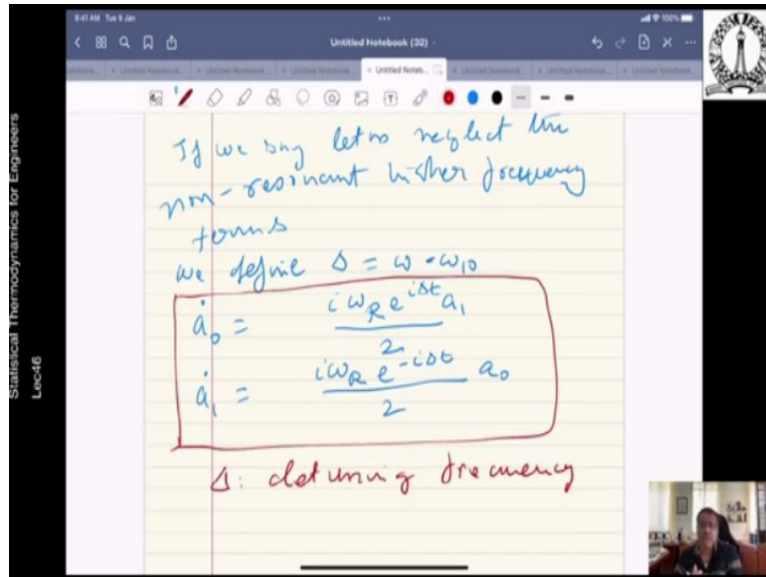


The Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bangalore
Lecture 57
The Rabi frequency and Beer's Law

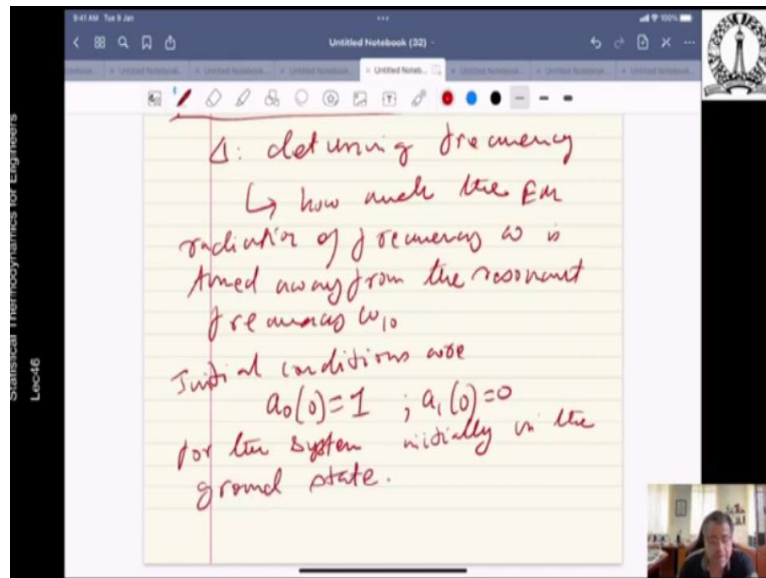
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Welcome to lecture number 46 of the Statistical Thermodynamic course. Now, as you can see over here, so, the non-resonant, so if we see these expressions that we wrote of a_1 and a_0 , so if we look at this, it is now seen that the non-resonant higher, if we, now, if we say let us neglect the non-resonant higher frequency terms. So, as their effects essentially average to 0, because they are rapidly oscillating functions of time.

