Time Dependent Quantum Chemistry
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Module 08 Lecture 45
Quantum Dissipative Dynamics

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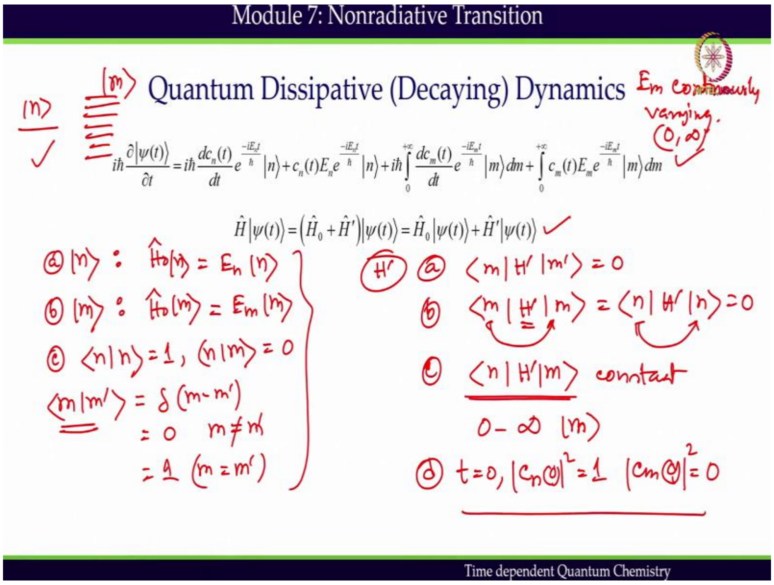

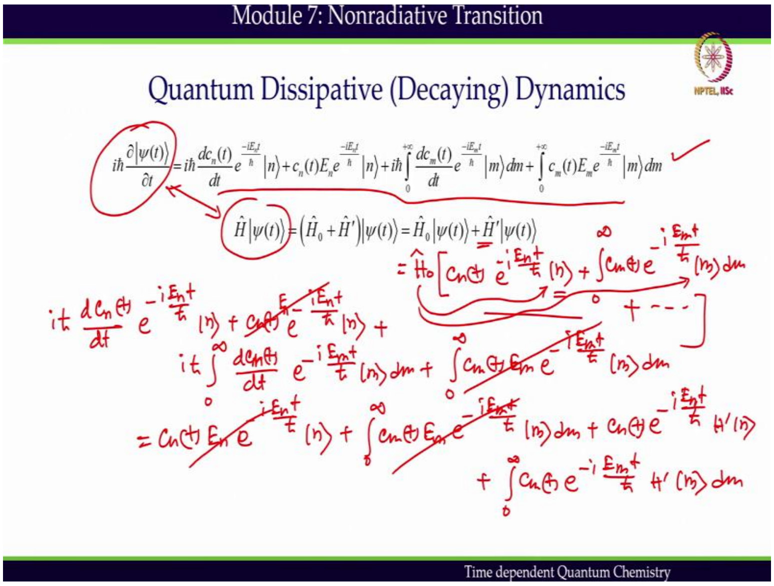

So, this is another initial condition we have defined. So, based on these assumptions, we will move forward and we will take a look at the remaining part. So, this is the Time Derivative part of the TDSE and this is the right hand side of the TDSE, the right hand side of the TDSE can be written as follows.

I can explicitly write down as

$$H\Psi(t) = H_0\{c_n(t)e^{-\frac{i2\pi E_n t}{h}}|n> + \int_0^{\infty} c_m(t)e^{-i\frac{2\pi E_m t}{h}}|m> dm] + H'[c_n(t)e^{-\frac{i2\pi E_n t}{h}}|n> + \int_0^{\infty} c_m(t)e^{-i\frac{2\pi E_m t}{h}}|m> dm]$$

And if we do that, then finally, we have to equate because this a TDSE we have to equate the left hand side and right hand side if we equate them, then what I get here is that this part would be equal to this part and one can now use this employ this operator on this |n> state and we know that is going to be an Eigen value equation again this operator on this |m> state will get the Eigenvalue equation and if we do that, then we have following terms

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

So, this is the left hand side and right hand side would be

$$= c_n(t)E_n e^{\frac{i2\pi E_n t}{h}}|n> + \int_0^{\infty} c_m(t)E_m e^{-i\frac{2\pi E_m t}{h}}|m> dm += c_n(t)e^{-\frac{i2\pi E_n t}{h}}H'|n> + \int_0^{\infty} c_m(t)E_m e^{-i\frac{2\pi E_m t}{h}}H'|m> dm]$$

So, we can see that there are few terms which will be cancelling out. So, this term E_m term this term will be cancelling out and this term here I had another term E_n. So, this term will also cancel out.

