Time Dependent Quantum Chemistry

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Module 11 Lecture 53

Absorption and Stimulated Emission

Welcome back to Module 8 of the course Time Dependent Quantum Chemistry. In this module, so far we have discussed light atom interaction and we have shown that if we use first order perturbation theory, time dependent first order perturbation theory, where we are assuming that the population was in n th state and is undergoing a transition from n state to the m state, what would be the population at the final state, m state, after the perturbation is turned off.

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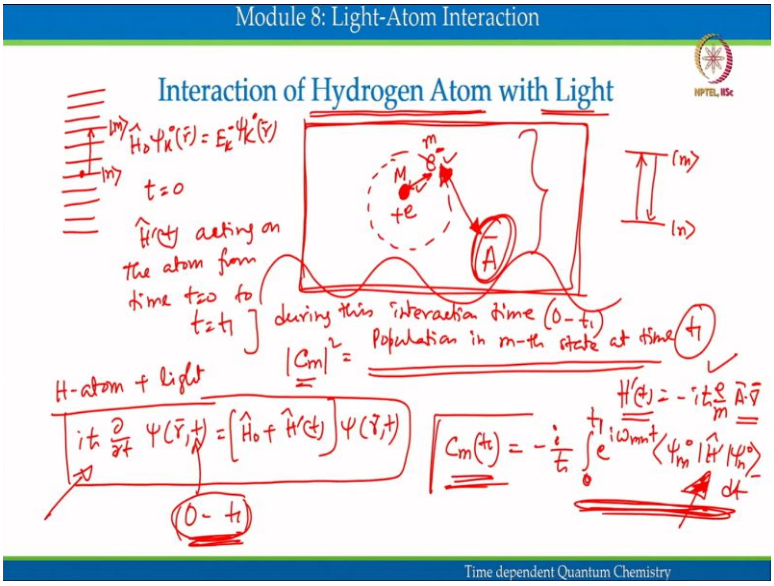

And we have already shown that this perturbation, time dependent perturbation which can be expressed in terms of the vector potential. Vector potential which is created by light when it is propagating through vacuum.

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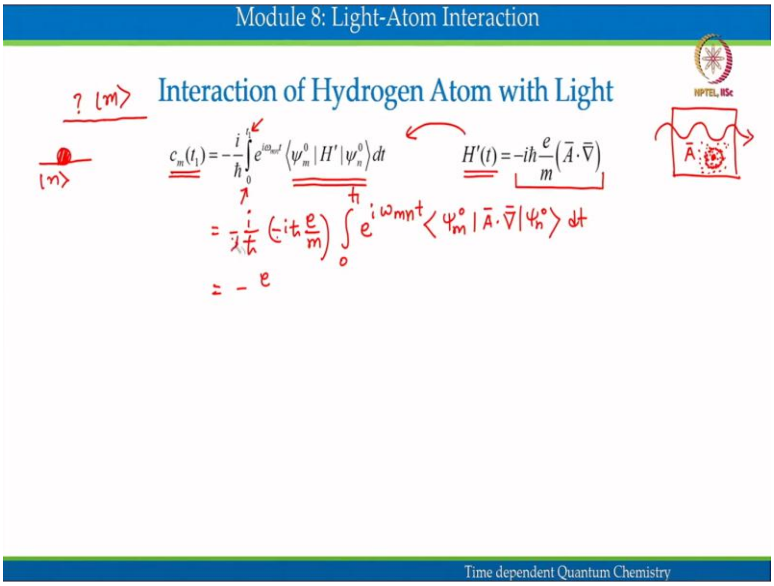

So, we will move on and we will now, explicitly look at the terms. This is the population. This will give me population. Actually, square of the absolute value of this term $c_m(t_1) = -\frac{i}{\hbar}\int_0^{t_1} e^{i\omega_{mn}t}\left\langle \psi_m | H' | \psi_n \right\rangle dt$ will give me the population at the m'th state. So, what we are assuming here is that we had an n state and then m state can be higher than (in energy) higher than n state or it can be lower than n state.

