Quantum Mechanics and Molecular Spectroscopy
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Lecture No -19
Einstein's Coefficients (Part-2)

Hello, welcome to the lecture number 19 of the course quantum mechanics and molecular spectroscopy. As usual, we will have a quick recap of the previous lecture. In the previous lecture, I was talking about Einstein's coefficients.

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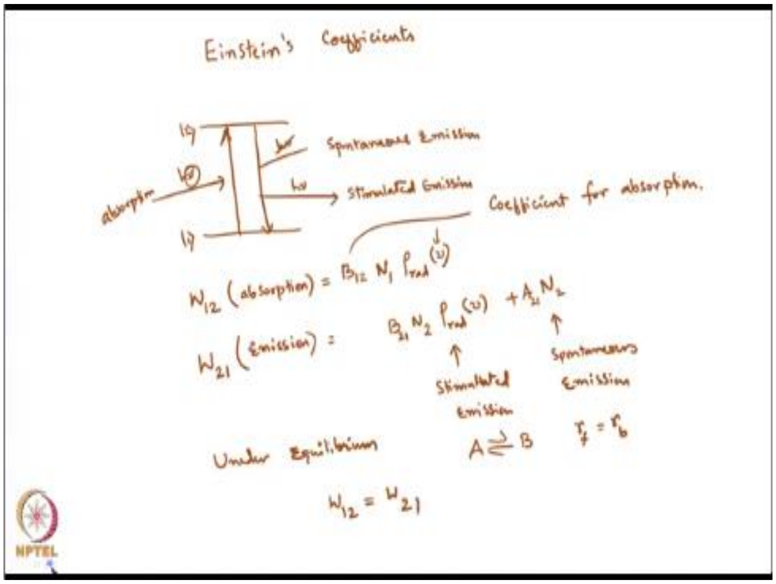

Einstein's Coefficients

W_{12} (absorption) $= B_{12} N_1 \rho_{rad}(\nu)$

W_{21} (Emission) $= B_{21} N_2 \rho_{rad}(\nu) + A_{21} N_2$

Stimulated Emission

Spontaneous Emission

Under Equilibrium $A \rightleftharpoons B$ $r_f = r_b$

$W_{12} = W_{21}$

These are just given by, you there are two states, one and two. So the rate of absorption in the presence of a photon h nu or rate of spontaneous stimulated emission h nu and spontaneous emission in the absence of h, nu we have rates, so let us call it rate W12, so going from state 1 to state 2 that is absorption, corresponds to absorption, will depend on the number of molecules in the state 1.

And the radiation density at the frequency nu and this frequency is same as the h nu, this frequency and this frequency has same and the proportionality constant is called B12 that is the Einstein's coefficient for absorption. Similarly W21 that is emission. Now emission will consist of both spontaneous emission and stipulated emission, so this will be equal to N2 the population, radiation density radiation nu.

And this will correspond to the stimulated emission plus into spontaneous emission does not need the radiation, so it does not need or it in happens in the absence of h nu, therefore it does not need h, rho radiation, so this is for this spontaneous emission. And the proportionality constraints are B21 and A21. Now under equilibrium condition, the rate of forward reaction we know if A and B are in equilibrium, so the rate of forward reaction must be equal to rate of backward reaction. So rate forward must be equal to rate backward, so that means W12 must be equal to W21.

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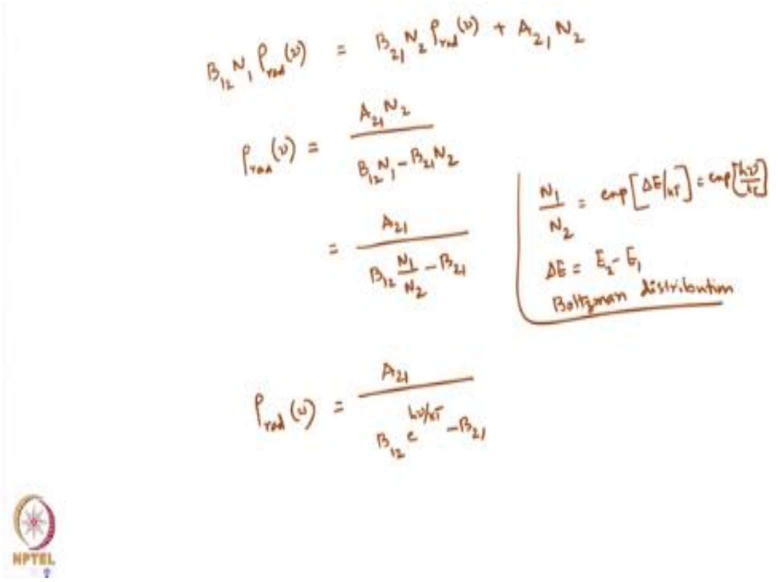