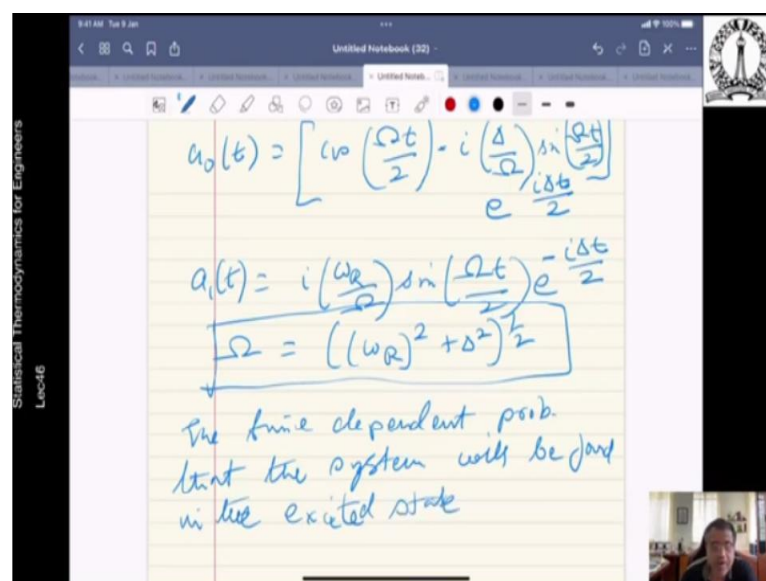
So, we define $\Delta = \omega - \omega_0$. So, therefore the equations for a_0 that is the variation of a_0 that is $\dot{a}_0 = \frac{i\omega_R e^{i\Delta t} a_1}{2}$. \dot{a}_1 is equal to $i e^{-i\Delta t} \omega_R a_0 / 2$. So, these two equations that you see over here, they can be actually solved analytical. The difference Δ is often called, this is called the detuning frequency. Since it measures how far the electromagnetic radiation of angular frequency ω is tuned away from the resonant frequency.

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Because this tells us that how much the Electromagnetic Radiation, EM radiation of frequency ω is tuned away from the resonant frequency ω_0 . So, this is called the detuning frequency. And you also realize that why the non-resonant higher frequency terms can be neglected because they essentially average out to 0 because of their fast, because they are really rapid in nature. So, now that we know the solution, to these 2, first order simultaneous equations is a two first order s differential equations with initial conditions are, initial conditions are a_0 at 0 is equal to 1 and a_1 at 0 is equal to 0 for the system initially in the ground state, t equal to 0.

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9:47 AM Tue 9 Jan

Untitled Notebook (32)

$$\vec{r} = (L\omega_R \dots)$$

The time dependent prob. that the system will be found in the excited state is given by

$$|a_1(t)|^2 = \frac{\omega^2}{\Omega^2} \sin^2\left(\frac{\Omega t}{2}\right)$$

corresp. time dependent prob. that system will be in ground

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$$|a_0|^2 = 1 - |a_1|^2 = 1 - \frac{\omega^2}{\Omega^2} \sin^2\left(\frac{\Omega t}{2}\right)$$

At resonance $\delta = 0$

$$\Omega = \omega_R$$

$$|a_1|^2 =$$

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Untitled Notebook (32)

At resonance $\delta = 0$

$$\Omega = \omega_R$$

$$|a_1|^2 = \sin^2\left(\frac{\omega t}{2}\right)$$

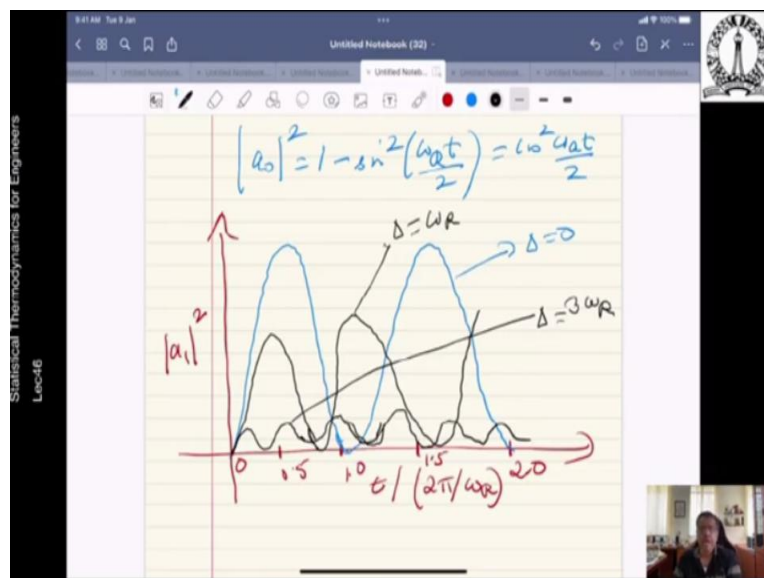
$$|a_0|^2 = 1 - \sin^2\left(\frac{\omega t}{2}\right) = \cos^2\left(\frac{\omega t}{2}\right)$$

So, therefore, now a naught t u can solve equal to cos, if you write it down and then we will go term by term mu i by 2 and a1 t sin omega t 2 e delta t by 2, in which, where omega into omega R square plus delta square half. That is what your omega is. So, this solution, if you just substitute, you will see that they actually agree with equations that we are talking about. So, the time dependent probability that the system would be found in the excited stage, so the time dependent probability, probability that the system will be found in the excited state is given by is equal to omega a square sine square.

