Time Dependent Quantum Chemistry
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Module 11 Lecture 54
Absorption and Stimulated Emission

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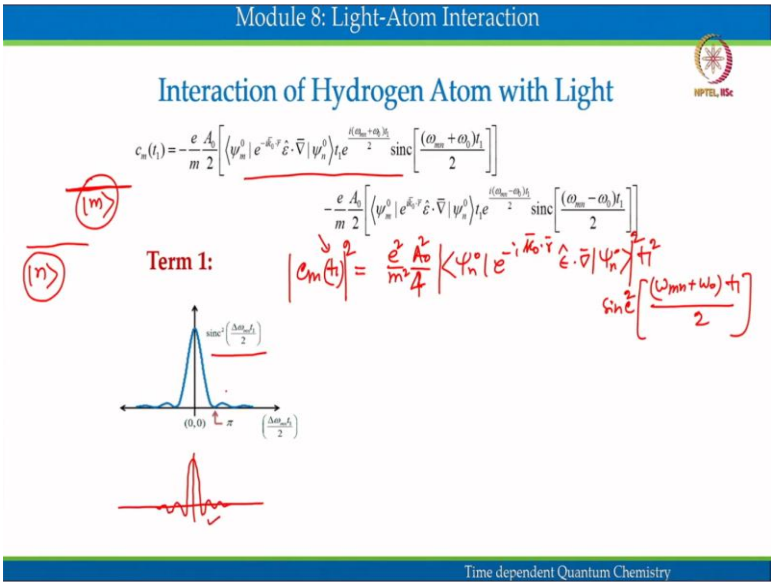

So, we look at the term 1. The first term, we will look at it. And the first term is, can be expressed as

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

These two terms, we will see that, these two terms cannot be satisfied simultaneously. One of the terms will be satisfied at a time. So, that is why we are looking at the each term separately. So, I have this c_m, this coefficient term.

So, I started with n state and I am, my final state is m state. But I really do not know yet, whether the final state would be, has to be higher in energy or lower in energy. That we do not know yet. We will just prove it right now, what is going to happen. Both transition are possible and each term is called corresponding to one type of transition.

So, first, this term will look at it. And if we write it down then it is going to be

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

And probability of transition from n state to final m state at time t_1, So, once I have turned off the interaction process, I am just trying to find out, immediately after the interaction process has been turned off, what is the final population? And the population in the final state is corresponding to the probability of transition. So, that population I will call it, let us say that population will be given by square of absolute value of this term. And if we take the square of absolute value of this term, what we get?

Immediately, $|c_m(t_1)|^2 = \frac{e^2}{m^2}\frac{A_0^{\ 2}}{4}$. And square of the cardinal sin functions is plotted here. So, previously I plotted the cardinal sin function itself. It was like this oscillation (see slide below). But, because I am squaring it, there will be no negative values. So, it is going to be all positive values.

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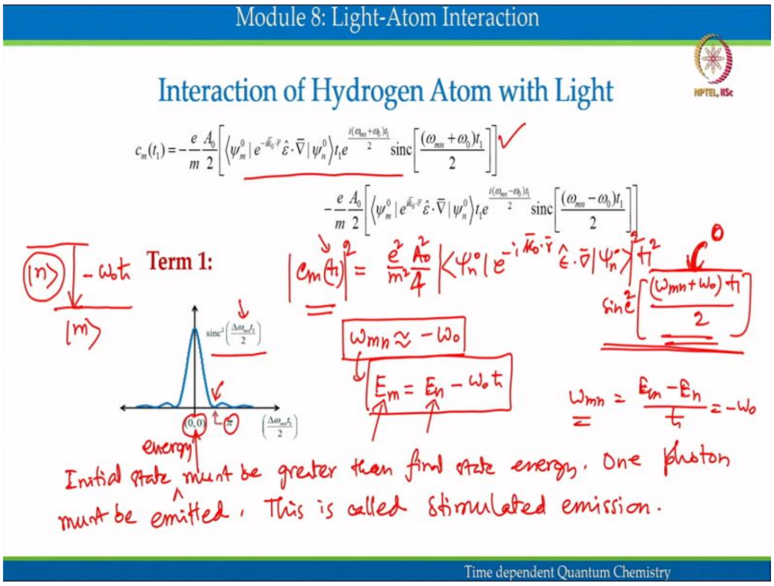

And we are getting it, what we have shown here, it is taking maximum value at the 0, variable equals zero. So, this is the variable right now. And it takes the 0 value at when it is π. So, what we see here is that this cardinal sin function, this will be negligible. It will make the population negligible unless we have $\omega_{mn} \approx -\omega_0$.