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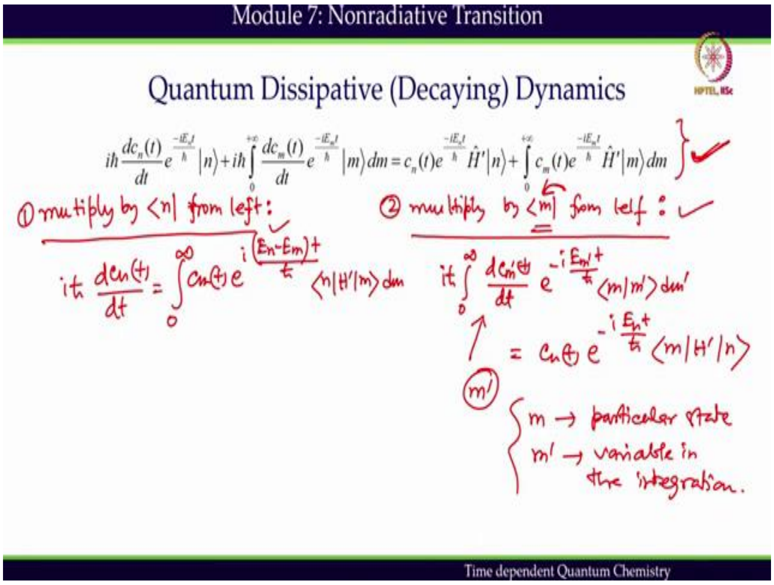

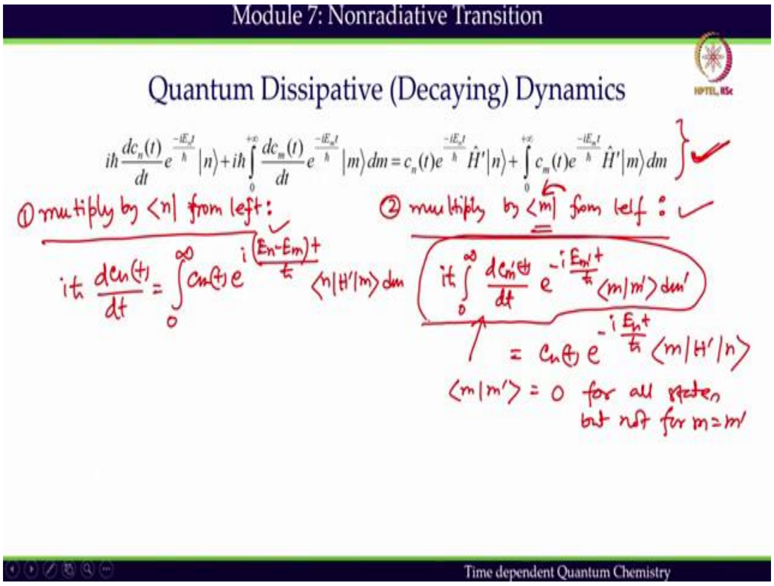

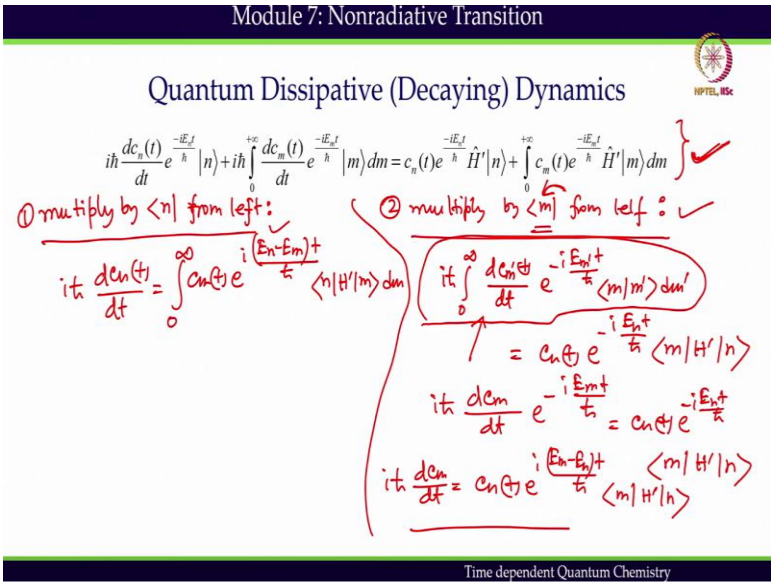

So, finally what I get is this expression.

