Quantum Mechanics and Molecular Spectroscopy

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Lecture No -16
Absorption Probability (Part-2)

Welcome to the lecture number 16 of the course quantum mechanics and molecular spectroscopy. We will just look at the final equation that we derived in the previous lecture and proceed with that.

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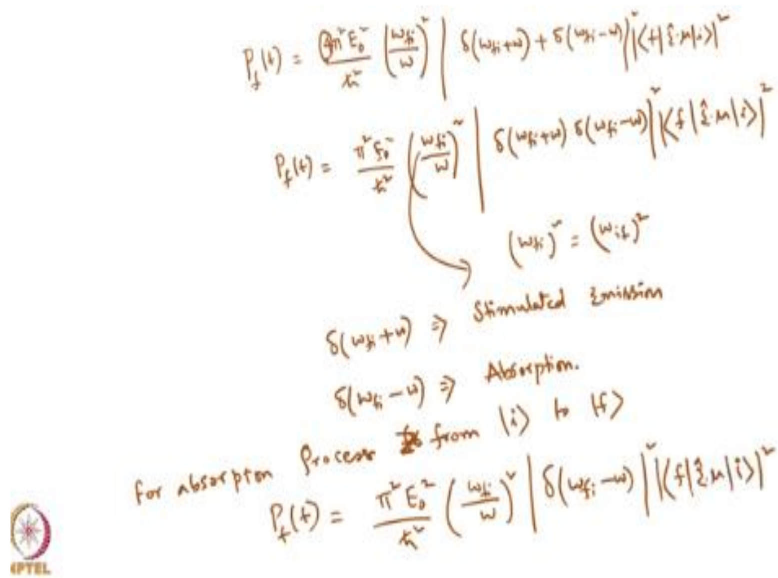

At the end of the last lecture we showed that the probability of transition to a final state f is given by 4 pi square E0 square by h bar square omega fi pi omega square del omega fi + omega + del omega fi - omega square f epsilon dot mu i whole square. I made a small mistake in the last lecture is that this 4 does not exist because you know when you write cos omega t you have 1 over 2 so that one comes out of this this square or absolute square.

Cancel the score so there is a small mistake but that is not going to change the way we look at the entire problem. So P of t is just given by pi square E0 square by h bar square into omega fi by omega square del omega fi + omega del omega fi omega square modulus of epsilon mu by whole square. Now there is one more thing is when you are squaring this so omega fi square of course is equal to omega if square.

So the transition whether it is going from the state f to state i or state i to state f this will remain the same. Now the other thing that we said that when you have del omega fi + omega this will correspond to Stimulated emission and del omega fi - omega this will correspond to absorption and we said this cannot happen simultaneously either stimulated emission will happen or absorption will happen.

So only one of the process can happen at a given point of time and both cannot happen simultaneously, so if we consider for absorption process from initial state i to a final state f then Pf of t is given by pi square E0 square by h bar square omega fi pi omega square omega fi - omega square f epsilon dot mu i whole square, that is the transient probability for absorption process going from an initial state i to a final state f.

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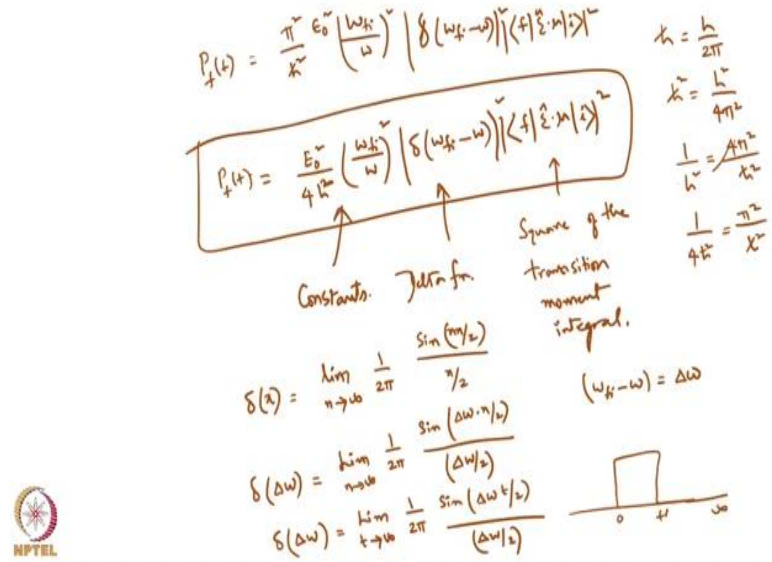

Now one can also write very simply slight rearrangement so Pf of t, now we know h bar is nothing but h by 2 pi. So when we had pi square by h bar square so h bar square is equal to h square by 4 pi square or 1 over h square is equal to 4 pi square by h bar square. So, one can think of this as if I take this 4. So 1 over 4 h bar square is equal to pi square by h bar square. So you can always write this so your P f of t can also be written as E0 square omega fi by omega square del omega f i - omega square f epsilon dot mu i whole square.

