Time Dependent Quantum Chemistry
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Lecture 52
Hamiltonian for Light-Atom Interaction

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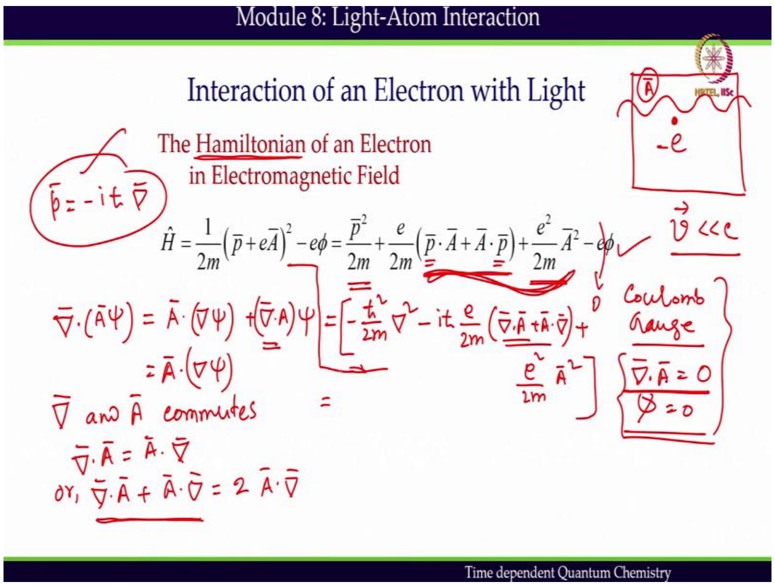

So, definitely ϕ is 0, which means that this term $e\phi$ would be 0 from the Hamiltonian and then we will see what is the consequence of this divergence less A, $\vec{\nabla}.\vec{A} = 0$ that we will see. The consequence is following we will be able to write down this. So, this is plugged in. So, I will be able to get this this is the kinetic energy operator we get in general in absence of the interaction between electromagnetic field and an electron and then this part will be taken to be e/m.

This is going to be we will see that what would be this part and that we have to figure out here. So, we will write down slowly , first of all, this vector quantity can be written as this is another vector identity basically can be written as $\vec{\nabla}.\left(A\psi\right) = \vec{A}.\left(\nabla\psi\right) + \left(\vec{\nabla}.\vec{A}\right)\psi$. And because this is divergence less one, $\vec{\nabla}.\vec{A} = 0$ can write down this to be like this $\vec{\nabla}.\left(A\psi\right) = \vec{A}.\left(\nabla\psi\right)$. So, one can conclude that if it is so, then one can conclude that this for the given coulomb gauge this del operator $\vec{\nabla}$ and vector potential $\vec{A}$ commutes.

And because it commutes one can write down $\vec{\nabla}.\vec{A} = \vec{A}.\vec{\nabla}$ or one can write down one can write down this one $\vec{\nabla}.\vec{A} + \vec{A}.\vec{\nabla} = 2\vec{A}.\vec{\nabla}$. So, this is exactly what we have here, if this is the momentum operator this is momentum operator. So, one can convert this momentum operator and we can use it.

So, I can use the explicit form of the momentum operator and one can write down as $-\frac{\hbar^2}{2m}\nabla^2 - i\hbar\frac{e}{2m}\left(\vec{\nabla}.\vec{A} + \vec{A}.\vec{\nabla}\right) + \frac{e^2}{2m}\overline{A}^2$ and $e\phi$ this term is 0. So, we are neglecting it. So, this is the Hamiltonian, we have current Hamiltonian we have here and because of this vector identity one can plug this one here, this part here. So, finally one can write down.