So, so that this is the time dependent probability that a system will be found in the excited state, where the corresponding time dependent probability that the system will be found in the ground state, corresponding time dependent probability. That system will be in ground state is given as 1 minus a1 square is equal to 1 minus omega R square, the square sin square. So, at resonance, delta detuning frequency is equal to 0. This is equal to omega R.

So, in that case, your a1 square becomes sin square omega R t by 2 and a naught square becomes 1 minus sin square omega R t by 2 is equal to cos square omega R t by 2. So, this transition probability, now the, the probability, the transition probability a1 square can be now plotted for 2, 3 different detuning frequencies.

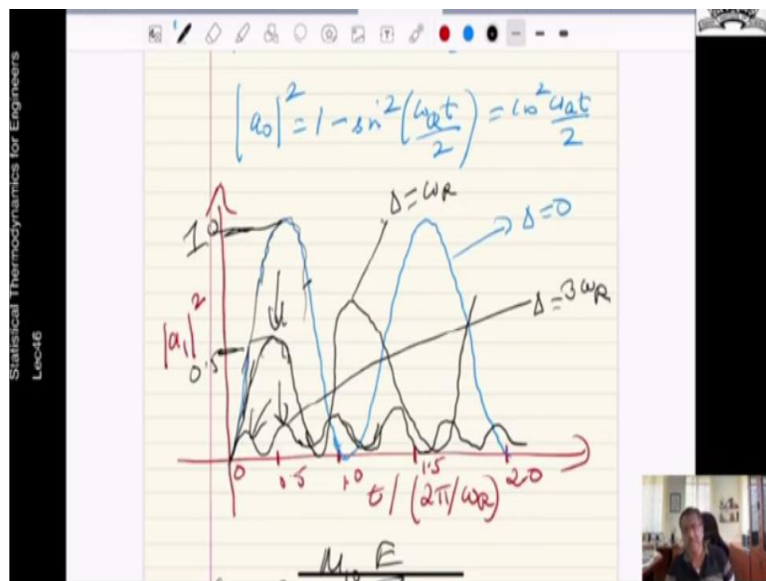
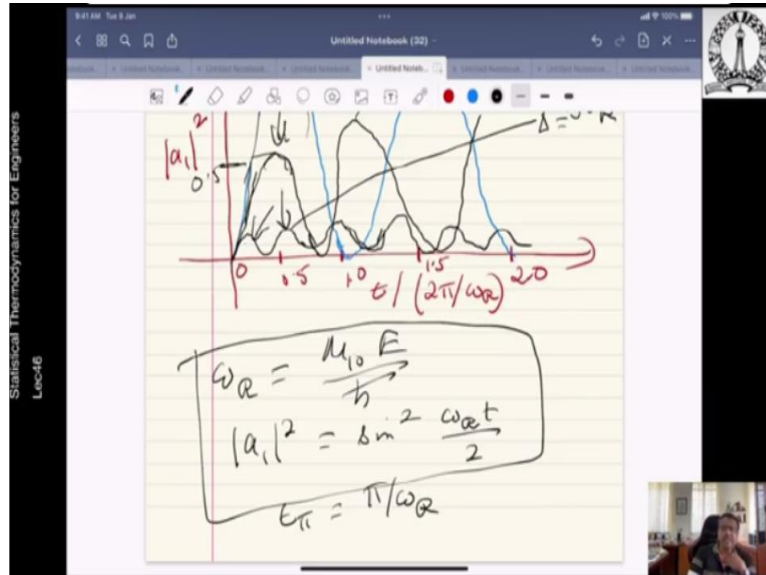
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So, let us draw that. So, this access now has a1 R, and this is t divided by 2 pi omega R. And this is 0.5, 1, 1.5, 2. So, when the detuning frequency is 0 in 0, so let us draw like this, this has a detuning frequency 0. Then let us take detuning frequency, go to the Rabi frequency. So, that will be given as, a little bit like this, so on and so forth.