Because the entire term has to be close to 0. And if the entire term has to be close to 0 then ω_{mn} has to be $-\omega_0$. Or in other words, we know that ω_{mn}, what does it mean by ω_{mn}? It is actually.

The difference between the energies and that if we employ that then I can get $E_m = E_n - \omega_0 \hbar$ and $\omega_{mn} = \frac{E_m - E_n}{\hbar} = -\omega_0$. So, I get the maximum population when this term becomes 0. Because, this has to be 0.

And if I have this term to be 0 then ω_{mn} has to be like this. So, $E_m = E_n - \omega_0 \hbar$. It shows that E_m energy has to be less than E_n. If it is deviating too much from 0, this entire term, then the cardinal sin function will become 0.

It has to be very close to 0. This entire term. Then only I get the maximum population. So, which suggests that the initial state must be greater, Initial state energy must be greater than final state energy. Which means that one photon in this process, so I have a situation where initial state energy is greater than final state energy. And atom will be making this transition.

If the atom is making this transition then one photon has to be emitted that is $-\omega_0 \hbar$. That one photon has to be emitted. One photon must be emitted. This process is called stimulated emission. So, what we are seeing here, the first term which we have got, it is indicating a behaviour of a stimulated emission and stimulated emission is possible only when the this cardinal sin function, this entire term in within this cardinal sin function, that term has to be very close to 0. And if we consider 0, it means that the one photon will be emitted.

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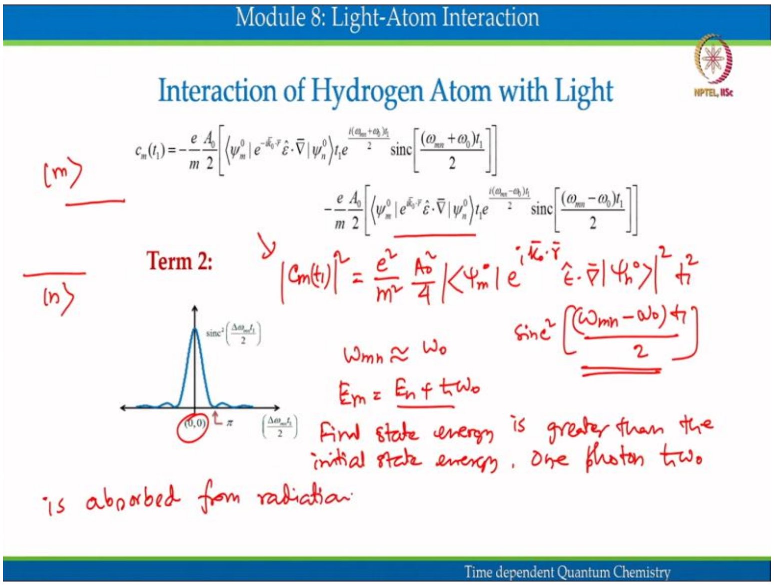