$$B_{12} N_1 \rho_{rad}(\nu) = B_{21} N_2 \rho_{rad}(\nu) + A_{21} N_2$$

$$\rho_{rad}(\nu) = \frac{A_{21} N_2}{B_{12} N_1 - B_{21} N_2}$$

$$= \frac{A_{21}}{B_{12}\frac{N_1}{N_2} - B_{21}}$$

$$\frac{N_1}{N_2} = \exp\left[\Delta E/kT\right] = \exp\left[\frac{h\nu}{kT}\right]$$

$$\Delta E = E_2 - E_1$$

Boltzmann distribution

$$\rho_{rad}(\nu) = \frac{A_{21}}{B_{12} e^{h\nu/kT} - B_{21}}$$

In such scenario, so the B12 N1 rho a radiation at nu must be equal to B21 N2 rho radiation nu + A21 N2, okay? I will rearrange this equation as, rho radiation nu equals to A21 N2 divided by B12 N1 - B21, which can further be written as A21 divided by B12 N1 by N2 - B21. Now we know that N1 by N2 that is the population of the ground state with respect to excited state in Boltzmann is E equal to exponential delta E by KT or exponential h nu by KT, where delta e is equal to E1, sorry E2 – E1.

So this is nothing but from the Boltzmann distribution. Now when I plug in this, so this should be equal to A21 divided by, N1 by N2 I will use this equation, so B12 e to the power of h nu by KT-B21 rho radiation.

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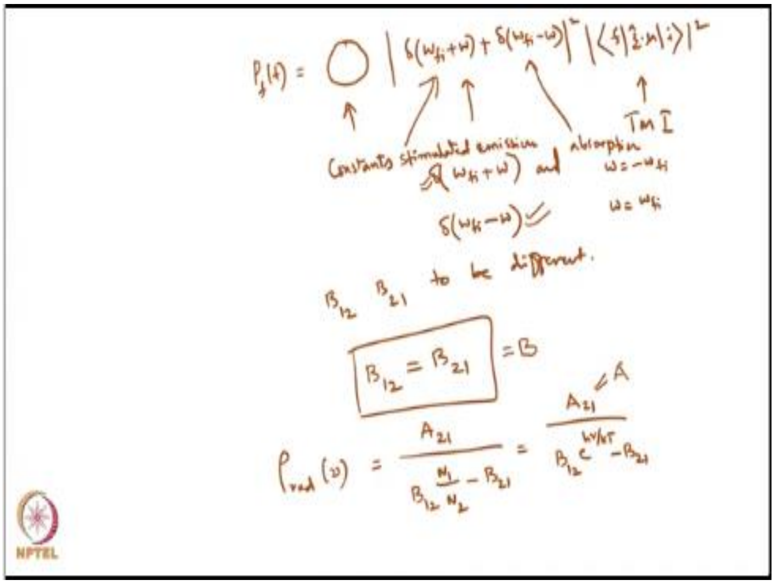

$$P_f(t) = \bigcirc \left|\delta(\omega_{fi}+\omega) + \delta(\omega_{fi}-\omega)\right|^2 \left|\langle f|\hat{\varepsilon}\cdot\mu|i\rangle\right|^2$$

Constants stimulated emission absorption TmI

$\cancel{\delta}(\omega_{fi}+\omega)$ and $\omega = -\omega_{fi}$

$\delta(\omega_{fi}-\omega)$ ✓ $\omega = \omega_{fi}$

B_{12} B_{21} to be different.

$$\boxed{B_{12} = B_{21}} = B$$

$$\rho_{rad}(\nu) = \frac{A_{21}}{B_{12}\frac{N_1}{N_2} - B_{21}} = \frac{A_{21}}{B_{12}e^{h\nu/kT} - B_{21}}$$

A

Now if I go back little bit ahead and look at the transitions, transition probability, then I had one term, so your Pf of t was equal to some constants, I do not, you can go and look it up, multiplied by what you had is delta nu fi + nu, sorry omega fi + omega + omega fi - omega square and f epsilon or nu i square. So this we know is transition moment integral and there were some constants and there was this term which is the delta function.