So, this is drawn for delta is equal to omega R and then if you go to the detuning, even smaller detuning frequency, so this is with the delta equal to 3 omega R. So, this is the plotting. So, the meaning of the Rabi frequency now becomes clear if you look at these two equations.

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So, the, if we look at this equation, which was E by \hbar , and if you look at the equation, which is $|a_1|^2$ is equal to $\sin^2 \omega_R t / 2$? So, the Rabi frequency is being cleared from this. The system is coherently cycled, coherently cycled. That is with no abrupt changes in the phases of amplitude, the wave functions between the ground state and the excited state by an electromagnetic radiation. And resonance, the system is completely inverted after a time of π by πR .

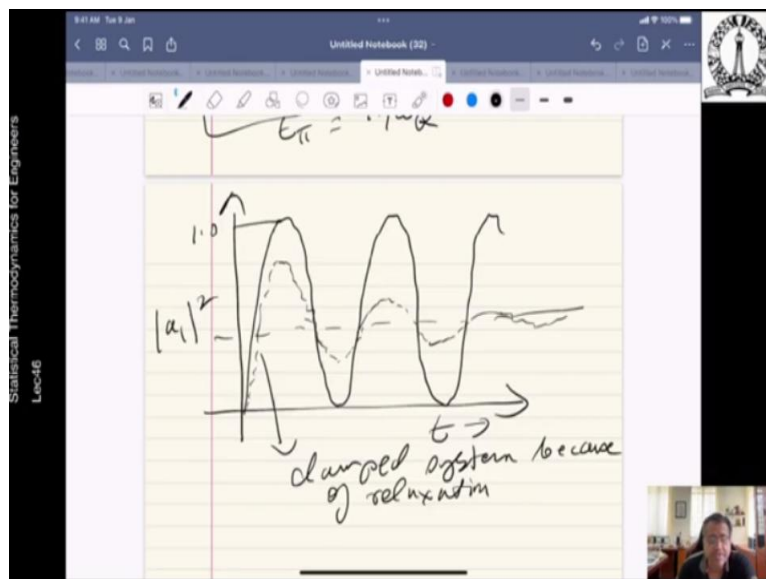
So, if we look at it, this is basically your 1. So, at the resonant frequency, the system is inverted. We can see it is inverted completely at the resonant condition. So, it is completely inverted between the ground and the excited stage. And this inversion happens after the time, which is given as $t = \pi / \Omega R$. The off resonance, while at off resonance, there is a reduced probability of finding the system in an excited stage, which is also shown in this particular figure that these are at detuning cases.

When the incident radiation is detuned by that particular amount, you will find that a system will have a reduced probability to begin with. The system will have a reduced probability to begin with, and that is exactly what happens over here. This probability is reduced if you further detune it, it is the probability of system existing in that particular excited stage. This is about 0.5. You can imagine how low this is.

So, we have got two things; at resonance, the system is completely inverted, after a specific timescale, we also understood the meaning of the Rabi frequency. If you look at these two troughs over here, these two expressions and off resonance there is a reduced probability because of the detuning nature.

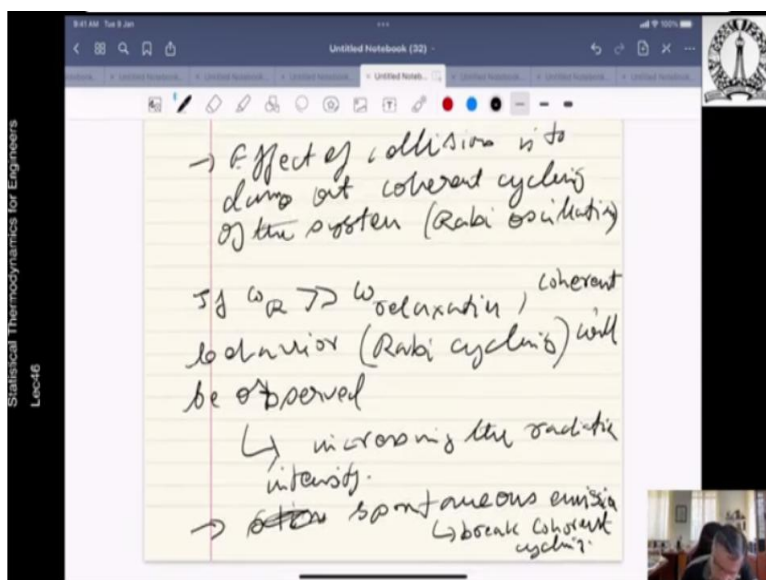
So, this is a picture of coherently driven system that has ignored all decay processes such as spontaneous emission from the excited stage. So, the spontaneous emission of a photon will bring the coherence of the emission, coherence of the excitation and reset the system to the ground state. Similarly, collisions can also cause relaxation in the system. In fact, collision can reset the phase of the wave functions without changing any of the population. So, this phase changing collisions also interact the coherent cycling of the system. So, all these things, all these things are actually present.

