Time Dependent Quantum Chemistry
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Lecture 39
Derivation of Quantum Adiabatic Theory

Welcome back to module 6, we have we are presenting quantum adiabatic theorem. And one thing we tried to emphasize here is that when there is a dynamical evolution going on in quantum system, just before initiation of the dynamical evolution the system is in a stationary state it can be in a single state let us say ground state, but after the dynamical evolution is turned off, immediately after that point, point of time the system is not in the stationary state. System is in a non-stationary state and that non-stationary state has to be expressed in terms of the linear combination of the stationary states available for the system. And that is exactly what we have done here.

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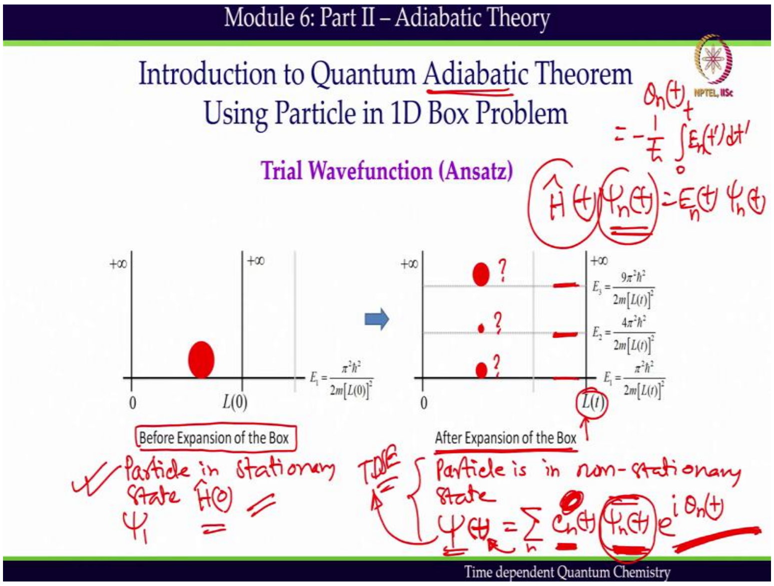

And this is general consensus of general way of doing the calculating quanta exploring the quantum system in the which is using TDSE Time Dependent Schrodinger equation. So, what we are saying is that just before the expansion it was in the stationary state and the stationary states are given by H_0 but after immediately after the expansion we cannot give more time after the expansion it is just exactly immediately after the expansion of the box the particle is in non-stationary state and that non stationary state which means that I may have population in different states that is why it is non stationary.

If it is in the with a population staying in the same state then it is not as non-stationary state anymore, but if the population has staying in different states, it means that all states are going to contribute it is more like a superposition and the moment I have superposition it is called non-stationary state. So, this non-stationary state will be defined as linear combination of all stationary states present at that time at that L(t) distance.

And L(t) distance which means that H(t) Hamiltonian will give me that stayed stationary states. So, those stationary states may be occupied and we need to find out the population of each occupancy of the states. So, that is the basic idea, which we have to follow and we have clarified that due to this non-adiabatic sorry, due to this adiabatic change this temporal change from 0 to T the total accumulated phase would be this one for each nth state.

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

Each stationary state is accumulating our temporal phase of this kind, because E_t is changing $E_n(t)$ is changing. So, instead of writing this expression, this entire thing, we will assume that θ_n we will define a quantity called

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

that is the θ_n . So, basically this entire integration is θ_n. So, we will just replace this by θ_n ,i does not have that.

So, it is theta n is actually

$$\theta_n = -\frac{2\pi}{h}\int_0^t E_n(t')dt'$$

So, in that case I will be able to write on iθ_n or phase factor total phase factor which is accumulated by the n th stationary state at that time a t L(t) distance for the L(t) of the box. Each stationary state is accumulating the phase this is the phase each stationary state wave function is given by this at that time and its contribution to the total wave function which is a non-stationary state.

So, what we need to do now, as is usual for any Schrodinger way of solving the problem, we have to insert this 1 to TDSE to get this unknown C_n part to find out what is the population, each state contributing how much each state is contributing to the non-stationary state of the particle.