Now we see, we said that the omega fi + omega delta and delta omega fi - omega cannot be simultaneously correct. So you cannot fulfill these two conditions simultaneously because in this case omega should be equal to -omega fi and in this case omega must be equal to omega fi. So simultaneously this cannot be right, so we said this one will correspond to absorption and this one will correspond to stimulated emission.

So a molecule can either go absorption or stimulated emission at a given point of time. In general, it can happen both things can happen, but at a given instance only one of the processes will, either it will go from the ground state to excited state or come back from the excited state to ground state, it cannot happen simultaneously. So for absorption process we only took this one, so for the stimulated emission process it should.

So if you look at the equation, if you now look at the stimulated emission everything else will remain the same except that this delta function will change. So, if only the delta function is changing, that will depend whether the; you are going up or coming down. So there is no reason for B12 or and B21 to be different. Therefore B12 must be equal to B21 because essentially all the other integrals and the constants are exactly the same, it is just the delta function that is going to be changing.

So if the probability is going to same, then the rate and the rate constant must be the same. So B21 must be equal to B12. Now if I go back and look at this equation and now I plug in, rho radiation nu is equal to A21 divided by B12 N1 by N2-B21, this was equal to A21 by B12 e to the power of h nu by kt-B21, but I said B21 is equal to B2, so this is equal to I will call it as B, similarly A21 I will just call it as A because spontaneous emission will only happen from the upper state to the lower state and it cannot happen from the lower state to the upper state.

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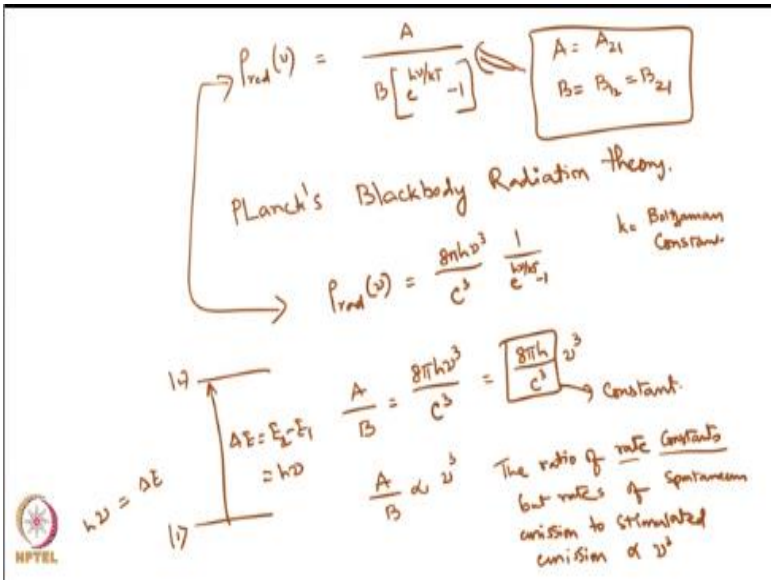

$$\rho_{rad}(\nu) = \frac{A}{B\left[e^{h\nu/kT} - 1\right]}$$

$$\boxed{\begin{aligned} A &= A_{21} \\ B &= B_{12} = B_{21} \end{aligned}}$$

Planck's Blackbody Radiation theory.

$$\rho_{rad}(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}$$

k = Boltzmann Constant.

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \boxed{\frac{8\pi h}{c^3}}\nu^3$$

→ Constant.

$$\frac{A}{B} \propto \nu^3$$

The ratio of rate constants but rates of spontaneous emission to stimulated emission $\propto \nu^3$

$\Delta E = E_2 - E_1 = h\nu$

$h\nu = \Delta E$

So essentially what you have is rho radiation nu equals to A divided by B into e to the power of h nu by KT – 1, where A is equal to A21, B is equal to B12 is equal to B21 under that approximation. So if you have this, then you have this. Now according to Planck's Blackbody Radiation theory, rho radiation nu is given by 8 pi h nu cube by C cube into 1 over e to the power of h nu by kt – 1. Now in all these case, of course k is Boltzmann constants.

