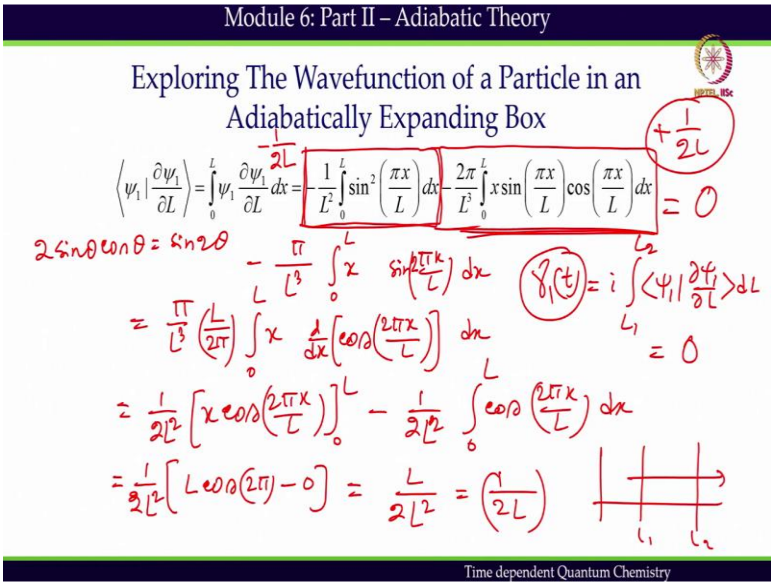

So, we will perform it step by step first to look at this integration the right this first integration, in order to do this first integration, we will use trigonometric identity as

$$\cos 2\theta = 1 - 2sin^2\theta$$

$$or, -2sin^2\theta = \cos 2\theta - 1$$

we will use this one. Because in this part if we look at this part

$$-\frac{1}{L^2}\int_0^L \quad sin^2\left(\frac{\pi x}{L}\right)dx = -\frac{1}{2L^2}\int_0^L [\cos\frac{2\pi x}{L} - 1]dx$$

So, if we do that,

$$-\frac{1}{L^2}\int_0^L \quad sin^2\left(\frac{\pi x}{L}\right)dx = -\frac{1}{2L^2}\int_0^L [\cos\frac{2\pi x}{L} - 1]dx = -\frac{1}{2L}$$

The other integration, this integration, Now, we are looking at this integration, in order to do this integration, we will be able to write down.

$$2\sin\theta\cos\theta = \sin 2\theta$$

So,

$$-\frac{\pi}{L^3}\int_0^L x\,2\sin\frac{\pi x}{L}\cos\frac{\pi x}{L}dx$$

that is the integration I have, which is which can be written as

$$= -\frac{\pi}{L^3}\int_0^L x\sin\frac{2\pi x}{L}\,dx$$

So-

$$= \frac{\pi}{L^3}\left(\frac{L}{2\pi}\right)\int_0^L x\frac{d}{dx}\left[\cos\left(\frac{2\pi x}{L}\right)\right]dx$$

By integration by parts-

$$= \frac{1}{2L^2}\left[L cos\left(\frac{2\pi L}{L}\right) - 0\right] - \frac{1}{2L^2}\int_0^L \cos\left(\frac{2\pi x}{L}\right)dx$$

Finally ,

$$= \frac{L}{2L^2} = \frac{1}{2L}$$

$$< \Psi_1 \parallel \frac{\partial \Psi_1}{\partial L} > = 0$$

if this integration is becoming 0, then

$$\gamma_1(t) = i\int_{L_1}^{L_2} < \Psi_1 \parallel \frac{\partial \Psi_1}{\partial L} > dL = 0$$

So, what we are seeing here is that the geometric phase becomes 0 for an expanding box, when the box is expanding from L_1 to L_2 but it is accumulating dynamical phase but geometric phase becomes 0.