So P of this can also be written as E0 square by 4 h square omega fi by omega whole square del omega fi - omega whole square f epsilon dot mu whole square. Now you can see you can write in two different ways essentially the functional form still remains the same. So it will have the square of the transient moment integral and then you will have this delta function and some constants.

Now the problem here is this that how this equation will behave that is what we want to look at. Let us look at the delta function delta of some function x this can be written as limits n tends to infinity 1 over 2 pi sin mx by 2 divided by x by 2. This is a way one can write a delta function as well. Now one can also write delta omega fi - omega as delta omega if one writes that then your of delta omega can be written as limit n tends to infinity 1 over 2 pi sin of delta omega to n by 2 divided by delta omega by 2.

But what is your n here n is just the time. So I can still rewrite as delta omega is equal to limit t tends to infinity is equal to 1 over 2 pi sine of delta omega t by 2 by delta omega 2. Now why I am using limit t tends to infinity because you can I we have all but this is a valid limit because remember when we drew this perturbation curve from 0 to t prime and goes to infinity. So time can go up to infinity without any consequence.

Because after t prime it does not the perturbation does not exist. So one can think of this limit to be taken over, so this same as extending our integral.

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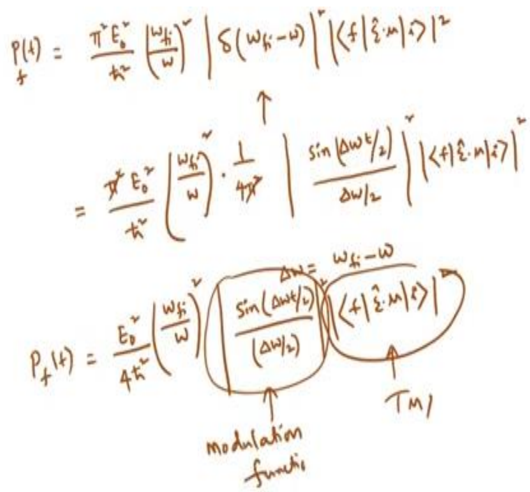

So which means I can rewrite P of t of f this is equal to pi square E0 square by h bar square omega fi by omega square. I had, del of omega fi minus omega square integral f epsilon dot mu i whole square. Now this i will write in terms of the limit, so this will come out to be there was a 2 pi 1 or 2 pi so that I can bring it outside. So pi square E0 square by h bar square omega fi by omega whole square into 1 over 4 pi square cos and this pi square and this pi square will get cancelled.

And this one will be sin of delta omega t by 2 divided by delta omega by 2 whole square f epsilon mu i square, where delta omega is nothing but omega fi minus omega. Now so I am going to slightly rewrite this equation so Pf of t is equal to E0 square by 4h bar square omega fi pi omega square modulus of sine del omega t by 2 by del omega by 2 square f whole square, so this is the probability.

So now you can see the probability of a transition or an absorption from initial state final state will depend on this, will depend on this transition moment integral and will get modulated by this function. So this is nothing but TMI transient moment integral and this is nothing but your modulating function. I will come back to what modulation function really means but just you know for a minute let us keep it, let us look at it. So I am going to tell now what does it really mean it means that your probability of function f of t equals to;

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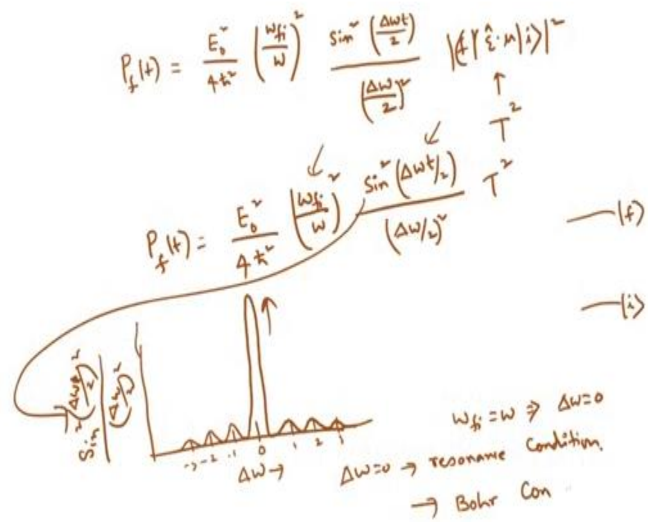