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So, if you have a system now, if you consider a system in which there is a relaxation process going on, let us draw this. This is time and this is once again a_1 time. So, that is the probability. So, undamped system will have very nice. So, this is one. Moment, you start have damping. This will start to decay and so forth. So, at the relaxation processes, so these are the damped systems because of relaxation.

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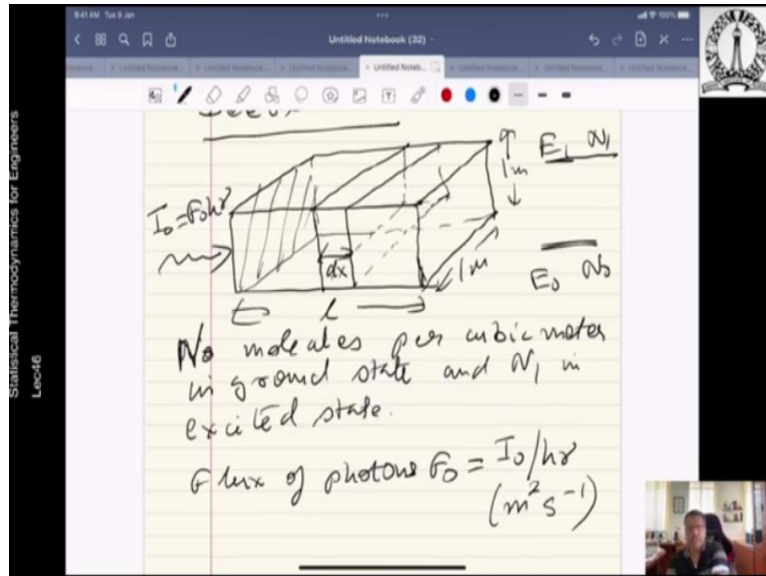
So, so the effect of, for example, collisions of collisions and other relaxation phenomena is to damp out coherent cycling of the system. The system also called the Rabi oscillations. However, the Rabi oscillations can be observed in a unique quantum system by just increasing the intensity of the radiation. This increases the applied electric field. So, at some

point, the Rabi cycling frequency exceeds the relaxation frequency and the coherent behaviour will be observed, and the coherent behaviour will be observed. So, if ω_R is much, much greater than ω_{relax} , a coherent behaviour or which is for the Rabi cycling will be observed. Sometimes you do it by increasing the radiation intensity. Increasing the radiation intensity.

Now, there are NMR and other processes which can actually do that. So, the, so we can see that how collisions processes and even like stimulated or rather spontaneous emission can also, you know, break this cycle, break the coherent cycle of the system. So, that is good. So, now that we know that what it is, so we can now then, got an idea, fairly good idea of what. So, next we are going to do something called, which is very relevant to absorption spectroscopy. So, that will be, called the Beer's law.

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The image shows a digital notepad interface with a handwritten note titled "Beer's Law". The note includes a diagram of a rectangular volume with dimensions l and l . An incident radiation beam $E_0 N_0$ enters from the left, and a transmitted beam $E_l N_l$ exits from the right. The text below the diagram states: "No molecules per cubic meter in ground state and N_1 in excited state." Above the diagram, there are handwritten notes: "break coherent cyclin?" and "I₀ = I₀ N₀". The notepad interface includes a toolbar with various drawing tools and a small video feed of a person in the bottom right corner.



So, let us take a look at something that we are going to do next. Beer's law. So, consider a system, like this, draw it first. So, this is like the 1 meter, and there are 2 energy levels say E_1 , N_1 like that. And there is radiation, which is coming at this. So, this is a system where there are N naught molecules, this is N naught, not no molecules, N naught molecules per cubic meter in the ground state and N_1 molecules in excited stage, state.