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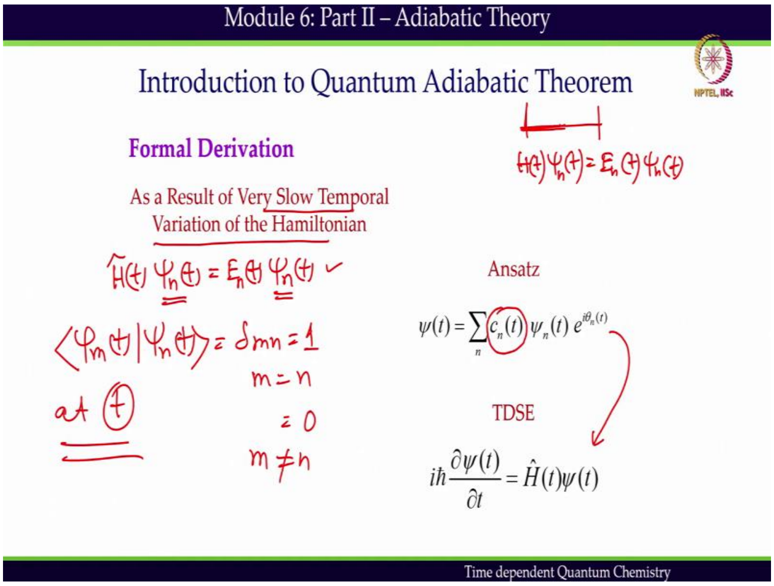

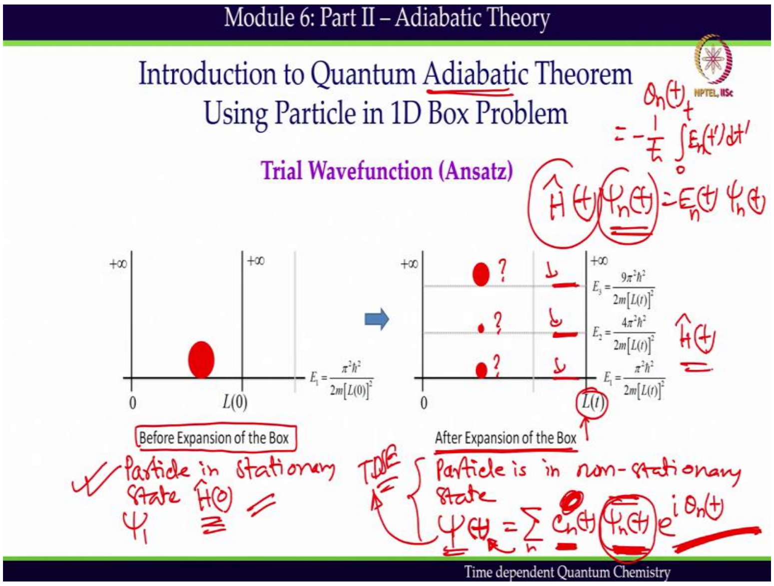

So, that is exactly what we are going to do right now. For the subsequent mathematical derivation further we will write down few things, we will write down that as a result of slow temporal variation of the Hamiltonian, this at time t, which is immediately after the process is turned off, this eigenvalue equation is valid

$$H(t)\Psi_n(t) = E_n(t)\Psi_n(t)$$

this eigenvalue equation is valid and this is this is one thing which we have already said that before the expansion, the eigenvalue equation was

$$H(0)\Psi_n(0) = E_n(0)\Psi_n(0)$$

And after the expansion I have now this is t this is instead of 0 I have now t instead of 0 I have now t instead of 0 I have now t and instead of 0 I have now t immediately after the expansion is turned off. So, this part is valid. And when this is valid, then we assume that at time t which is L(t) is the distance rather the dimension of the box for this dimension of the box, the all this $\boldsymbol{\Psi}_n$ which you have written it is actually the states here not states here, these are not the these states are given by H(0).

But these states stationary states are given by H(t) that is the Hamiltonian at time t. So, those states are orthonormal to each other. So, I can write down that.

$$< \Psi_m(t) \parallel \Psi_n(t) > = \ \Psi_{mn} = 1 \ when \ m = n \ , = 0 \ when \ m \neq n$$

So, they remain. So, those states are remained orthonormal at any at that time.

So, at time t immediately after the process has been turned off those stationary states remain orthonormal. So, these are the facts we have been considered to solve this problem. And now, all we need to do is that this is the ansatz which is a trial with function we have to insert to this TDSE and get the solution. Solution which means that we will be looking for what the expression we have for C_n. C_n will give me the population of each state each available state.