It does not matter where it is. So, we will just assume that it is somewhere. This is another m state (follow slide figure or the lecture 53 at 02:05). And system is undergoing a transition due to this coupling term $\left\langle \psi_m | H' | \psi_n \right\rangle$. When system is undergoing the transition, we will assume that the perturbation started. Which means the interaction, light matter interaction or light atom interaction started at t = 0, ended at t = t_1.

And immediately after we turn off the perturbation, we would like to know what is the population. So, we started with the population in the n state. And after the perturbation, after this interaction, what is the population in the m state that is exactly what we are trying to find out here.

So, as I have mentioned that before is that this perturbation part can be expressed in terms of this vector potential $H'(t) = -i\hbar\frac{e}{m}\vec{A}.\vec{\nabla}$. Vector potential is coming in entirely from the fact that the light is propagating through the vacuum medium and when it is propagating through the medium, it is creating this vector potential, is associated with this vector potential.

And this vector potential is now interacting with a hydrogen atom, where I have, this is classical way of showing, I have a nuclear center and an electron orbiting the nucleus. But this is a classical picture Bohr atomic model but in the quantum model, it is going to be and cloud of electron. So, I have nucleus and then there is a cloud of electron around it. And there will be a place or position in the cloud where the cloud would be dense otherwise, it is like this (follow slide 03:50). So, this is the interaction we are looking at, and we are trying to find out what kind of transition we can have.

So, vector potential, once we express the perturbation in terms of the vector potential, one can write down this, insert this one $H^{'}(t) = -i\hbar \frac{e}{m}\vec{A}.\vec{\nabla}$ here $c_m(t_1) = -\frac{i}{\hbar}\int_0^{t_1} e^{i\omega_{mn}t}\left\langle \psi_m{}^0 \,|\, H^{'} \,|\, \psi_n{}^0 \right\rangle dt$,

and one can write down $c_m(t_1) = -\frac{i}{\hbar}\left(-i\hbar\frac{e}{m}\right)\int_0^{t_1} e^{i\omega_{mn}t}\left\langle \psi_m{}^0 \,|\, \vec{A}.\vec{\nabla} \,|\, \psi_n{}^0 \right\rangle dt$.

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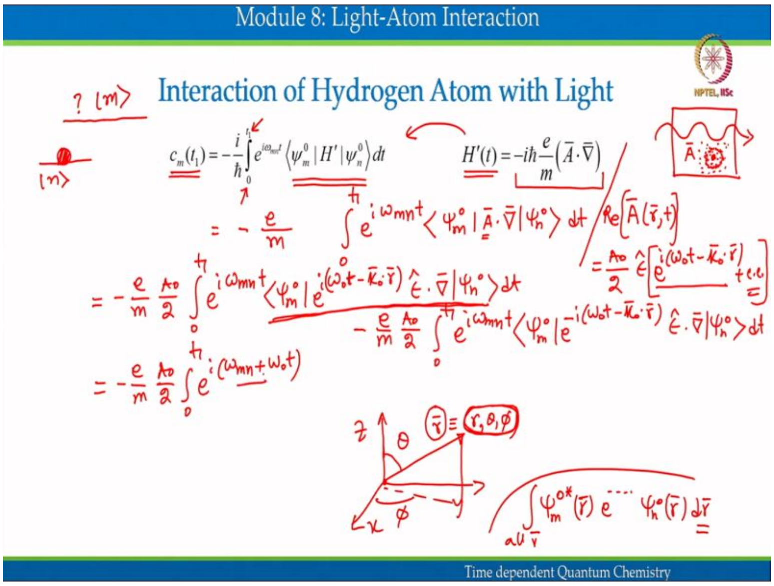

So, that is why, finally, what I will get here is, this term will be reduced to $c_m(t_1) = -\frac{e}{m}\int_0^{t_1} e^{i\omega_{mn}t}\left\langle \psi_m{}^0 \,|\, \vec{A}.\vec{\nabla} \,|\, \psi_n{}^0 \right\rangle dt$. That is the integration what we get. Now, A has a particular expression, we have seen. A will be expressed as (as A is a vector and A depends on the position), so will explicitly write down as $\mathrm{Re}\left[\vec{A}\left(\vec{r},t\right)\right]=\frac{A_0}{2}\varepsilon\left[e^{i\left(\omega_0 t-k_0\vec{r}\right)}+c.c.\right]$.

