Quantum Mechanics and Molecular Spectroscopy
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Lecture No -18
Einstein's Coefficients (Part-1)

Hello welcome to the lecture number 18 of the course quantum mechanics and molecular spectroscopy.

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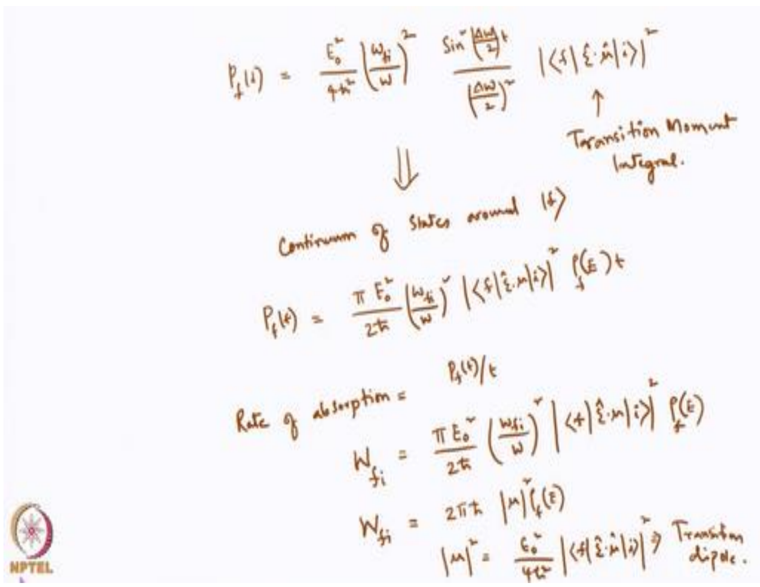

In the last class we looked at the transition probability to state f from state t and this was given by E0 pi square by 4 h bar square omega f i by omega square, sin square del omega by 2 into t divided by delta omega by 2 whole square modulus of f epsilon dot mu i whole square and we know this is the transition moment integral and this for a continuum of states around f, we showed that this P f of t was equal to pi E0 square by 2 h bar omega f phi by omega square modulus of f epsilon of mu i square rho e f i into t.

And, from here we defined rate of absorption is equal to p f of t divided by t, so that was nothing but pi epsilon0 by 2 h bar omega f i by omega square modulus of f epsilon dot mu by i whole square rho E f so row f, small mistakes. So, we call it as rho f of e and rho f of E this we finally wrote as this is nothing but w f. So this was equal to from state i so rate from state i to state f that is buried in a continuum is equal to 2 pi h bar mod mu square rho f of E.

And, where mod mu square was given by E0 square by 4 h bar square modulus of f epsilon dot mu i square and this we call it as transition dipole or square of the transition dipole because mu is the transition dipole.

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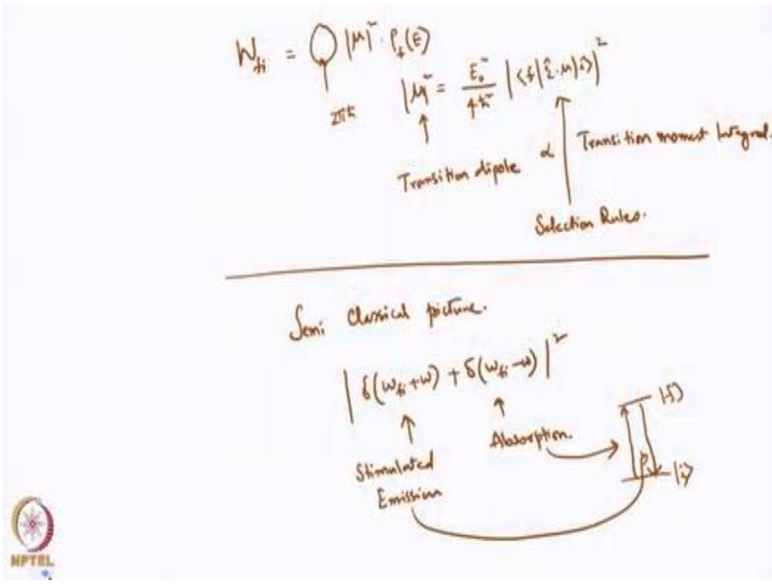

So, now we know two things that the rate of absorption from a state i to f is given by mu square and some constants that publish multiplied by density of states at f. Now, these constants turn out to be 2 pi h bar and that mu square i just wrote is equal to E0 square by 4 h bar square and your transition moment integral square. So this is called transition modulus of this is transition dipole and this transition dipole is proportional to transition moment integral.