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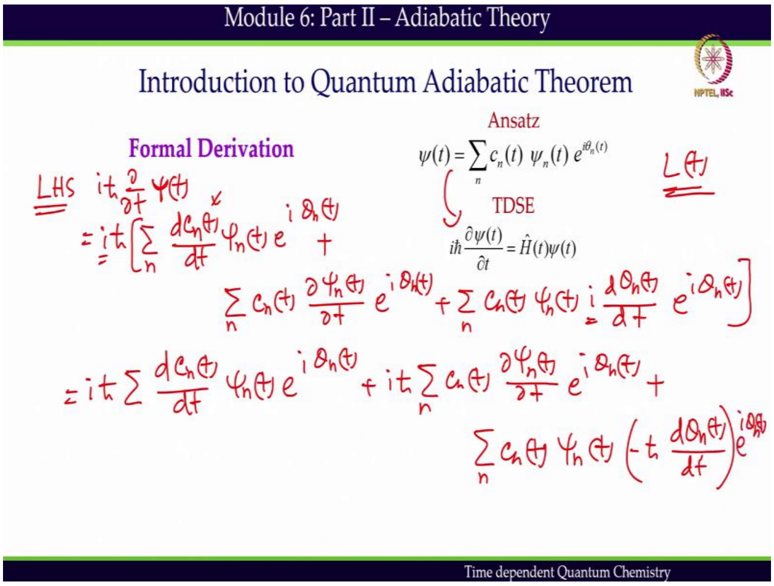

So, let us look at the derivation, we will first insert this to the right-hand side. So, the left-hand side so, left hand side for left hand side what I get is that i h cut partial derivative with respect to t $\boldsymbol{\Psi}$(t) equals i h cut now, summation over n this is d C_n (t) this is not a partial derivative anymore because C_n depends on all the on time. But this is partial derivative because although explicitly not showing it x depends on the variable x sorry the psi depends on variable x.

So, it should be written like this way $\boldsymbol{\Psi}$(x;L(t)) instead of writing like this way we are just writing $\boldsymbol{\Psi}$ (t). So, we should not get confused. What is the notation what does it mean by this notation and that is why we are using the partial derivative here. But C_t depends on time so that is why this is total derivative we are considering here. Now, this is

$$\frac{h}{2\pi}\frac{\partial\Psi(x,t)}{\partial t} = i\frac{h}{2\pi}[\sum_n \frac{dc_n(t)}{dt}e^{i\theta_n(t)} + \sum_n c_n(t)\frac{\delta\Psi_n(t)}{\delta t}e^{i\theta_n(t)} + \sum_n c_n(t)\Psi_n(t) i\frac{\partial\theta_n(t)}{\partial t}e^{i\theta_n(t)}]$$

Now, this is going to be also the not going to be the partial derivative is going to be total derivative because $\theta_n$depends on the energy and energy depends on does not depend on x energy depends on only L(t). So, that is what this is, this is going to be total derivative. So, this is what I get.

So, if I simplify a little bit further, I will get

$$\frac{h}{2\pi}\frac{\partial\Psi(x,t)}{\partial t} = i\frac{h}{2\pi}\sum_n \frac{dc_n(t)}{dt}e^{i\theta_n(t)} + i\frac{h}{2\pi}\sum_n c_n(t)\frac{\delta\Psi_n(t)}{\delta t}e^{i\theta_n(t)} + \sum_n c_n(t)\Psi_n(t)(-\frac{h}{2\pi}\frac{\partial\theta_n(t)}{\partial t})e^{i\theta_n(t)}]$$

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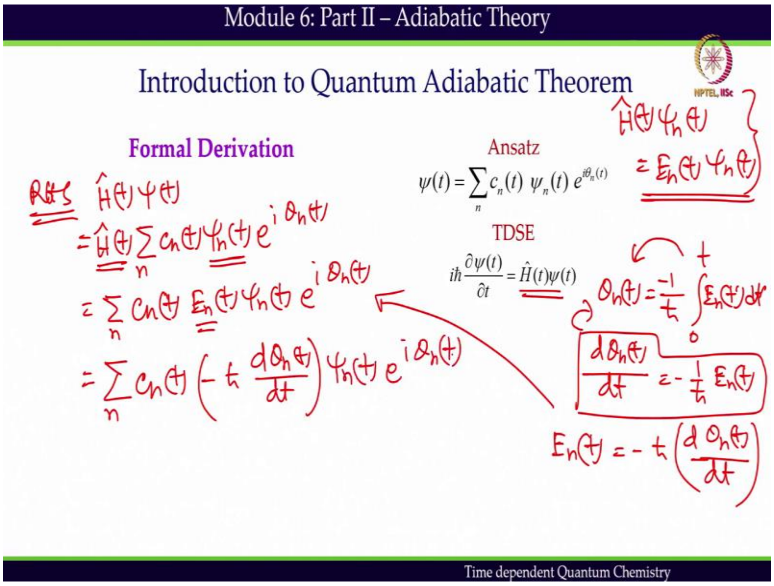