$$\frac{ih}{2\pi}\frac{dc_n}{dt}e^{-\frac{i2\pi E_n t}{h}}|n> + \frac{ih}{2\pi}\int_0^\infty \left\{\frac{d}{dt}c_m(t)\right\}e^{-i\frac{2\pi E_m t}{h}}|m>dm == c_n(t)E_n e^{\frac{i2\pi E_n t}{h}}H'|n> + \int_0^\infty c_m(t)E_m e^{-i\frac{2\pi E_m t}{h}}H'|m>dm$$

Now, we will reduce it further we will do one thing we will first multiply by this [<n|] from left and then the same equation we will multiply by |m>. So, this is going to be complex conjugate of that <m| from left. So, this is the two mathematical tricks we will use. And this is something which we have not done in the Time Dependent Perturbation theory.

In the Time Dependent Perturbation theory, we have not tried to obtain a couple differential equation, which we are trying to do here, but up to this point, the derivation steps are quite similar to the what we have used in Time Dependent Perturbation theory.

So, if we do that, if I multiply by <n| by from the left and if I multiply <m| from the left then one can easily deduce this following thing making some using the assumptions we have made assumption is not the ortho normalization condition which we can use and also we can as we assume that the state are not getting coupled with itself.

So, those assumptions we will make and then we will be able to reduce it following way. So, if I use this then I get this equation

$$\frac{ih}{2\pi}\frac{dc_n}{dt} = \int_0^\infty c_m(t)e^{i\frac{2\pi(E_n - E_m)t}{h}} < n|H'|m >$$

So, this is one equation we get and if I multiply this one then I get following equation,

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

That is the equation we get.

So, if I and so, what we have done here when you are multiplying this equation with this <m| the complex conjugate of this state, Then, what we have used is that within this integration, the variable we have used as m’ dash to distinguish it from the state by which I am multiplying.

So, this is just a convenient way of representing the integration, we do not want to mix up two different m s here, here we are multiplying by a particular state m, this m is a particular state and that is why integration is running over the m states in the integration. So, we know that this equation can be further reduced, because we know that we assume that this <m|m’>=0 for all states for all states, except for, not for m=m’. So, this entire integration becomes 0 except for one term and the term is going to be m=m’.

And that if I use that condition, I will be able to write down

$$\frac{ih}{2\pi}\left\{\frac{d}{dt}c_m(t)\right\}e^{-i\frac{2\pi E_m t}{h}} == c_n(t)e^{-\frac{i2\pi E_n t}{h}} < m|H'|n >$$

So, this is the reduced form of this expression, for this part of the expression. Which is which can be again further reduced as

$$\frac{ih}{2\pi}\left\{\frac{d}{dt}c_m(t)\right\} = c_n(t)e^{\frac{i2\pi(E_m-E_n)t}{h}} < m|H'|n >$$

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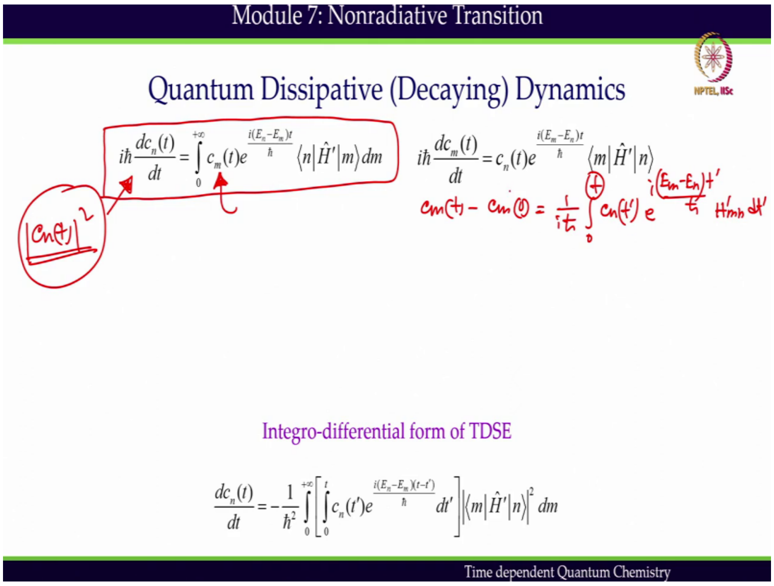