Now there is one thing that you must remember that is that this transition moment integral you know dictates what selection rules are going to be, of course in this course up till now we have not come across the selection rules but i will come to selection rules towards the end of this course. Last few lectures will be based on the selection rules of rotation vibration and electronic transitions.

Now, this is something that is rate of absorption in semi classical picture we had two things remember when you had this delta functions you here two of the delta functions delta omega f i + omega + delta omega phi minus omega modulus square may be couple of lectures below you can go and look at it and this i told you corresponds to stimulated emission and this will correspond to absorption.

So the stimulated emission and absorption are a similar process, so in the presence of the classical light a molecule or an atom or a quantum mechanical particle can absorb energy and go from a ground state to the excited state or can come back from the excited state to the ground state. So if you have state i in state f you can either go up that is your absorption and or come down that is your stimulated emission.

And, this is in the presence of however when you excite a molecule it does not stay there forever it has to come back even if you switch off the light and that is called spontaneous emission. So emission can happen by two different pathways one is the stimulated emission and the other is a spontaneous emission. Unfortunately in semi classical picture spontaneous emission cannot be dealt with directly.

So it has to be introduced in an ad hoc manner and that ad hoc manner was developed by Einstein it is called Einstein's coefficient. So we will look into that now.

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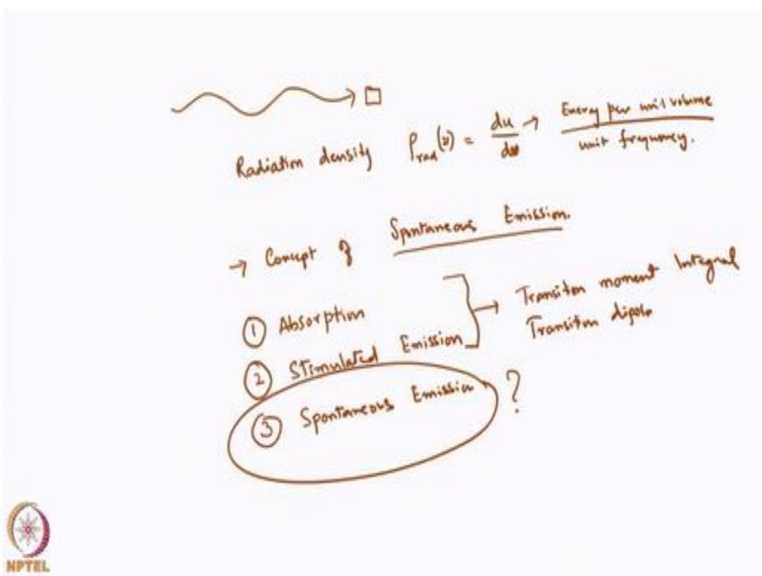

Now for example if you have a light impinging on a particle, so of course it is never going to be a single photon generally when you do spectroscopic measurements you will have bunch of photons some intensity of light and you have to that intensity of light you have some radiation density. So I will define a quantity called radiation density, that is nu radiation density rho or rho radiation density at some frequency nu this is given by du by dv d nu, du by d nu where u is the energy per unit volume by unit frequency.

Now why I want to do this, so the reason why I want to do it is that; I want to in introduce a concept of spontaneous emission because I told you that in presence of light in a semi classical picture there is no spontaneous emission there is only stimulated emission but we all know that the spontaneous emission does happen. So we have to introduce the concept of spontaneous emission.

So there are totally three processes that happen when the light is absorbed by when light is impinged on a particle. So one is the absorption second one is the stimulated emission and third one is spontaneous emission and both of these can be related to the transition all transition dipole but I still do not know how to look at this and that is what we are looking at.