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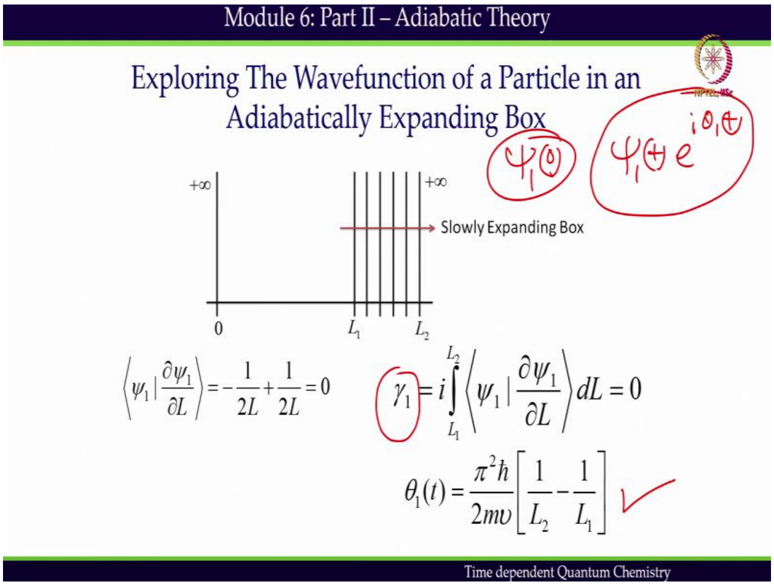

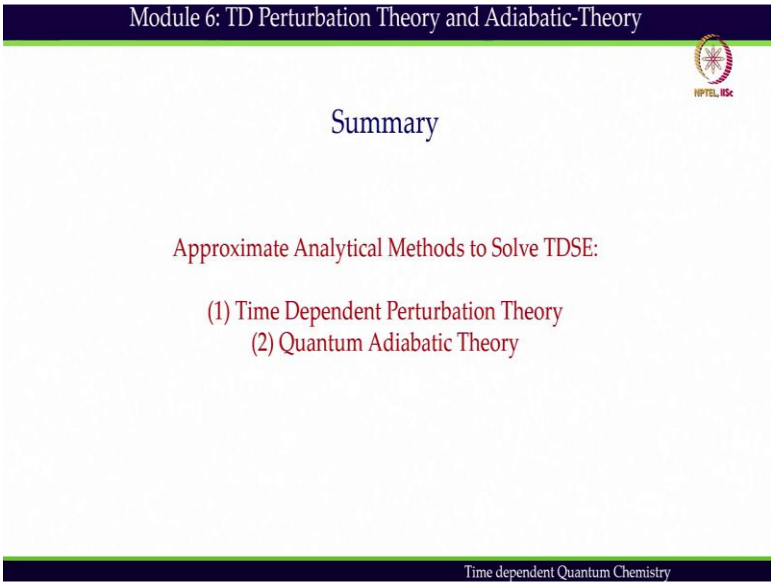

So, what we have observed is summarized here the wave function initially the wave function was this [$\mathbf{\Psi}_1(0)$]. Finally, the wave function would be $\Psi_1(t)e^{i\theta_1(t)}$ because we started with the ground state wave function, so, it is going to be $\Psi_1(t)e^{i\theta_1(t)}$ and γ_1 vanishes. So, this is the final wave function after the expansion and $\theta_1(t)$ is given by this expression.

When we see this geometric phase to be 0, we can remember that anytime if the wave function is real, then the geometric phase after the adiabatic expansion is going to be 0. That is another consequence of adiabatic theorem which we can prove actually but we will not do it immediately, we have come to the end of this present module. In this module, we have given theories which can be used to solve analytically the TDSE Time Dependence Schrodinger Equation to explore the dynamics of a quantum system.

We have presented time dependent perturbation theory where we have which can be used to find out the dynamical evolution of a system time dependent perturbation theory will be very frequently used for light absorption, light emission and non-radiative transition. In addition to this time dependent perturbation theory, there is another analytical approach which is available which is called quantum adiabatic theory, which we have presented in the light of expanding one dimensional box. We will end this session and we will meet again in the next module.