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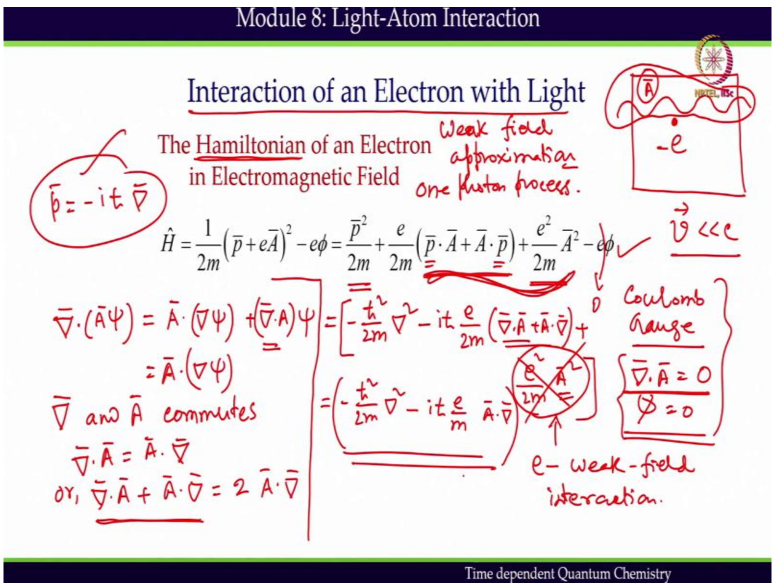

$-\frac{\hbar^2}{2m}\nabla^2 - i\hbar\frac{e}{m}\vec{A}.\vec{\nabla}$. So, this is the Hamiltonian. When you are doing this Hamiltonian, we are neglecting this part as well. We are neglecting this part $\frac{e^2}{2m}\overline{A}^2$ saying that because we will say that light's this field strength or the potential strength is so weak, it is we are actually working on electron and a weak field interaction electromagnetic field interaction.

So, we are saying that the vector potential field itself is so weak that its square terms would be even weaker than that. So, those terms are neglected and that is called weak field approximation.

So, the interaction of an electron with light when you will be presenting here, we are actually using weak field approximation.

And in terms of photon, what does it mean? We are actually treating one photon process, that means, I can have absorption of one photon or emission of one photon but I cannot have two photon processes like two photon absorption or two photon emission process those in those case I need a stronger field and the stronger field for stronger field this term cannot be neglected this term has to be included. So, finally, this is my Hamiltonian. $H = -\frac{\hbar^2}{2m}\nabla^2 - i\hbar\frac{e}{m}\vec{A}.\vec{\nabla}$

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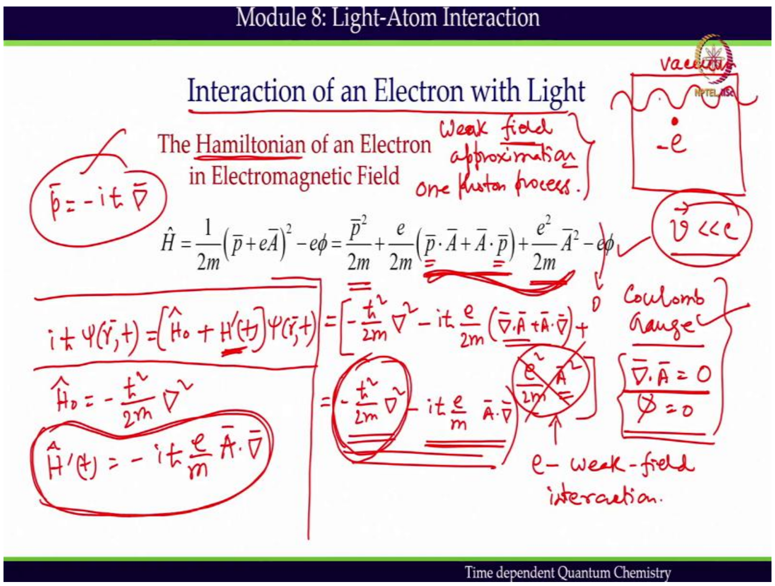