So, this is the left hand side right hand side one can insert here right hand side right hand side is going to be

H(t) $\boldsymbol{\Psi}_n$(t) which is nothing but H(t) summation of C_n(t) $\boldsymbol{\Psi}_n$(t) $e^{i\theta_n(t)}$ equals H(t) now, H(t) acting on $\boldsymbol{\Psi}_n$(t) we have shown we have previously said that some H(t) acting on $\boldsymbol{\Psi}_n$(t) will give me E_n(t) $\boldsymbol{\Psi}_n$(t) that is the time independent Schrodinger equation the eigenvalue equation at time t which is immediately after the adiabatic process is turned off this eigenvalue equation holds that is why we get the different eigenstates at that time.

$$H(t)\,\boldsymbol{\Psi}_n(t) = H(t)\sum_n c_{n(t)}\,e^{i\theta_n(t)}$$

And so, I can write down this is nothing but following this is nothing but C_n(t) then En(t) $\boldsymbol{\Psi}_n$(t) $e^{i\theta_n(t)}$. Now, because this θ_n (t) is nothing but $= -\frac{2\pi}{h}\int_0^t E_n(t')dt'$ one can write down that

$$\frac{d\theta_n(t)}{dt} = -\frac{2\pi}{h}E_n(t)$$

one can write down this. So, basically integration is now converted to its derivative form, from this derivative form only we get this integration so, we are getting the derivative form.

Once we get this derivative form one can write down this

$$E_n(t) = -\frac{h}{2\pi}\frac{d\theta_n(t)}{dt}$$

So, this can be inserted here we have E_b(t) this can be inserted here and what I get is that the right-hand side finally, transform to

$$H(t)\,\Psi_n(t) = \sum_n c_{n(t)}\left(-\frac{h}{2\pi}\frac{d\theta_n(t)}{dt}\right)\Psi n(t)\, e^{i\theta_n(t)}$$

that is what I get from right hand side. Because it is TDSC left hand side and right-hand side should be equal.

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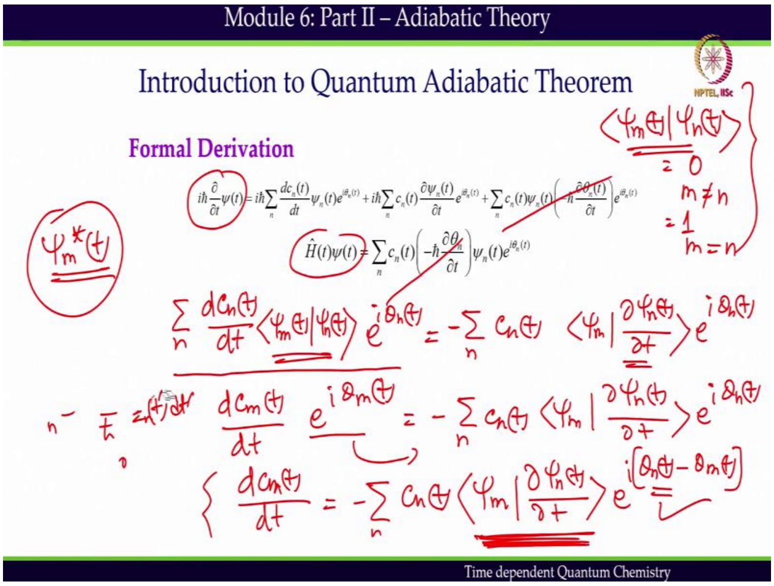

So, this part and this part should be equal and if we make it equal what we see here is that this part and this part will be cancelling each other and in the end what I get is I get

$$i\frac{h}{2\pi}\sum_n \frac{dc_n(t)}{dt}\Psi n(t)\, e^{i\theta_n(t)} = -i\frac{h}{2\pi}\sum_n c_n(t) \quad \frac{\delta\Psi_n(t)}{\delta t} e^{i\theta_n(t)}$$

this is what I get i end i h cut h cut will cancel out.