So, there is a flux of photons which is given us F naught is equal to I naught by h here, is incident on this left phase of the cube. So, if you consider this to be the left phase of the cube, this is the left phase of the cube where there is an incident photon, which is in the unit of meter square, second inverse which is incident upon the left phase.

So, all these photons, what they will do, they will travel through the system and they can be absorbed or they can induce stimulated emission. So, what is the intensity of the radiation after a distance, say l after a distance l and this is a differential section, which is dx . So, this is a distance l of the box. So, there is a flux of photons. These photons can either be absorbed or they can trigger stimulated emission. So, what is the intensity after a certain length l in this particular box?

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excited state.

Flux of photons $\rho_0 = I_0/h\nu$
($m^2 s^{-1}$)

$$\frac{dN_1}{dt} = -B_{1 \rightarrow 0} \rho N_1 + B_{0 \rightarrow 1} \rho N_0$$

$\rho = \frac{I}{c} = \frac{h\nu F}{c}$

$$\frac{dN_1}{dt} = \frac{2\pi^2 \mu_{10}^2}{3\epsilon_0 h^2} (N_0 - N_1) g(\nu - \nu_{10}) \rho$$

$$= \frac{2\pi^2 \mu_{10}^2 \nu}{3\epsilon_0 hc} (N_0 - N_1) g(\nu - \nu_{10}) F$$

$$\frac{dN_1}{dt} = \sigma F (N_0 - N_1)$$

$$\sigma = \frac{2\pi^2 \mu_{10}^2}{3\epsilon_0 hc} g(\nu - \nu_{10})$$

$\hookrightarrow m^2$
 \hookrightarrow effective area that a molecule presents to a flux of photons F .

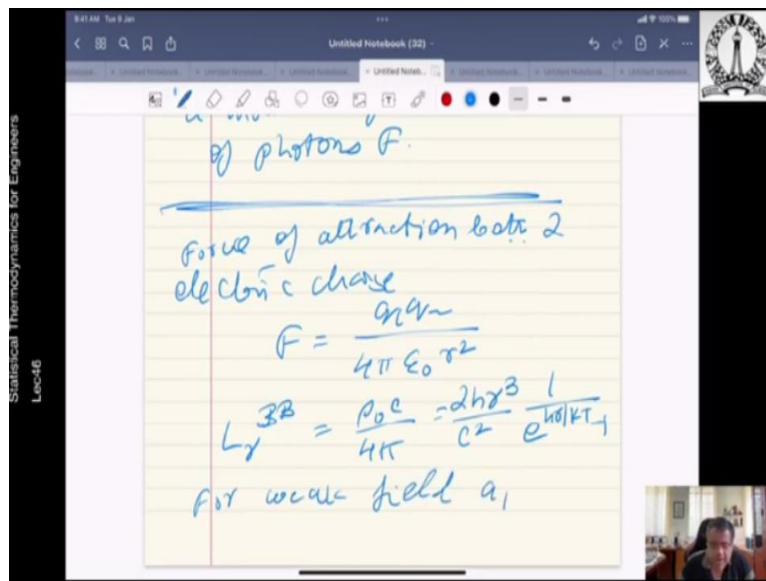
So, let us do that. dN_1 by dt is equal to minus $B_{1 \rightarrow 0} \rho N_1$ plus $B_{0 \rightarrow 1} \rho N_0$. We will see what, what ρ is. ρ is basically I by C is equal to $h F C$ by C . Now, coming from this expression, after this, what would happen? dN_1 by dt is equal to $2\pi^2 \mu_{10}^2$ naught square, $3\mu_{10}^2$ naught square, $3\mu_{10}^2$ naught square, $3\mu_{10}^2$ naught square. We will see how to get to this actual expression. So, that will be a part of a tutorial, $g V$ minus V naught ρ .

You may be thinking that what this g is and what this, other things are. So, we will take a detour right here. After this is done, after these expressions are done. So, this is μ_{10}^2 naught square π^2 $3\epsilon_0$ naught hc N naught by N_1 g 10 into F . This gives rise to dN_1 by dt is equal $2\sigma F N$ naught minus N_1 . Where σ is equal to $2\pi^2 \mu_{10}^2$ naught square divided by $3\epsilon_0$ naught hc $g(\nu - \nu_{10})$ (21:06). This has got a dimension of meter square. The

physical interpretation of sigma is as an effective area that the molecule represents like a stream of Planck's F. So, this is basically the effective area that, molecule present to a flux of photons F.