Now as I told you this will depend on E0 square by 4h bar square omega fi by omega square sin square del omega t by 2 divided by del omega by 2, because the square so I have just bought it out of square and multiplied by modulus of f epsilon dot mu i square. Now this I told you the transition moment its a definite integral, I just write it as t and I take a square of it so it will be t square.

So your Pf of t is equal to E0 square by 4h bar square omega fi by omega square sin del omega t by 2 square of that and del omega by 2 square of that into t square. Now you can see for a given omega, omega f is fixed because the energy difference between the two states is fixed so your initial state and the final states are fixed. So omega pi is a constant omega will vary because if your electromagnetic radiation varies that will vary.

Because you can tune the radiation you can go from some frequency to some other frequency or some wavelength to some other wavelength. For example if you are recording an absorption spectrum in the visible light then your wavelength will change from 400 nanometer to 800 nanometer and correspondingly the frequencies will also change. So omega will is a varying function. So this will get affected because omega fi is fixed but omega could vary.

So this ratio will vary apart from that this sine function will vary because you know as delta omega varies sine also will varies but you see sign function can only go from 0 to 1, so the sign square function also goes from only from 0 to 1. In fact sine function goes from -1 to +1 but sine square function can only go from 0 to 1. So this function is basically modulating between 0 and 1 and now if I plot delta omega this is 0 that means omega fi is equal to omega this is equal to delta omega is equal to 0.

And then you can think of some units 1, 2 - 1 - 2 - 3 and then 1, 2, 3 etcetera and if I plot this function here that is nothing but sine square del omega t by 2 whole square divided by del omega by 2 or rather there is not t, I just plot without the t then this function will look something like this. So this is kind of exaggerated view actually these will be even lower. So this will hit the roof this will go much more and this will.

So which means your absorption will also happen away from the resonance but so this is the resonance delta omega is equal to 0 is also called resonance condition. It can also happen away from the resonance however you will see that this will be very very low. So essentially away from the resonance will still not be able to see transitions. The major transition will happen or the maximum probability of transition will only happen at the resonance that is nothing but the omega fi is equal to omega and this is also called Bohr condition.

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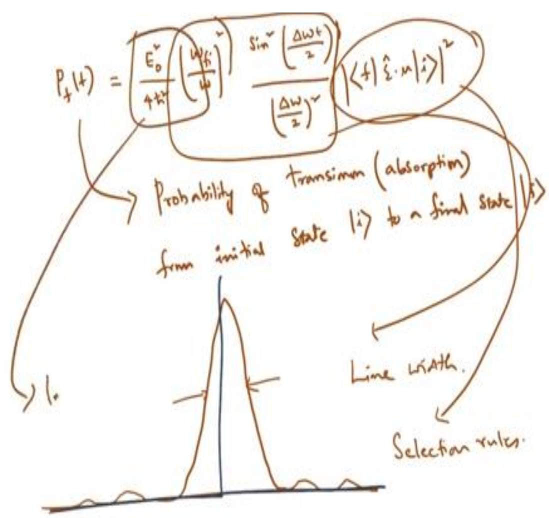

Essentially your Pf of t equals to E0 square by 4h r square omega fi by omega whole square sine square del omega t by 2 divided by del omega by 2 whole square if this is gives you probability of transition or absorption from initial state i to a final state if something like that. Now one interesting fact is that this has got width like that, it has got a width and this width has some important consequence you know we will go to the line widths and then we will discuss this and the line width comes from this function and this function will tell us selection rules.

So for a and this will tell you effectively tell you intensity. So essentially there are 3 factors that determine the probability of a transition from a ground state or initial state i to a final state. One is the transient moment integral that will tell you whether this action will be allowed or not if allowed what its value, second thing is your modulating function which will tell you how the line widths will come about and third one will be intensity that will depend on the how much light you are shining. So it will stop at this point of time and continue in the next lecture, thank you.