So, finally, I get after inserting that trial wave function which is also called ansatz that we get this expression.

$$\sum_n \frac{dc_n(t)}{dt}\Psi n(t)\, e^{i\theta_n(t)} = -\sum_n c_n(t) \quad \frac{\delta\Psi_n(t)}{\delta t} e^{i\theta_n(t)}$$

And we have to further reduce it and we will be able to reduce it further by multiplying the entire expression multiplying the entire expression by Ψ so, we will multiply by $\Psi^*_m(t)$ and make use of ortho normalization condition. So, I will multiply this one by $\Psi_m(t)$. So, I will just rewrite this one as follows. I will write down as and then integrate it over the spatial coordinate which is

$$\sum_n \frac{dc_n(t)}{dt} < \Psi_m(\mathrm{t}) \parallel \Psi_n(\mathrm{t}) > e^{i\theta_n(t)} = -\sum_n c_n(t) \quad < \Psi_m \parallel \frac{\delta\Psi_n(t)}{\delta t} > e^{i\theta_n(t)}$$

So, this is what I get to reduce it by multiplying by this complex conjugate of the psi n because we are going to make use of the orthonormal condition.

Orthonormal condition we have seen it is this is the orthonormal condition.

$$< \Psi_m(t) \parallel \Psi_n(t) > = \Psi_{mn} = 1 \; when \; m = n \, , = 0 \; when \; m \neq n$$

So, we make use of this and this is a trick which we use many occasions to reduce TDSE so, this is a very common trick. So, this expression this final expression will reduce down every other terms will be 0 because of this term, except for when n equals m.

So, I get only this term surviving $\frac{dc_m(t)}{dt} e^{i\theta_m(t)}$ will be surviving. On the other hand, right hand side, I cannot do anything because this is with respect to derivative I do not have any treat for the derivative yet. So, I have to keep it as it is

$$\frac{dc_m(t)}{dt} e^{i\theta_m(t)} = -\sum_n c_n(t) \quad < \Psi_m \parallel \frac{\delta\Psi_n(t)}{\delta t} > e^{i\theta_n(t)}$$

. And what we will do we will just take this 1 on the right-hand side. And finally, we will be able to write down

$$\frac{dc_m(t)}{dt} = -\sum_n c_n(t) \quad < \Psi_m \parallel \frac{\delta\Psi_n(t)}{\delta t} > e^{i[\theta_n(t) - \theta_m(t)]}$$

that is the final expression we get.

So, in order to reduce this expression, what we need to do, we need to find out this expression, if we get this expression because θ_n is has already an expression $\theta_n(t)$ we have seen is nothing but

$$\theta_n = -\frac{2\pi}{h} \int_0^t E_n(t')dt'$$

this is the integration to present material. So, this part is known, the C this part if we get an expression, we will be able to reduce the expression further.

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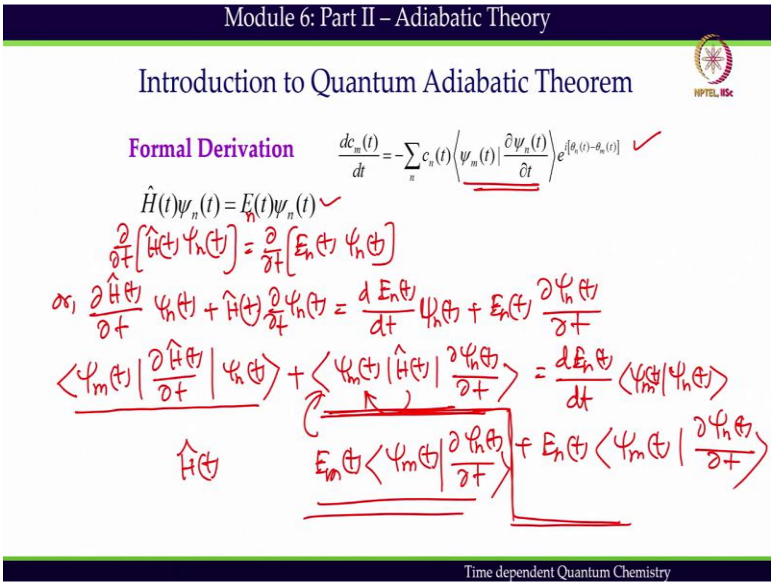