That is the way we have already seen it. So, if we insert that one here $c_m\left(t_1\right)=-\frac{e}{m}\int_0^{t_1}e^{i\omega_{mn}t}\left\langle\psi_m{}^0\,|\,\vec{A}.\vec{\nabla}\,|\,\psi_n{}^0\right\rangle dt$, we get now two terms. One term is $-\frac{e}{m}\frac{A_0}{2}\int_0^{t_1}e^{i\omega_{mn}t}\left\langle\psi_m{}^0\,|\,e^{i\left(\omega_0 t-k_0 z\right)}\varepsilon.\vec{\nabla}\,|\,\psi_n{}^0\right\rangle dt$

Another term would be, the c.c complex conjugate $-\frac{e}{m}\frac{A_0}{2}\int_0^{t_1}e^{i\omega_{mn}t}\left\langle\psi_m{}^0\,|\,e^{-i\left(\omega_0 t-k_0 z\right)}\varepsilon.\vec{\nabla}\,|\,\psi_n{}^0\right\rangle dt$.

And this can be further reduced in a following way. I can write down. $-\frac{e}{m}\frac{A_0}{2}\int_0^{t_1}e^{i(\omega_{mn}+\omega_0)t}dt......$

This integration, this is an integration within the bracket notation what we have written it is the integration over the entire space. So, basically this is an integration, something like this. I have integration over all, $\int_{all}^{t_1}\psi_m{}^{0*}\left(\vec{r}\right)e^{\cdots}\psi_n{}^0\left(\vec{r}\right)d\vec{r}$. So, it is the entire space.

So, if I have a three-dimensional space, this is x, y, z, three-dimensional space and this is the r vector I have, then r vector can be in any direction and this r vector can be very conveniently written in terms of scalar. So, either I have to express this integration in terms of vector.

So, this vector, r vector can be expressed in terms of scalar quantities, r which is the distance from the center and then θ is this angle and ϕ is going to be this angle. How to do that we will find out later. But the bottom line is that this integration or whatever is written in this bracket notation that is the integration over the space. That is why this time part, temporal variation part, the time dependent part can be taken out of that integration. And that is exactly what we have done here.

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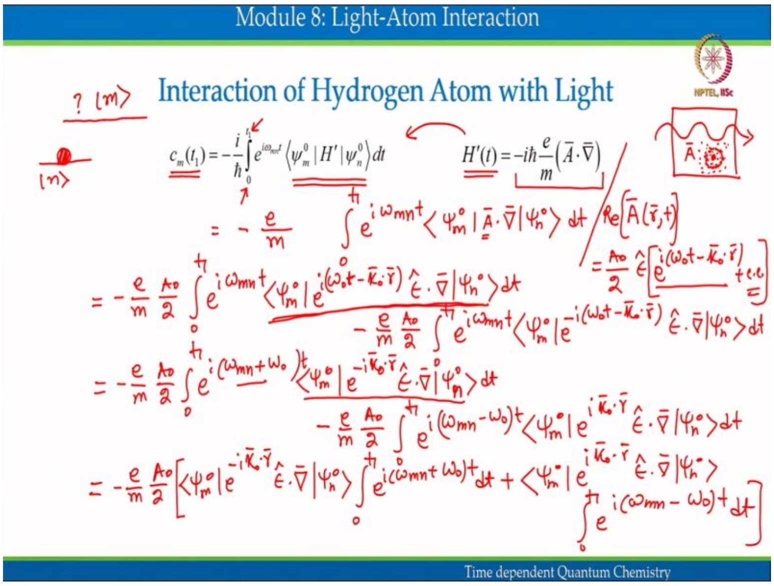

So, once we have done it, we will be able to just reduce it further, to get a convenient expression for our treatment. So, we have this, this one and then the integration is going to be

$$= -\frac{e}{m}\frac{A_0}{2}\int_0^{t_1} e^{i(\omega_{mn}+\omega_0)t}\left\langle \psi_m{}^0 \,|\, e^{-i\vec{k}_0\cdot\vec{r}}\,\varepsilon.\vec{\nabla} \,|\, \psi_n{}^0\right\rangle dt - \frac{e}{m}\frac{A_0}{2}\int_0^{t_1} e^{i(\omega_{mn}-\omega_0)t}\left\langle \psi_m{}^0 \,|\, e^{i\vec{k}_0\cdot\vec{r}}\,\varepsilon.\vec{\nabla} \,|\, \psi_n{}^0\right\rangle dt$$

That is the, we can write it down. And what we see that now one can find out one fact that this integration, this is bracket, what I have written in the bracket, this integration is over the space, entire space.