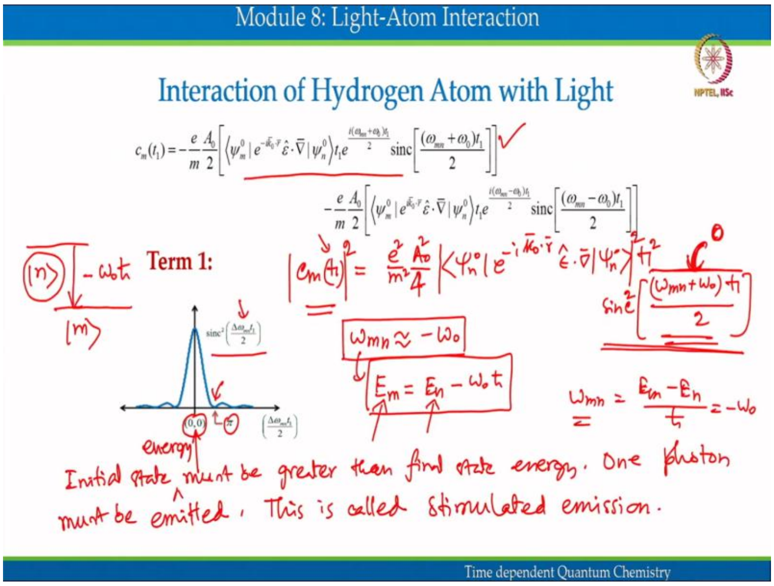

Let us look at the second term. The second term is going to be here $-\frac{e}{m}\frac{A_0}{2}\left[\left\langle \psi_m{}^0 \,|\, e^{i\vec{k}_0.\vec{r}}\,\varepsilon.\vec{\nabla} \,|\, \psi_n{}^0 \right\rangle\right] t_1 e^{\frac{i(\omega_{mn}-\omega_0)t_1}{2}} \sin c\left[\frac{(\omega_{mn}-\omega_0)t_1}{2}\right]$

And we can again write down. So, we can directly write down, because square of absolute value of this c_m, this coefficient is related to the population in the emit state after that the interaction has been turned off. So, that is going to be $\frac{e^2}{m^2}\frac{A_0{}^2}{4}\left[\left\langle \psi_m{}^0 \,|\, e^{i\vec{k}_0.\vec{r}}\,\varepsilon.\vec{\nabla} \,|\, \psi_n{}^0 \right\rangle\right]^2 t_1{}^2 \sin c^2\left[\frac{(\omega_{mn}-\omega_0)t_1}{2}\right]$.

So, again the same argument is valid. This value has to be very close to 0. If it is deviating little bit then the cardinal sign function is zero and if it is 0 then population will be 0.

So, there will not be no population in the final state. So, in order to have the population in the final state, this is the initial state and to have a population in the final state, this has to be 0. And if it is 0 or close to 0 then $\omega_{mn} \approx -\omega_0$. And if it is so, then I will be able to write down $E_m = E_n + \omega_0 \hbar$. This shows that the final state energy, this is m state energy is higher than this.

So, final state energy is greater than the initial state energy. So, previously, we have seen the initial state energy was greater than the final state energy. Now, this time we are seeing the final state energy is greater than the initial state energy. And as a result one photon which is $\hbar\omega_0$ is absorbed from radiation.

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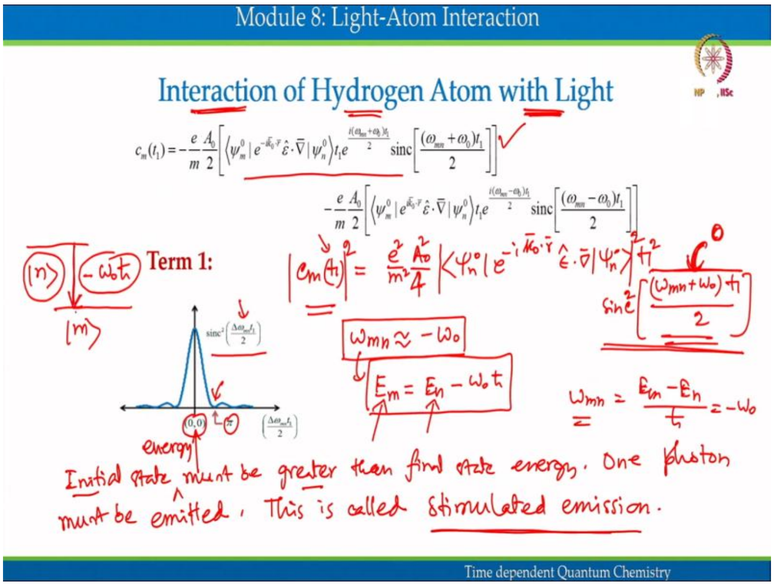

So, always in, both scenarios, previously also there is an interaction of light and atom. Due to the, during this interaction, due to that interaction there will be new photon which will be emitted. That is why it is called stimulated remission. This stimulated emission is different from spontaneous emissions. For spontaneous emission, I do not need an interaction of light and atom.

Even if you turn off the radiation, the system which is electronically excited or vibrationally, they will spontaneously come back to the lower energy state. That is called by emitting photon, which has called spontaneous emission. For stimulated emission, I need interaction of the atom and light. And due to this interaction, another photon can be emitted, that is called stimulated emission.