Now both these equations give rho radiation nu, so one can equate both of them, so it turns out that A by B is equal to 8 pi h nu cube by C cube. Now we know 8, pi, h and C, they are all constants. So one can write it as a by 8 pi h C cube into nu cube. So A by B is proportional to nu cube because you know these are constants. So what is A? It is the rate constant for spontaneous emission and what is b? It is the rate constant for stimulated emission.

So the ratio of rate constants, actually because both rate constants, both the A and B, the rate constants for the stimulated emission and the rate constant for the spontaneous emission will act only on the population of the excited state, so not only rate constants but rates as well, so ratio of the rate constants or rates of spontaneous emission to stimulated emission is proportional to nu cube. That means nu is nothing but, nu if you multiplied by h, it is the energy.

So if you have two states 1 and 2 and this is delta E, this is equal to E1, E2-E1, this is equal to h nu, as you keep increasing the energy difference between states 1 and 2, the spontaneous emission becomes more and more probable, because the rate constant will increase, keep increasing with nu. So if you keep increasing the value of nu, these spontaneous emissions becomes more and more probable.

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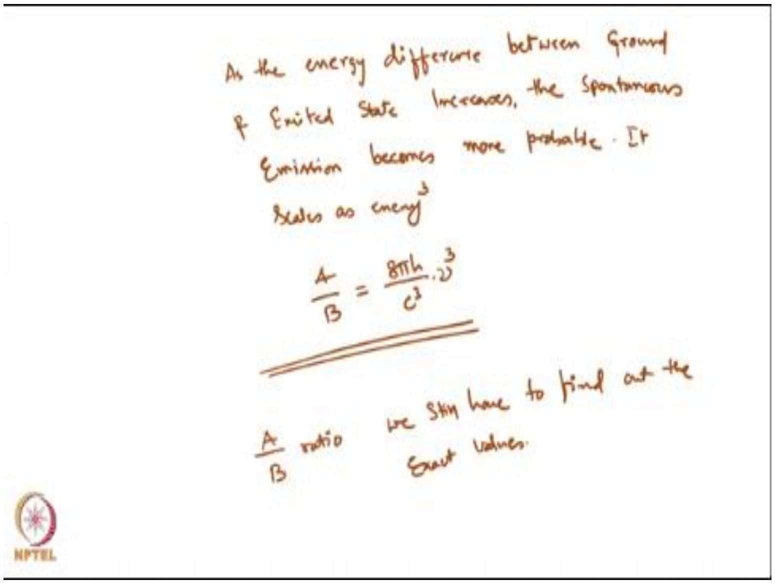

As the energy difference between Ground & Exited State Increases, the Spontaneous Emission becomes more probable. It Scales as energy^3

$$\frac{A}{B} = \frac{8\pi h}{c^3} \cdot \nu^3$$

$\frac{A}{B}$ ratio we still have to find out the Exact values.

So which simply means that as the energy difference between ground and excited state increases, the spontaneous emission becomes more probable and it scales as energy cube. So A by B as you know is equal to 8 pi h by C cube. So this is an important. But this is only the ratio, but we really, we only know what is the ratio of A to B but we have to get the value of each. See for example, if I say ratio is 2, then I can have, if ratio of A to B is 2, then I can say that you know A can be 10 and B can be 5 or A can be 2 and Be can be 1.

So you know the ratio, but you do not know the absolute values. So we still have to find out the values.

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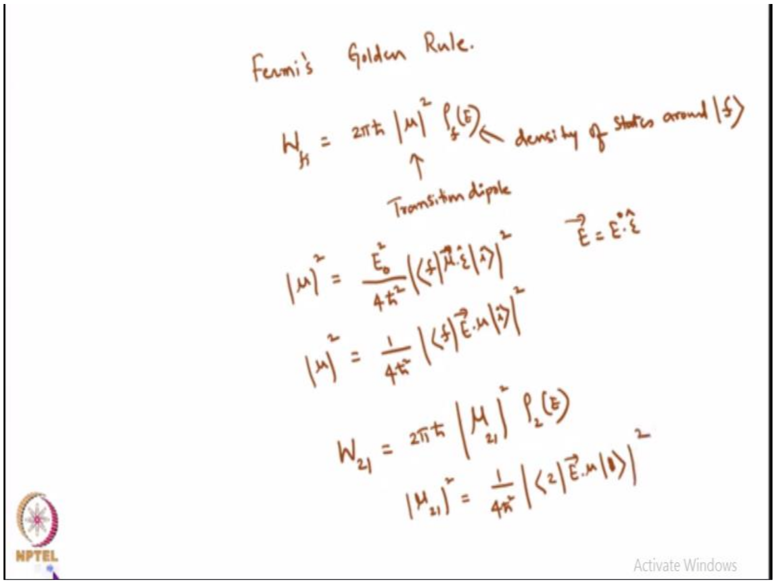