What the entire r space? An r is a vector right now. And this integration is over time, that is why this spatial integration can be taken out, and one can write down in a following way. One can finally write down as

$$c_m(t) - \frac{e}{m}\frac{A_0}{2}\left[\left\langle \psi_m{}^0 \,|\, e^{-i\vec{k}_0\cdot\vec{r}}\,\varepsilon.\vec{\nabla} \,|\, \psi_n{}^0\right\rangle\right]\int_0^{t_1} e^{i(\omega_{mn}+\omega_0)t}dt - \frac{e}{m}\frac{A_0}{2}\left[\left\langle \psi_m{}^0 \,|\, e^{i\vec{k}_0\cdot\vec{r}}\,\varepsilon.\vec{\nabla} \,|\, \psi_n{}^0\right\rangle\right]\int_0^{t_1} e^{i(\omega_{mn}-\omega_0)t}dt$$

So, this is what we finally get after the, after reducing the equation.

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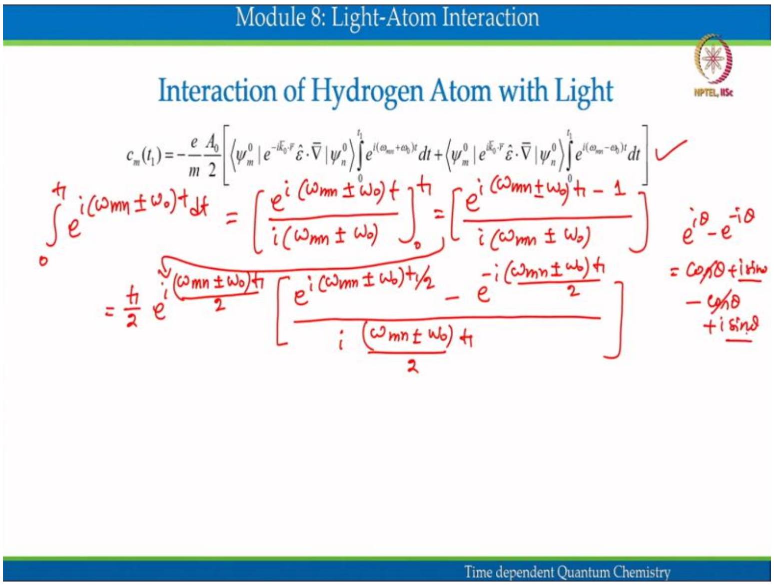

We will further reduce the equation. This is what we have got already in the previous slide, but we will now focus on the time integration part first. So, together this time integration is. So, together I can express it together to, instead of writing twice, I can actually express the integration as $\int_0^{t_1} e^{i(\omega_{mn} \pm \omega_0)t} dt$.

So, if I do this integration, the simple integration, we have already seen this kind of integration before. This is the integration $\int_0^{t_1} e^{i(\omega_{mn} \pm \omega_0)t} dt = \left[\frac{e^{i(\omega_{mn} \pm \omega_0)t}}{i(\omega_{mn} \pm \omega_0)}\right]_0^{t_1} = \left[\frac{e^{i(\omega_{mn} \pm \omega_0)t_1} - 1}{i(\omega_{mn} \pm \omega_0)}\right]$

So, now I will just make one trick, and the trick is this is a trick which we have used before as well. This is going to be

$$= \frac{t_1}{2} e^{\frac{i(\omega_{mn} \pm \omega_0)t_1}{2}} \left[\frac{e^{\frac{i(\omega_{mn} \pm \omega_0)t_1}{2}} - e^{-\frac{i(\omega_{mn} \pm \omega_0)t_1}{2}}}{\frac{i(\omega_{mn} \pm \omega_0)t_1}{2}}\right]$$