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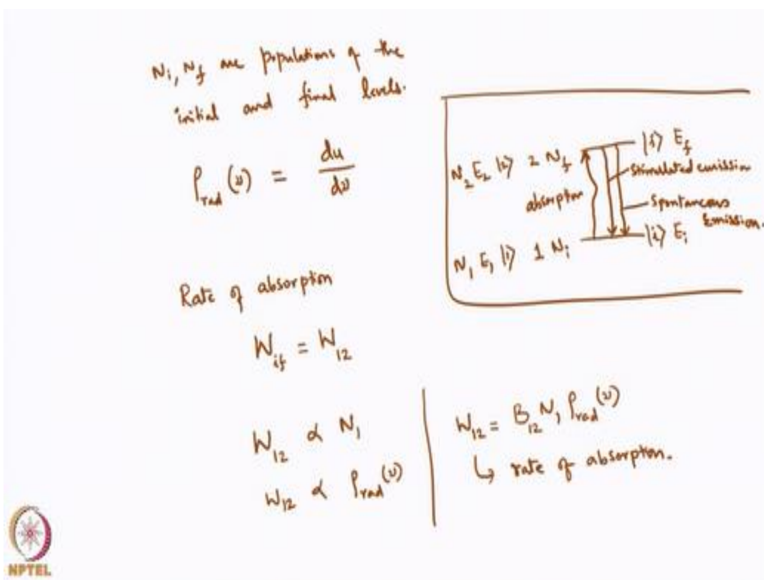

Now, let us consider two levels, so let us start with the simplest of the problem there are two levels. Let us call it as in initial level i with energy Ei and final level f with energy Ef and let Ni be the population of the lower level and Nf be the population of the so Ni, so Ni, Nf are the population operations of the initial and final levels and we have radiation density rho radiation at a nu frequency is d u by d nu.

Now, if you have that then what can happen there are three processes that can happen, so the particle can go from top to bottom that is absorption and it can come down from top to bottom by stimulated emission and it can come down from top to bottom by spontaneous emission. Now, let us look at the rate of functions, now if I want to go from Ni to from top to bottom so that means rate of absorption.

So the rate of absorption w going from the initial state to final state for the sake of convenience and the way it is written in the textbooks will I also call i as 1 and f as 2, so initial state is 1 and final state is 2. So we can also write 1 and 2 and corresponding energies are E2 and E1. Now, if you have omega f5s this is nothing but rho w f i, i f; this is nothing but w, w12 that is rate constant from going from level 1 to level 2 that is given by this rate will of course depend on number of particles there are or now what is the population in the ground state.

And, the population the ground state is N1 and indexed state is N2, so this is proportional to number of molecules or the population the ground state. So this is proportional to N1 and it is also proportional to let me write this way; so w12 is proportional to N1, now w12 is also proportional to amount of radiation if the more radiation is there if you have more intensity more number of more intensity of light more number of transitions will so it is proportional to radiation density.

So that means it is proportional to at the appropriate frequency nu. So it is proportional to two quantities N1 that is the population of the ground state and the radiation density mu, so instead of this so I need to remove the proportionality constant, so what I will get is w12 equals to proportional constant I will call it as B12, N1 rho rad. So this is rate of absorption, so that is when process are when the when the process of going from the state 1 to state 2.

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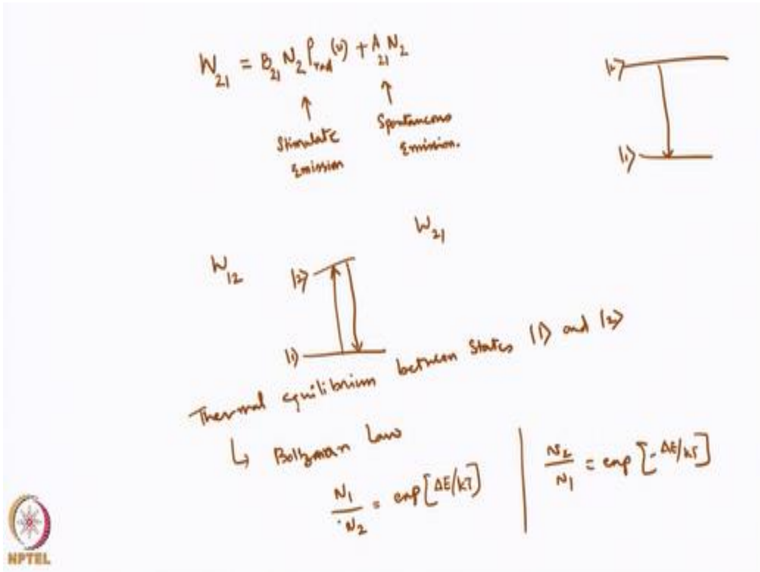

Now under same condition if I want to come back from state 2 to state 1. So rate of absorption for coming down w21 a rate of coming down w21 that is means that this means you have state 2 and state 1 and you have to come down, so this coming down is by two processes one is the spontaneous emission, other is the stimulated emission. In the case of stimulated emission it will be proportional to the population N2 and it will be proportional to radiation density.