That is exactly what we will do. We have now, this expression already given. And we need to know this one. So, in order to get this one, what we will do, we will first take the time derivative of this expression time derivative of this expression, this is the eigenvalue equation at time t, immediately after the adiabatic process is turned off. So,

$$\frac{\partial}{\partial t}[H(t)\Psi_n(t)] = \frac{\partial}{\partial t}[E_n(t)\Psi_n(t)]$$

So, it is going to be now, first it is going to be this is going to first term would be partial derivative, because Hamiltonian depends on x plus wave function also depends on x, that is why it is going to be partial derivative equals this is going to be total derivative, because energy depends on the length adopted at that time t. So, it depends on time only and this remains plus I have now, partial derivative $E_n(t)$ partial derivative of $\boldsymbol{\Psi}_n(t)$ dt.

$$\frac{\partial H(t)}{\partial t}\Psi_n(t) + H(t)\frac{\partial}{\partial t}\Psi_n(t) = \frac{dE_n}{dt}\Psi_n(t) + E_n(t)\frac{\partial \Psi_n(t)}{\partial t}$$

So, this is the expression what we what we get. Now, if we multiply again we will use the same trick if we multiply from left hand side this if we multiply then what I get is that

$$< \Psi_m(t) \parallel \frac{\partial H(t)}{\partial t} \parallel \Psi_n(t) > + < \Psi_m(t) \parallel H(t) \parallel \frac{\partial}{\partial t}\Psi_n(t) >= \frac{dE_n}{dt} < \Psi_m(t) \parallel \Psi_n(t) > + E_n(t) < \Psi_m(t) \parallel \frac{\partial \Psi_n(t)}{\partial t} >$$

so, this is the expression finally, we get.

And we have to note that this is the integration of our coordinate space coordinate space which means that this is nothing but $\int_0^L \Psi_m^* \frac{\partial H(t)}{\partial t} \Psi_n(t)\, dx$ that is the integration. So, this is this integration. This is the meaning of this Dirac notation. So, we will go ahead and we will be able to reduce it because H is an Hermitian operator.

It can actually act because it is Hermitian operators the property of Hermitian operator we know that it can act from right hand side so, it can actually act on this. And if it is acting on this, then what I get from this is that this part is nothing but $E_m(t) < \Psi_m(t) \parallel \frac{\partial}{\partial t}\Psi_n(t) >$. So, this part can be written like this.

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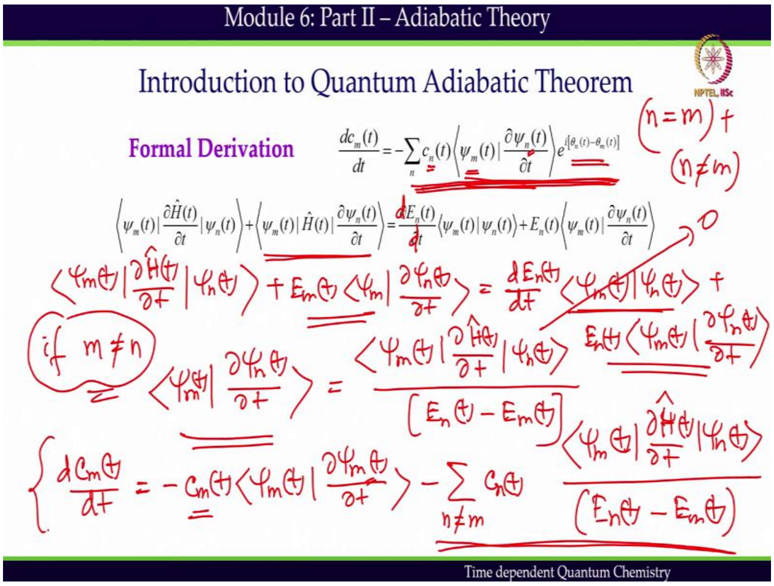