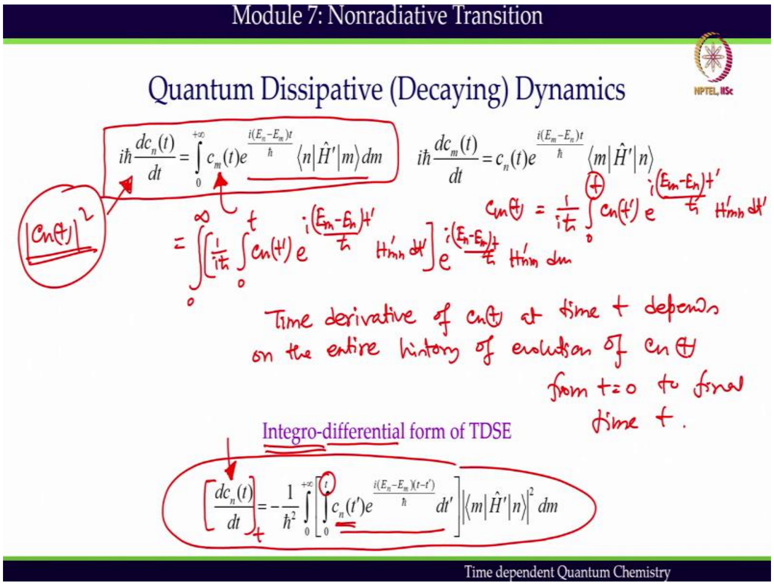

So, what do we get finally, after doing all these things, we get two differential equations, coupled equations, one is depends on the other. So, these are the two couple differential equations we have obtained after inserting that initial trial function wave function to the TDSE. And if we have this to couple of differential equations, question is how do I solve these two equations because our target is to find out $c_n(t)$, we want to find out how the population in the initial state doing as a function of time.

So, that is exactly what we are trying to find out. So, what we should do here is that we have to find out and in order to find out this population, so, from this equation I can get it but the difficulty in this derivation is that I have to find out an expression for c_m, then only I will get that and cm expression can be obtain from this equation.

So, from this equation, I get that c_m expression, I insert that expression here, then I will be able to integrate this equation to get the population in the n th state. That is exactly what we are going to do. So, let us integrate this part. We will be able to integrate this part very easily. It is going to be nothing but

$$c_m(t) - c_m(0) = \frac{2\pi}{ih} \int_0^t c_n(t') e^{\frac{i2\pi(E_m - E_n)t}{h}} < m|H'|n > dt'$$

,this is the integration I have.

And we know that the $c_m(0)$ by initial condition, I have assumed that the no population was present in the final state. So, this is going to be 0, so, this part is gone. And I have this expression, the cm t expression like this.

$$c_m(t) = \frac{2\pi}{ih} \int_0^t c_n(t') e^{\frac{i2\pi(E_m - E_n)t}{h}} < m|H'|n > dt'$$

And what we need to do, as I have mentioned before, this expression now needs to be inserted here, so that I can get the expression for this.

So, what I will do right now, I will insert it, if I insert it, then what I get is

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

that is the total integration I have.

So, it is just rewriting if I rewrite this one to some extent, I get this this form the integro-differential form of this equation

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

where I have this change in population, this integration what we get here is that change in population this expansion coefficient as a function of time and that is given by this entire expression, this expression is an interesting form it is a differential form this differential equation definitely is a differential equation, but at the same time this differential equation depends on the entire.

So, this is the differential equation this derivative depends at time t, this entire derivative at time t depends on this integration over time t. So, time derivative, so, basically this equation shows that time derivative of $c_n(t)$ at time t depends on the entire history of evolution of $c_n(t)$, this is $c_n(t)$ from t equals 0 to final time t. Because it depends on entire history.

That is why it is called integro-differential form of the TDSE. It is the same TDSE form, but it is an integro-differential form of the TDSE assuming that the wave function was expressed as a linear combination of the initial state and all final states. We will stop here and we will continue this discussion of this integro-differential form of the TDSE in the next session.