Fermi's Golden Rule.

$$W_{fi} = 2\pi\hbar\,|\mu|^2\,\rho_f(E) \leftarrow \text{density of states around } |f\rangle$$

$\uparrow$ Transition dipole

$$|\mu|^2 = \frac{E_0^2}{4\hbar^2}\left|\langle f|\vec{\mu}\cdot\hat{\varepsilon}|i\rangle\right|^2 \qquad \vec{E} = E_0\cdot\hat{\varepsilon}$$

$$|\mu|^2 = \frac{1}{4\hbar^2}\left|\langle f|\vec{E}\cdot\mu|i\rangle\right|^2$$

$$W_{21} = 2\pi\hbar\,|\mu_{21}|^2\,\rho_2(E)$$

$$|\mu_{21}|^2 = \frac{1}{4\hbar^2}\left|\langle 2|\vec{E}\cdot\mu|1\rangle\right|^2$$

For this we will return to one of our older derivation, that is the Fermi's golden rule. So let us now look at the Fermi’s golden rule. The Fermi’s golden rule is given by W that is rate, fi is equal to 2 pi h bar modulus of nu square rho f and this we call it as transition dipole. And this is the Rho fi is nothing but density of states around f. Now where modulus of nu square was given by E0 square by 4 h bar square into f nu dot epsilon i whole square, which can also be written as 1 over 4 h bar square.

If I take E not square multiplied by epsilon that becomes you know, electric field. So modulus of f E dot nu i square, where E is equal to E0 t. So this is your modulus nu square that is my rate. But in the Einstein coefficients, we are using rate between states 1 and 2. So I am going to rewrite this equation slightly differently. W21 equals to 2 pi h bar. I will call it as mu21 square rho 2 E.

So this will be and where modulus nu 21 square equals to 1 by 4 h bar square 2 E dot nu 1 whole square.

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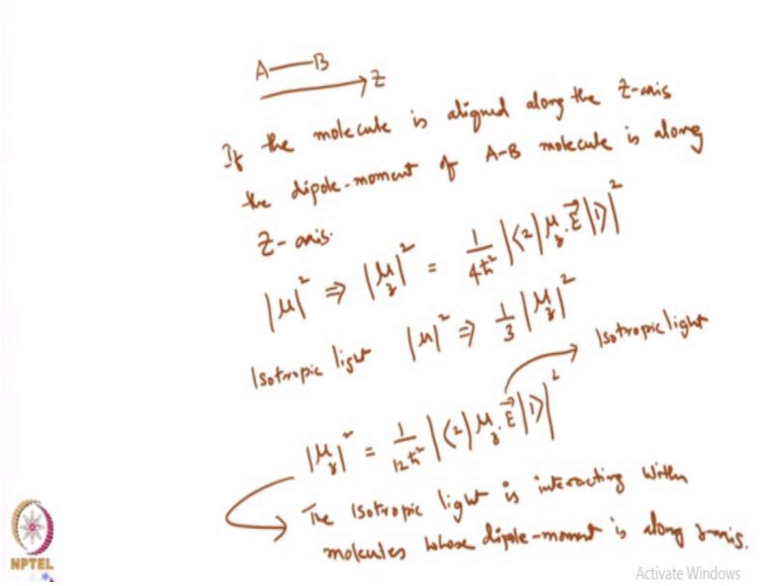

A—B

$\longrightarrow z$

If the molecule is aligned along the z-axis the dipole-moment of A-B molecule is along z-axis.

$$|\mu|^2 \Rightarrow |\mu_z|^2 = \frac{1}{4\hbar^2}\left|\langle 2|\mu_z\cdot\vec{E}|1\rangle\right|^2$$

Isotropic light $|\mu|^2 \Rightarrow \frac{1}{3}|\mu_z|^2$

Isotropic light

$$|\mu_z|^2 = \frac{1}{12\hbar^2}\left|\langle 2|\mu_z\cdot\vec{E}|1\rangle\right|^2$$

The Isotropic light is interacting with molecules whose dipole-moment is along z-axis.