And if this integration can be written like this way then I can replace this part here and if I replace this part here, I can replace this part here. So, what we will do is following I have this one which can be written as now

$$\Psi_m(t) \parallel \frac{\partial H(t)}{\partial t} \parallel \Psi_n(t) > + E_m(t) < \Psi_m(t) \parallel \frac{\partial}{\partial t}\Psi_n(t) >$$

$$= \frac{dE_n}{dt} < \Psi_m(t) \parallel \Psi_n(t) > + E_n(t) < \Psi_m(t) \parallel \frac{\partial \Psi_n(t)}{\partial t} >$$

So, what we get now, if we consider that m naught equals n if m not equals n this integration $\frac{dE_n}{dt} < \Psi_m(t) \| \Psi_n(t) >$ will become 0 this goes to 0 if m not equals n then

$$< \Psi_m(t) \| \frac{\partial}{\partial t} \Psi_n(t) > = \frac{< \Psi_m(t) \| \frac{\partial H(t)}{\partial t} \| \Psi_n(t) >}{[E_n(t) - E_m(t)]}$$

Because this part and this part we are clubbed together and we are finally writing down.

But this can be written only when m not equals n. So, and this is exactly what we have here, this this part so, we can insert it and if we insert it what we get here is that

$$\frac{dc_m(t)}{dt} = -c_m(t) < \Psi_m(t) \| \frac{\partial}{\partial t} \Psi_m(t) > - \sum_{n \neq m} c_n(t) \frac{< \Psi_m(t) \| \frac{\partial H(t)}{\partial t} \| \Psi_n(t) >}{[E_n(t) - E_m(t)]}$$

So, what we have done? This entire summation we have divided into two parts one part for n equals m another part for n not equals m. For n not equals m we have written this part entire part but for n equals m what will happen if n equals m then this is going to be C_m that is we have written one term we will get to n equals m, and then this is going to be m but the n equals m. So, this part is m and this part will go 0 because $\theta_m - \theta_m$ will be 0. So, that part will not exist anymore. So, finally, we have found that the expression can be reduced to this.

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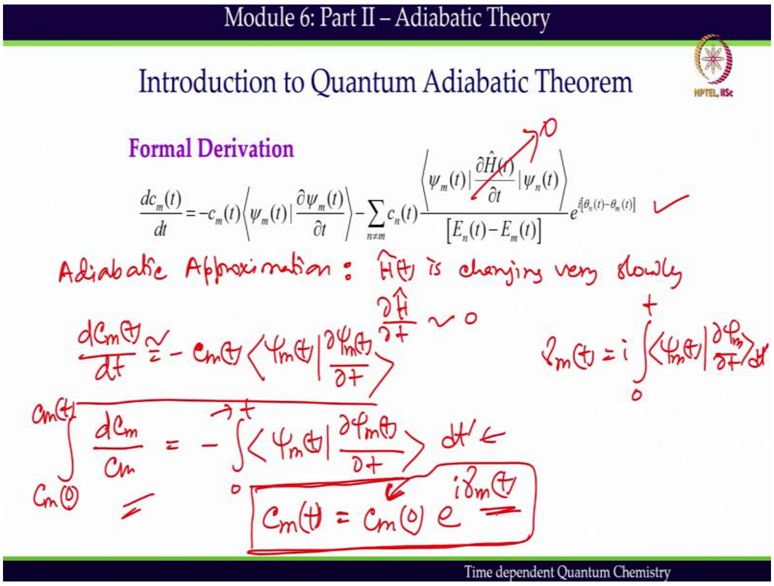

And once we have reduced to this expression, we will be able to do now, at adiabatic approximation, that adiabatic approximation is following a adiabatic approximation assumes that because H is changing very slowly, one can write down $\frac{\partial H(t)}{\partial t}$ to be negligible or 0. So, this part becomes 0 and if this part becomes 0, I get the expansion coefficient equals $-c_m(t) < \Psi_m(t) \| \frac{\partial}{\partial t}\Psi_m(t) >$ this is the approximate under a adiabatic approximation we get this expression.

And once we get this expression one can now integrate this expression as follows this is going to be

$$\int_{c_m(0)}^{c_m(t)} \frac{dc_m(t)}{c_m(t)} = -\int_0^t < \Psi_m(t) \| \frac{\partial}{\partial t}\Psi_m(t) > dt'$$

So, we have again distinguished the variable for the integration and the limit for the integration. So, limit is showing that I am looking at the integration from 0 to t.

And if I do that integration, then immediately I get this value $C_m(t)$ at time t which is immediately after the adiabatic process is turned off. This will give me the population at the n th state that will be controlled by C_m (0) at time t equals 0, what was the population multiplied by e to the power so, this part is going to be L (n).