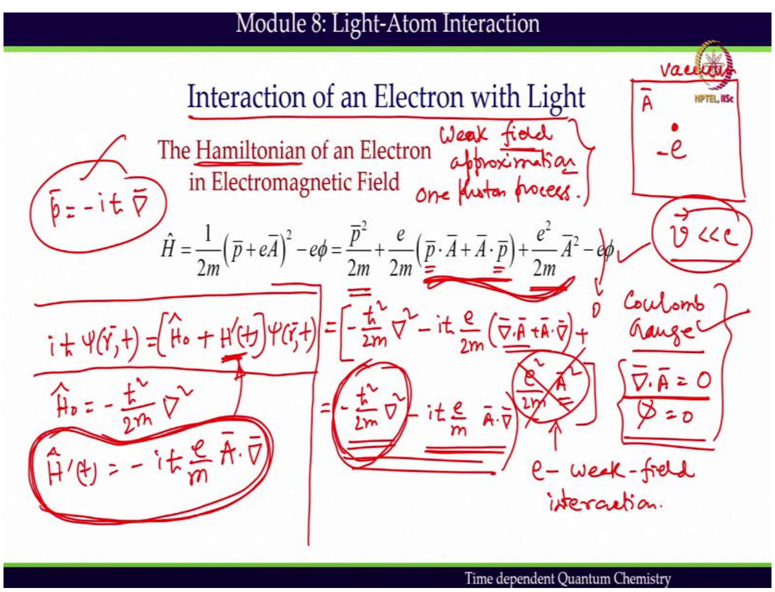

And I will just erase the parts and I will clearly write down final time dependenT Schrodinger equation, how does it look like with this approximation and the total interaction Hamiltonian. So, I have, this is three dimensional wave function, which is nothing from this part you can imagine if the electron was present only electron was present in the medium there is no interaction then I should have got this kinetic energy part of the electron just like a free particle electron is a free particle.

So, it will have a kinetic energy part. So, that is I am calling it H_0 plus due to this interaction I now have this time dependent this potential part. So, this is the first time we are introducing time dependent potential and time dependent potential comes from this vector potential or the light interaction. $i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}=\left(H_0+H'(t)\right)\psi(\vec{r},t)$

So, here H_0 for the three particle is nothing but $\frac{\hbar^2}{2m}$ kinetic energy operator which we see always in the for the free particle. But in addition to this free particle Hamiltonian, we have the interaction Hamiltonian which is a time dependent Hamiltonian which is represented by

$$H'(t)=-i\hbar\frac{e}{m}\vec{A}.\vec{\nabla}$$

So, that is the nature of the interaction Hamiltonian we have under coulomb gauge condition under weak field approximation. So, these are the approximations we have made to specify the time dependent Hamiltonian. And one can say that, because it is weak field, this is weak, this is already weak, and that is why higher order terms is neglected.

One can use this time dependent perturbation theory to solve this equation and that is exactly what we will do. So, what is the perturbation? What is the nature of the perturbation? The nature of the perturbation is given here in terms of vector potential. So, to clarify one more time, the entire problem for getting all these mathematical rigorous here, I have an electron sitting in vacuum,

It is traveling with particular velocity, it can have the velocity is must be less than much less than c so that it is non relativistic electron, but it is in the vacuum and then light is also propagating through the medium, when light is propagating through the medium it is creating the vector potential or in other word, the field is created by the vector potential.

So, inside the medium now, I have a vector potential in the medium and that vector potential is going to interact with that electron and that interaction potential is given by this term interaction potential $H^{'}(t) = -i\hbar \frac{e}{m}\vec{A}.\vec{\nabla}$. So, that interaction potential time dependent interaction potential has to be included in the total Hamiltonian to get the solution of this problem.

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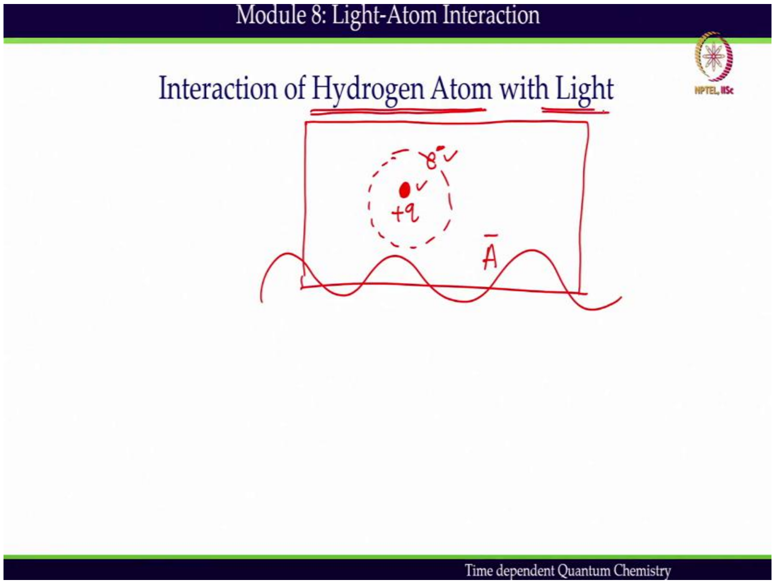