Now if that is the case now, let us look at slightly in a different way. Now, let us assume that my molecule or the transition dipole is along the xz axis. So let us just imagine there is a molecule A-B and is aligned along z axis. So the dipole moment effectively will be along the z axis. So if the molecule is aligned along the z axis or the dipole moment of A-B molecule is along z axis. Now your mod nu square will now then become mod nu z square because the dipole moment is along z axis.

So this will be equal to 1 by 4 h bar square modulus of, sorry, integral of 2 now nu z dot E 1 square because the essentially all the molecules is along z axis. So you know only that projection of the dipole moment or the dipole moment along z axis will get projected onto the electric vector E. Now if that is the case in such scenario and when we take isotropic light, now what is isotropic light? Isotropic light means light that is spreading in all directions x y z.

So let us suppose, you know, you have a lamb or a candle in the middle of the room, then what will happen? The light will go in all sorts of directions x y and z. So the projection along the z axis will only be one third of the total light. In such scenario if you use isotropic right, then you get there is a coefficient one third. So your nu square now be replaced by one third of nu z square.

Because the 2 things that are happening first is the light is along the all the directions and the second is the dipole moment of the molecule is only along the z direction. So basically you are wasting the one you know, basically you are wasting the two thirds of the light, that is along x and y projections and you are only utilizing the light that is along the z direction. Therefore if I use all this then by nu z square will be now one twelfth of h bar square 2 nu z dot E whole square where this will corresponding to isotropic light.

So what am I doing now? I am using isotropic light to interact with molecules that are aligned along the z axis. So, essentially this tells us that the isotropic light is interacting with molecules whose dipole moment is along z axis.

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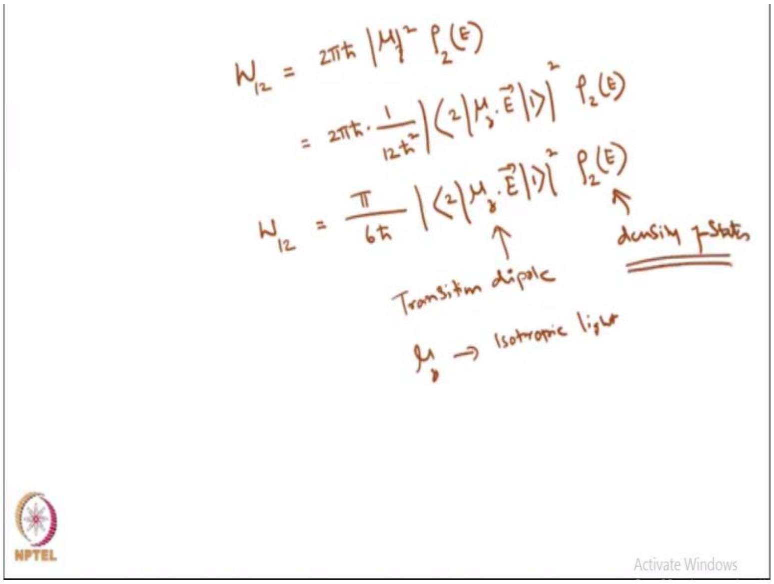

$$W_{12} = 2\pi\hbar\,|\mu|^2\,\rho_2(E)$$

$$= 2\pi\hbar\cdot\frac{1}{12\hbar^2}\left|\langle 2|\mu_z\cdot\vec{E}|1\rangle\right|^2\rho_2(E)$$

$$W_{12} = \frac{\pi}{6\hbar}\left|\langle 2|\mu_z\cdot\vec{E}|1\rangle\right|^2\rho_2(E)$$

Transition dipole

density of States

$\mu_z \rightarrow$ Isotropic light

So in such scenario your W12 will be equal to what was this 2 pi h bar? Modulus nu square Rho 2. So that was our equation. So in such scenario what will have is, 2 pi h bar into 1 over 12 h bar square 2 nu z dot E 1 whole square rho 2. So this will be nothing but, so this h bar and that h bar, so rearranging what will get is, pi by 6 h bar 2 nu z into 1 square rho 2. So, this is your rate. So now we know this is nothing but transition dipole with nu z interacting with isotropic light and this is density of states. We will stop here and continue in the next lecture. Thank you.