And, the proportionality constant i will call it as B21 while the spontaneous process will only depend on the population it does not depend on the radiation density because spontaneous emission does not need radiation. If you excite the molecule and switch off the light it will come down by itself and that is the spontaneous emission. So you will have N2 but you do not need radiation density but it should be proportional constant and that proportional constant calculus is A21.

So that is the A21 that is nothing but your so this will this rate will be for the stimulated emission and this rate for B will be spot. Now you have two rates you have two rates one is w12 that go takes molecules from top to bottom, sorry bottom to top and then you have w21 which brings molecule. Now if let us assume there is a thermal equilibrium between states 1 and 2, so this is 1 this.

Now, if you take thermal equilibrium then you will have to follow Boltzmann law and what the Boltzmann population distribution law says that N1 by N2 equals to exponential delta E by kt by the way it is slightly written usually written as other way round N2 by N1 is equal to exponential - delta E by kt, so I am just writing the inverse of this. Now this delta E is equal to E2 – E1.

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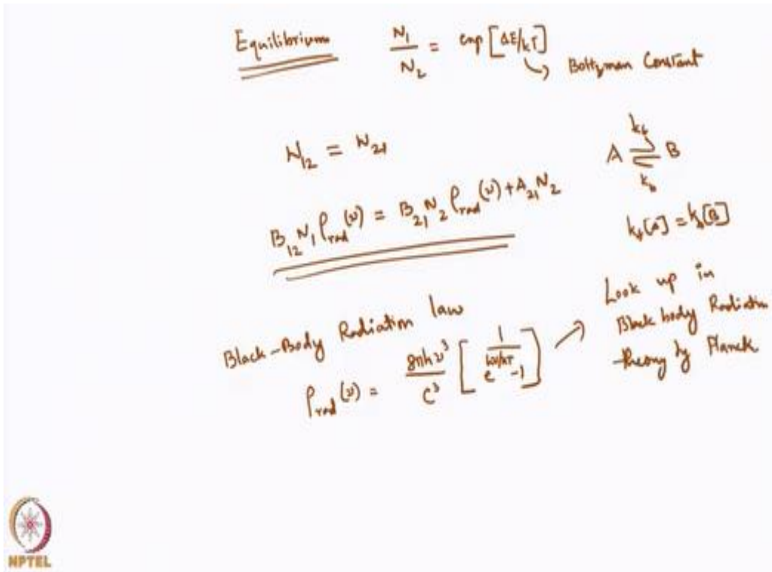

So, if you there is equilibrium and what you have is N1 by N2 is equal to exponential delta E by kt by the way this kt is nothing but your Boltzmann constant. Equilibrium also means rate of transitions going from bottom to top is equal to rate of transients going from top to bottom. So that is nothing but w12 must be equal to w 21 equilibrium line you have, let us suppose you have an equilibrium between A and B so that means so there is a k forward and k backward multiplied by rate constant.

So rate of forward reaction must be equal to rate of backward reaction, so simply means k f into A should be equal to k B into B, so that is what I am doing so in under equilibrium rate of absorption should be equal to rate of spontaneous and stimulated emission put together. So when I put do this will be equal to B12, N1 rho rad mu must be equal to B21 into rho rad nu + A21 N2, so this is the equilibrium.

So we have now have two equations for the equilibrium, so that is the equilibrium according to Boltzmann law and this is the equilibrium because of the radiation that is present and that is making things go up and down. Now according to blackbody radiation law this is given by Planck rho radiation mu is given by 8 pi h nu cube by c cube into 1 over e to the power of h nu by kt – 1. So this derivation we have to look it up.

Look up in blackbody radiation theory by Planck by the way there was something called you know ultraviolet catastrophe you know this equation was proposed by Planck where the energy is given in terms of h nu for avoiding the black ultraviolet catastrophe in the blackbody radiation.