Now, as we are interested in atom now going from this electron to atom, only thing we need to change is that for an atom I have nucleus with a positive charge, I have an electron with a negative charge and then the entire system is in the vacuum now. And now, I have light is propagating through the medium, that is why I have vector potential, which will be interacting with both charges I have this charge I have discharge, both charges will be affected by the vector potential inside this medium. So, that is the situation for let us a hydrogen atom, there is a simplified atom with light interaction.

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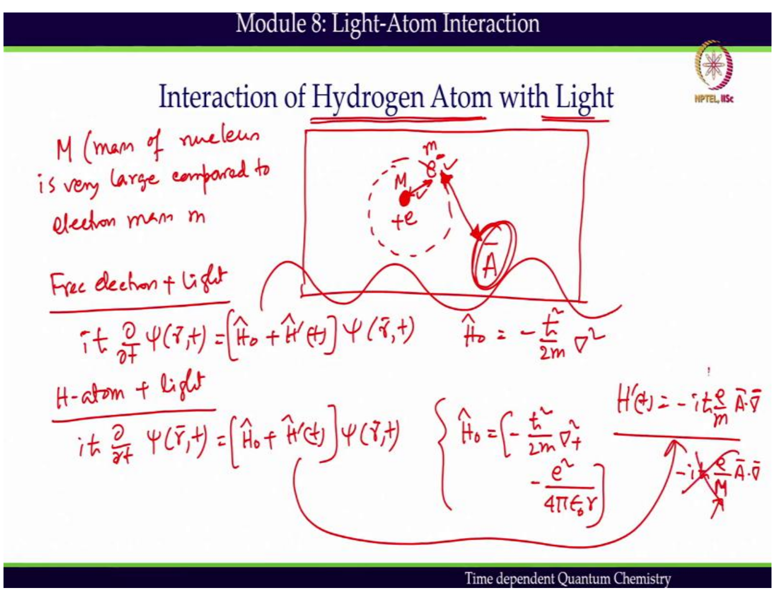

Now, to describe a hydrogen atom in an electromagnetic field, we must take into account the presence of nuclear charge nuclear charge positive charge I have included here so because it is negative charge here, so it is going to be positive plus e charge and also it has a mass M (nucleus) and this has a mass m (electron). Now, since M that is the mass of the nucleus is very large compared to electron mass m. So, we will say that the interaction between radiation field and nuclear charge can be neglected. It is not displaced by it is not affected by this vector potential or the light field.

So, one can say that M does not move this nuclear does not move it does not affect. It can affect if the potential distributor potential the field strength is so high extremely high, then it can affect. But we have already considered this is a weak field approximation and in the weak field approximation, this nuclear charge is not getting affected by the vector field. So, we can ignore that. So, this charge and light field interaction can be neglected. So, we neglect that part. It does not have any effect with this interaction.

Only thing which will be interacting is this electron and this. But at the same time, the unperturbed Hamiltonian has an interaction term between this is the coulomb interaction term between the nucleus and the electron. So, previously for the free electron + light we have written the time independence Schrodinger equation time dependence Schrodinger equation as this

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}=\left(H_0+H(t)\right)\psi(\vec{r},t).$$

Now, and H_0 , unperturbed Hamiltonian was nothing but the kinetic energy operator of a free particle and $H'(t)=-i\hbar\frac{e}{m}\vec{A}.\vec{\nabla}$. Now for hydrogen atom + light, we will be able to write down the same thing, I have unperturbed Hamiltonian + this is a perturbation - time dependent perturbation or the interaction part of the Hamiltonian.