So,

$$c_m(t) = c_m(0)e^{i\gamma_m(t)}$$

where

$$\gamma_m(t) = i\int_0^t < \Psi_m(t) \| \frac{\partial}{\partial t}\Psi_m(t) > dt'$$

so, this is the solution. So, what we are getting is that the expansion coefficient for each state is given by this expression it will depend on the initial population at that state. And it will depend on the another phase factor which is going to be introduced due to this adiabatic change.

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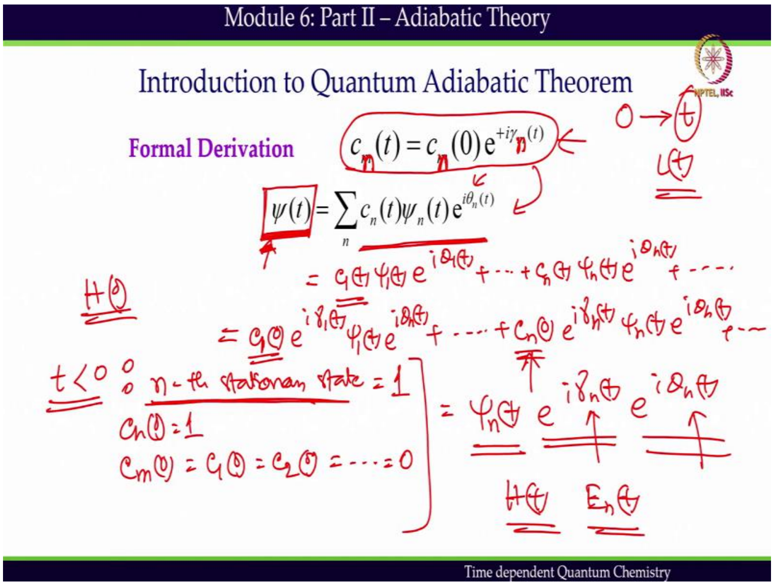

So, we can now write down all everything all together this was the wave function of the stationary or non-stationary state immediately after them. So, it started at 0 time it ended at time t and immediately after the adiabatic process ended, I would like to know the wave function which is representing the particle, but the wave function is no longer a stationary state with functional it is a non-stationary state wave function and a non-stationary state wave function is represented as some linear combination of all stationary state available at that time only at this t time which is for the box L t dimension.

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

And that depends on this particular phase factor which we have seen already and now C_n has a particular value. Now, for a general this part is for the for any m state. So, this can be also converted to n state also any n state, so I can convert it and the moment I convert it, I will be able to plug that in. And if I plug that in, I will be writing it down

$$\Psi(t) = c_1(t)\Psi_1(t)e^{i\theta_1(t)} + \dots\dots\dots\dots\dots\dots + c_n(t)\Psi_n(t)e^{i\theta_n(t)}$$

And we know that each one each expansion coefficient will be given by this so, I can write down as

$$\Psi(t) = c_1(0)e^{i\gamma_1(t)}\Psi_1(t)e^{i\theta_1(t)} + \dots\dots\dots\dots\dots\dots + c_n(0)e^{i\gamma_n(t)}\Psi_n(t)e^{i\theta_n(t)}$$

Now, if we consider the initial condition, initial condition was the population before t equals t less than 0 before the process started, we assume that this particle was in the n th stationary state if the particle was n th stationary state, and that means the population is going to be then 1. So, $C_n(0)$ is going to be 1 remaining all others C(0) which is $C_1(0)$, $C_2(0)$ at 0 time all are going to be 0. So, as you can see that these all terms will be 0 except for this term.

So, in the end, what I get is that

$$\Psi_n(t)e^{i\gamma_n(t)}e^{i\theta_n(t)}$$

that is the that is the way it reduces. So, it shows that if I start with n th stationary state of H (0), the final finally the particle will stay under adiabatic approximation. This may not be true for if I do it quickly, the expansion happens very quickly.

But the expansion because the expansion happens very slowly. The particle remains in the n th state of H (t) discrete n th state of H(t) but it stays in the n th state that means the energy state will be defined by this time, but that wave function accumulates to different phases. And the phases the definition of these phases, this θ_n is called dynamical phase and these γ_n is called geometrical geometric phase. We will we will look at what is the meaning of this different phases in the next class.