We will be able to write this down this way. So, we do that then we can immediately simplify $e^{i\theta} - e^{-i\theta} = \cos\theta + i\sin\theta - \cos\theta + i\sin\theta = 2i\sin\theta$

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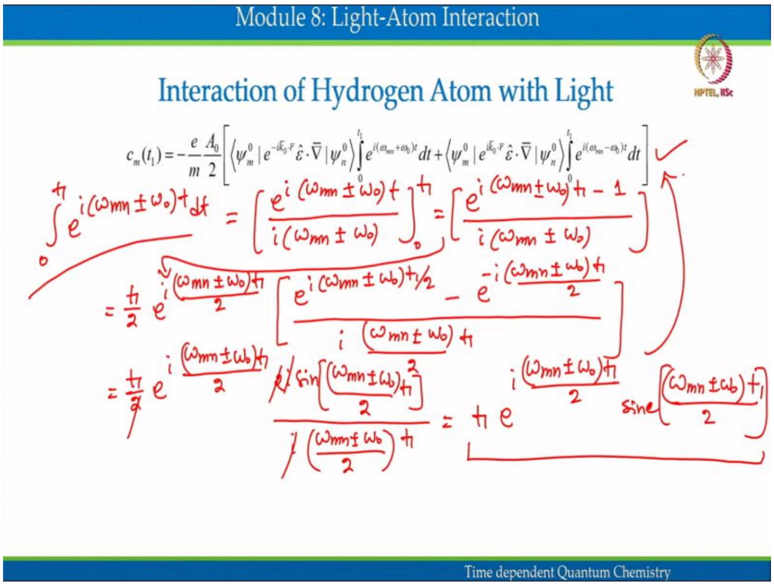

Similarly, that we can express this as t 1 by 2 e to the power i omega m n plus minus omega naught divide t 1 by 2. Then this part is going to be 2 i sin omega m n plus minus omega naught by 2. This is the sin function. Then divided by I have i omega m n plus minus omega naught divided by 2 t 1. So, what I get finally is that t 1. So, this 2 and 2 will be out. This i will be out. So, I get t 1 e to the power i omega m n plus minus omega naught t 1 by 2.

Then cardinal sin function which can be written as sin c omega m n plus minus omega naught t 1 by 2. This is the cardinal sin function. So, finally, what we are seeing is this. This time integral is giving me the response of a cardinal sin function. And we know that cardinal sin function is very very steep in his behavior. And we will it is very steep in its behavior. And we will now insert this into this equation.

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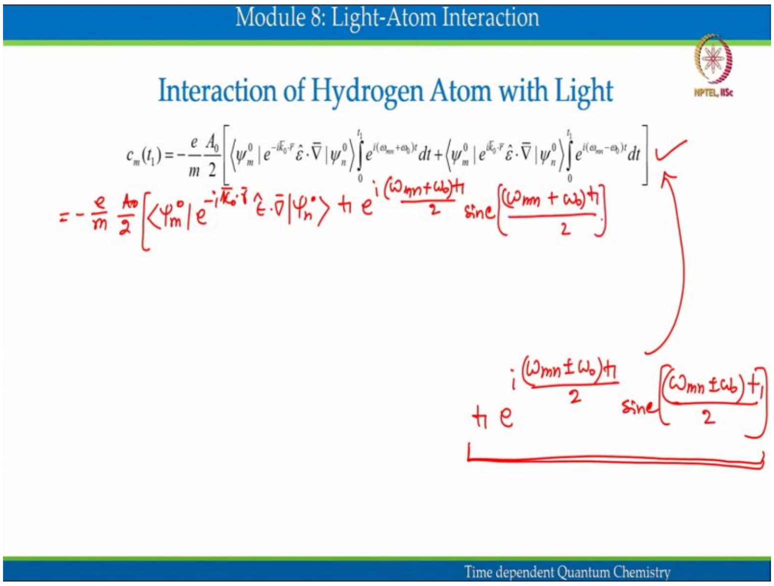

$$\frac{t_1}{2}e^{\frac{i(\omega_{mn}\pm\omega_0)t_1}{2}}\frac{2i\sin\left[\frac{(\omega_{mn}\pm\omega_0)t_1}{2}\right]}{\frac{i(\omega_{mn}\pm\omega_0)t_1}{2}} = t_1 e^{\frac{i(\omega_{mn}\pm\omega_0)t_1}{2}}\sin c\left[\frac{(\omega_{mn}\pm\omega_0)t_1}{2}\right]$$