In that case, I have this unperturbed Hamiltonian is going to be now kinetic energy part plus there is a potential energy part also which is present even I do not have the interaction in absence of light. But it is time dependent interaction term is remains to be the same. $H_0=-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{4\pi\varepsilon_0 r}$

So, unperturbed Hamiltonian the form of the unperturbed Hamiltonian has changed. And here I could have another term for the hydrogen atom, which is due to this charge of the nucleus, but because its mass is so heavy as you can see, that M comes in the So, if I want to write down that contribution I should have write written down like this way $-i\hbar\frac{e}{M}\vec{A}.\vec{\nabla}$, but M is so large that this part would be neglected because it is inversely proportional with respect to these parts.

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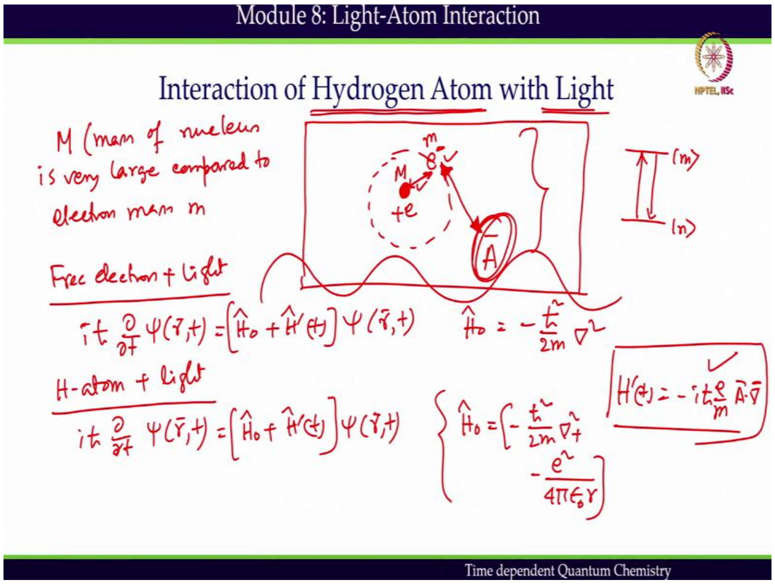

So, one can use only this part as an interaction Hamiltonian for the hydrogen atom problem as well hydrogen atom in in presence of the electric field. In presence of the electromagnetic field, which is showing up as a vector potential here. So, in light atom interactions, we are primarily interested in exploring different features which make decisive role for an atom to make transition from its own one stationary state to another stationary state. So, what happens in light atom interaction, because of this interaction, this atom can actually undergo a transition from one state to the another states.

Let us, say this is initial state this is final state. It will undergo transition or it can undergo this transition as well then it is going to be so, I should name it in a different way, initial final is different, I can have n state and I can have m state. So, one transition it can undergo. This transition process is often explored using the time dependent first order perturbation theory, which assumes that the atom was present in one of its stationary states before the light atom interaction process was initiated.

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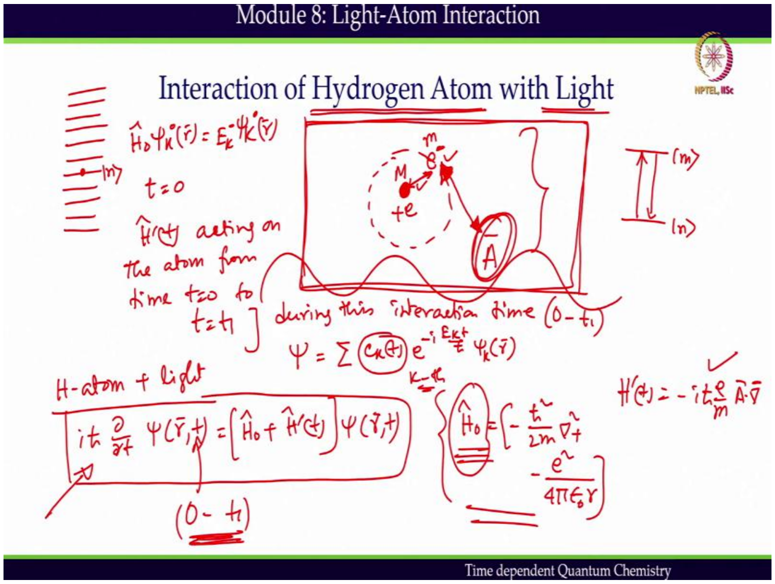

So, we will just go over one more time, because we are going to use this light atom in the time dependent perturbation theory to solve this problem, we will just go for the condition which we imply when we use this perturbation theory this time dependent perturbation theory. So, for that will just remind that perturbation theory assumes that the system was present in a particular stationary state.