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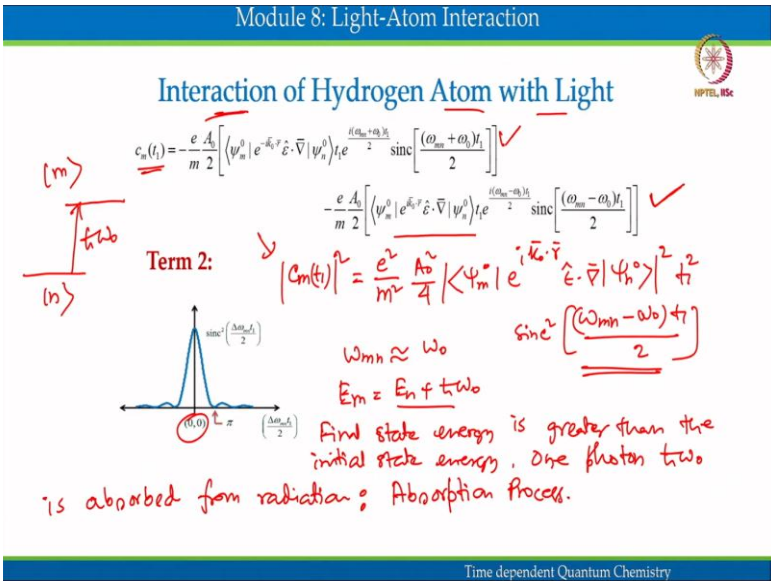

Here due to the interaction, because this entire term comes from the interaction term. So, interaction, due to interaction of atom with light, we have now photon absorbed from the radiation. And the photon amount is $\hbar\omega_0$. That is why this is called the absorption process. It is clear from here that there are only two terms I am getting from first order perturbation theory. And that we have mentioned before, one of them is showing stimulated emission, another one is showing absorption process. But this treatment directly does not show the possibility of spontaneous emission.

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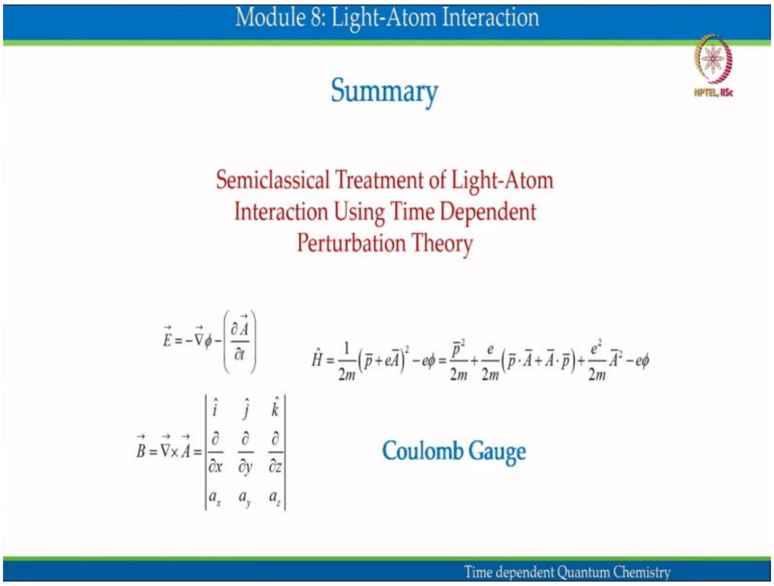

And that we have already mentioned that the semi-classical treatment does not include the spontaneous emission directly. We have to use statistical argument to get the spontaneous emission, the picture of spontaneous emission from semi-classical treatment. So, we have come to the end of this module.

In this module, we have discussed how an atom can interact with light with the help of the first order time dependent perturbation theory. And we have made use of this vector potential which is created by the light when is interacting with atom. So, atom when it is interacting with light, it is actually interacting with the vector potential of the light.

And we have seen that semi-classical treatment directly gives me two terms finally. Those two terms indicating that stimulated emission is possible and absorption is possible. But it does not show any term directly for the spontaneous emission. For the treatment of spontaneous emission, we have to use statistical argument. So, we will stop here. We will meet again for the next module.