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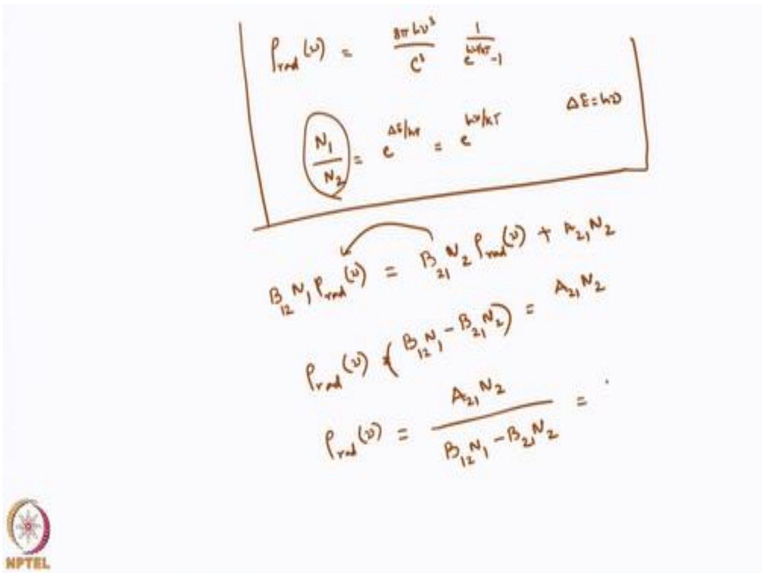

Now, let us look at this little bit more carefully rho radiation it knew a black body radiation is given by 8 pi h nu cube by c cube nu is the frequency h nu cube 1 over e to the power of h nu by kt – 1. Now we know that N1 by N2 is equal to e to the power of delta e by kt, so this is nothing but e to the power of delta e is nothing but h nu, h nu by kt. So these are the two equation that we have and that we need.

Now, let us go back to our equation N1, B12, N1 rho rad of nu is equal to B21 N2, rho rad nu + A12, N2. So I am going to slightly rearrange, I am going to bring this equation to this side, so that will be nothing but then I can take rho rad into nu as common is equal to I am sorry into B12, N1 - B 21, N2 equals to A 21, N2. So your rho rad mu is given by A21, N2 divided by B12, N1 - B21, N2.

Now, what I am going to do is the following is that now I am going to slightly rearrange this equation in such a way that I will be able to use this one. Now what I will do is I will divide by N2 all through, the denominator and the numerator. So this will be nothing but rho this implies rho rad of nu, let me do it in the next page.

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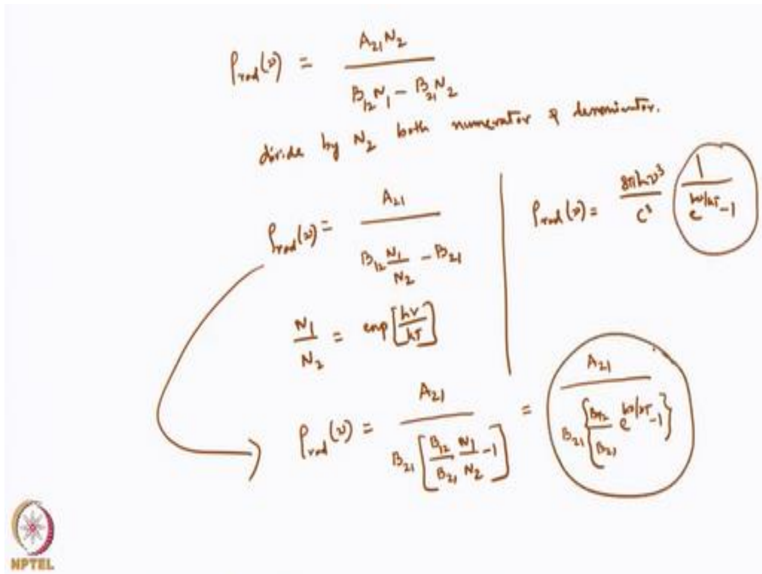

The rho rad of nu is equal to A 21 by N2 divided by B12, N1 - B21, N2. Now I will divide by N2 both numerator and denominator, so when I do that this is equal to A21 divided by B12, N1 by N2 - B21. Now that is the equation that we get of nu and my n1 by N2 is equal to exponential h nu by k t now and i also know further that rho rad of nu is equal to 8 pi h nu cube by c cube 1 over e to the power of h nu by k t -1.

Now, I am going to slightly rewrite this equation rho rad of mu is equal to A21 what I will do is I take B12 as common if I take B12 as common sorry B21 as common then I will get B12 by B21, N1, N2 – 1. Now, you can see N1 by N2 is this exponential h nu by kt, so this will give me A21 divided by B21; now N1 by N2 is divided by B12 by B21 to e to the power of h mu by kt – 1. Now, you can see quickly that there is some symbols between this and this.

So, we can see that these two equations are looking similar but they are not really similar yet, so we need to do little bit of more of mathematical manipulation to be able to look at that, which I will continue in the next lecture, I will stop it here and thank you very much.