So, if we insert this equation, we will be able to. So, this time derivative is now going to be, sorry, time integration which we had before that can be replaced by this cardinal sin function. So, when you replace this cardinal sin function, we get the behavior of the population. So, finally, the population will depend on this. The response of a cardinal sin function.

So, that is exactly what we are looking at right now. So, we will insert it and we will see that this is now, I can write down as minus

$$-\frac{e}{m}\frac{A_0}{2}\left[\left[\langle \psi_m{}^0 | e^{-i\vec{k}_0\cdot\vec{r}}\varepsilon.\vec{\nabla}|\psi_n{}^0\rangle\right]t_1 e^{\frac{i(\omega_{mn}+\omega_0)t_1}{2}}\sin c\left[\frac{(\omega_{mn}+\omega_0)t_1}{2}\right] + \left[\langle \psi_m{}^0 | e^{i\vec{k}_0\cdot\vec{r}}\varepsilon.\vec{\nabla}|\psi_n{}^0\rangle\right]t_1 e^{\frac{i(\omega_{mn}-\omega_0)t_1}{2}}\sin c\left[\frac{(\omega_{mn}-\omega_0)t_1}{2}\right]\right]$$

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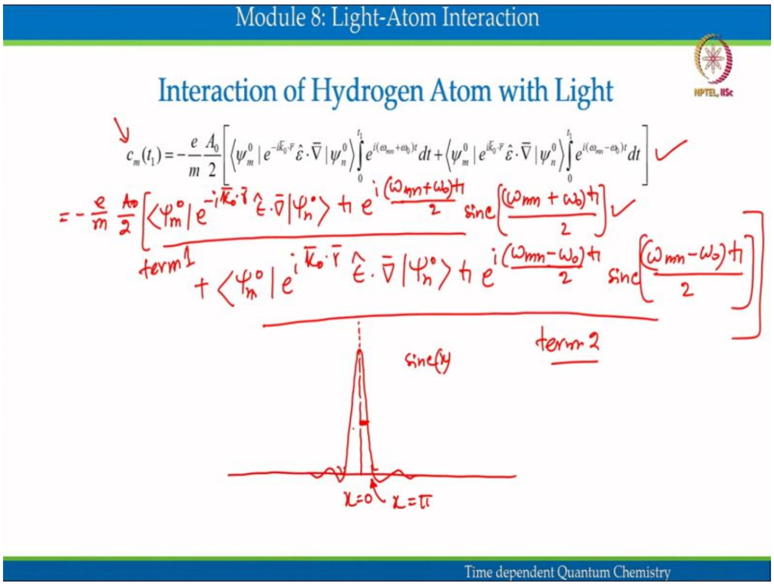

Then I have another term. And when we will writing the another term, This term, the first term, this one and the second term is here. There are two terms which is going to contribute to the population in the m'th state.

And if we look at the behavior of the cardinal sin function, we generally call it like this way. It is a very sharp function. It has a value to very close to this 0 point. Otherwise, it does not have the value. So, cardinal sin function if we plot, it will be like this. This is the cardinal sin function value. It gets value at x equals, near x equals 0 or to the limit x equals 0, it gets a maximum value. And it reduces, I mean, it goes to 0 very quickly, and when it goes to 0, I get $x = \pi$. So, $x = \pi$, I get the minimum value.

And so, we will find out, how this cardinal sin function is affecting these two terms. This is term number 1 and this is term number 2. We have to check individually, how these two terms are getting affected by the cardinal sin function. And remember, this width is very very narrow. It is very very narrow. It is only the cardinal sin functions mandates the values to be within a very narrow width.