Now of course, here you notice a few things like g and how did I get these expressions that you see over here. For that we need to take a little bit of a detour and try to understand that what happens on, when once radiation interacts with matter. Now, in order to do that, let us now take it case by case basis and well try to get a reasonable idea that how the built-up of the population in an excited state happens and how relaxation is actually important in taking away these transitions, breaking the coherency of these transitions and how they lead to what we call something called a line shaped function. So, for that we need to take a little bit of a detour. And try to find out that how this absorption coefficient, can be evaluated, from the, from the first principles.

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So, for that, we first, so here is this case for a small decay. So, if you recall that the magnitude of force of attraction between two electric charges, force of attraction between two electric charges are given as $F = \frac{q_1 q_2}{4\pi \epsilon_0 r^2}$. So, there is of course a half term, but you are not going to go over there. Since a typical electronic transition has a lifetime of about 10 nanosecond, the effect of Rabi cycling are already present at 1 watt, at megawatt or higher power levels of pulsed lasers, for example, what we get the coherent effect of strong radiations are even more pronounced, provided electrical breakdown is avoided.

At these high electric field strengths, however, the simple 2, 2-level model is not a good description of a molecular system. So, that is the pollute. So, you understand that a typical electronic transition lifetime is about 10 nanoseconds. So, the effect of Rabi cycling is present, which the coherent cycling. The higher pulse levels, higher power levels, we can see that the Rabi cycling can be even more pronounced. It is pronounced even at 1 watt.

So, there is also much confusion about the various terms and symbols in the field of radiometry, intensity of a laser beam can be called iluradiance in radiometry. In radiometry, the intensity and spectral intensity at used or power per steroid radium and power parts radiant for hertz respectively. So, there are all kinds of nomenclature issues as well. So, the, so these are the things, that are there. However, the spectral radiance of a black body is given as $\rho v c$ by 4π , which is equal to $2 h$ cube by C square into 1 by $h u$ by KT minus 1 .

So, the case of weak electromagnetic radiation interacting with the system is also common. In fact, before the de development of lasers in the 1960s, weak field case applied to all regions of the spectrum, except the radio frequency and the microwave region, for powerful, for which powerful coherent sources were available. In the weak field case, there is a negligible built-up of population in the excited stage. So, for weak field, non-laser, a_1 is almost equal to 0 and a_0 is almost equal to 1.

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The image shows a digital notepad with handwritten mathematical derivations. The first equation is $a_1 = \frac{i\omega_R}{2} \int_0^t e^{-i\delta t} dt$. The second equation is $a_1 = \frac{\omega_R}{-2\delta} (e^{-i\delta t} - 1)$. The third equation is $P_{1 \leq 0} = |a_1|^2 = \frac{\omega_R^2}{\delta^2} \sin^2\left(\frac{\delta t}{2}\right)$. The fourth equation is $= \frac{\mu_0^2 E^2}{\hbar^2} \frac{\sin^2((\omega - \omega_0)t/2)}{(\omega - \omega_0)^2}$.

As a result of that, a_1 dot is $i \omega_R$ by 2 , e minus $i \delta t$. So, this is, this can be readily integrated to get a_1 $i \omega_R$ by 2 0 to t e minus $i \delta t$, t dt . So, a_1 is ω_R by 2 δ e i minus δt minus 1 . So, probability of finding the, system in the excited stage after a time t is then obtained from this particular equation that we have written over here. So, $P_{1 \leq 0}$ to 1 ,

that is a probability, it is a_1^2 square, therefore, given as $\frac{\omega R^2 \sin^2 \Delta t}{2}$ is equal to $\frac{\mu_1 \hbar^2 \sin^2 (\omega - \omega_1) t}{2}$, divided by $\omega \omega_1$ square.

So, this formula is deceived because it is resumes monochromatic radiation and short interaction times. These requirements are inconsistent with one another because of Hilgenberg uncertain principles. So, in the next class we will see that how some of these things actually unfolds. But this is the probability of finding something in the excited stage for a weak field of radiation.