So, this Hamiltonian this in absence of light the unperturbed Hamiltonian can give me a number of states for hydrogen atom we know this is 1s, 2s, 2p like that different states I have. All these states can we obtain from time independent Schrodinger equation which is given by $H_0\psi_k(\vec{r}) = E_k\psi_k(\vec{r})$ this is time independent Schrodinger equation and from this time independent Schrodinger equation I can get all the possible stationary state.

And then we assume that the atom before the interaction in this vacuum medium, it is before the interaction of light it was present in one of the stationary states let us say. It can be in the ground state it can be somewhere. It was present in the one of the stationary states. And if it is present in the stationary state, one stationary state, then suddenly this light atom interaction was initiated.

And it was initiated at t = 0. So, this $H^{'}(t)$ acting on the atom from time t =0 to t = t_1 time it is acting interaction is going on. So, during this interaction time I will assume that it was in n state first first before the interaction started and during this interaction time which is 0 to t_1 time during this interaction time, if I have to present the wave function then that wave function will be represented by this time dependent Schrodinger equation.

So, this t has a limit of 0 to t_1 anytime t. So, at any time t how the system looks like that will be described by this time dependent Schrodinger equation within this time interval interaction time and the moment interaction is over. And, during this interaction time, this ψ would be represented as a linear combination of stationary states and this part is giving the population of a particular state here it is the kth state. $\psi = \sum c_k(t) e^{\frac{-iE_k t}{\hbar}} \psi_k(\vec{r})$

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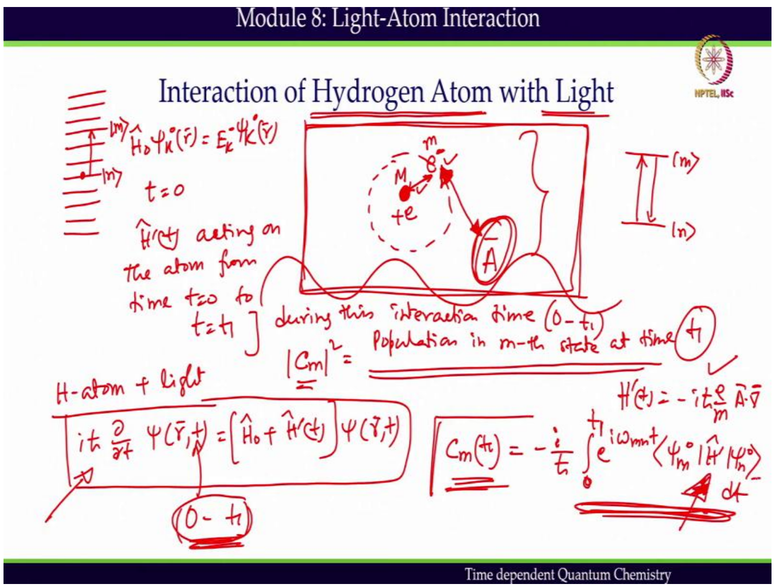

So, if the transition if this interaction light atom interaction which is happening for the interval 0 to t_1 time, if the system is undergoing a transition let us say from n state to m state then the $|c_m|^2$ the population of population at m th state that is the final state where the transition is occurring at time t_1, just immediately after the interaction has been switched off.

Immediately after that time, I will check the population and that population will be given by $|c_m|^2$ and that will be finally represented by the time dependent first order perturbation theory in terms of time dependent perturbation theory that is going to be given by $c_m(t_1) = -\frac{i}{\hbar}\int_0^{t_1} e^{i\omega_{mn}t} \left\langle \psi_m | H' | \psi_n \right\rangle dt$

So, C_m will depend on this population in the m th state (the final mth state) at time t_1 after the interaction, just switched off immediately after that, it will depend on the entire history of time and entire history of time it means that it is the integration between 0 to t_1 time. We have to do that and that is what does it mean.

So, basically, we are interested in this population final state population after the interaction and that interaction is given by first order perturbation theory where I have to I have this interaction term inside this integration this integration over the space. So, we will stop here and we will continue this session. We will continue this module in the next session.