Statistical Thermodynamics for Engineers
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Lecture 58
Insights into radiative spectral transitions

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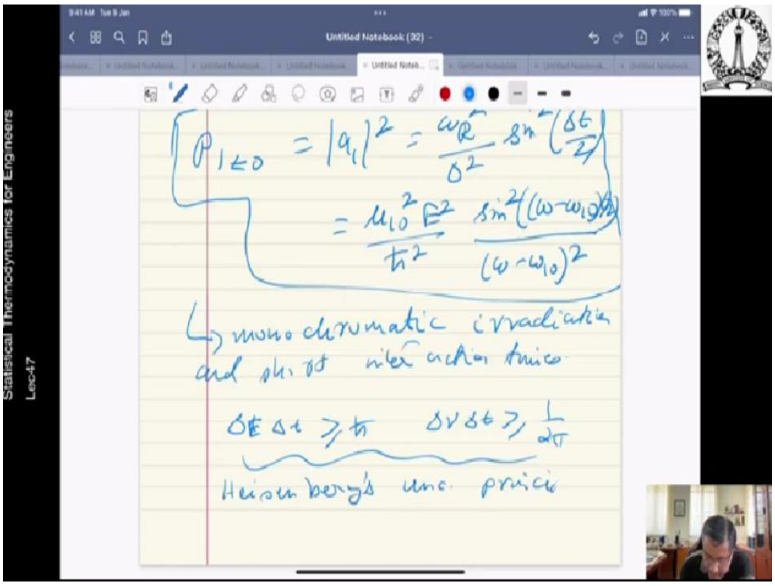

$$P_{1\leftarrow 0} = |a_1|^2 = \frac{\omega_R^2}{\delta^2}\sin^2\left(\frac{\delta t}{2}\right)$$

$$= \frac{\mu_{10}^2 E^2}{\hbar^2}\,\frac{\sin^2((\omega-\omega_{10})t/2)}{(\omega-\omega_{10})^2}$$

↳ monochromatic irradiation and short interaction times

$$\underbrace{\Delta E\,\Delta t \geq \hbar \qquad \Delta\nu\,\Delta t \geq \frac{1}{2\pi}}_{\text{Heisenberg's unc. princi}}$$

Welcome to lecture number 47. So, we already saw that how the probability for a weak electromagnetic radiation can be written says. But this formula, as we say it is very deceptive because it assumes monochromatic, monochromatic irradiation. And short interaction states over times. So, these two requirements are obviously inconsistent with one another because of Heisenberg's uncertainty principle; delta E into delta t has to be greater than equal to h bar or delta frequency into delta t has to be greater than equal to 1 over 2 pi. This must be always satisfied. This is by Heisenberg's uncertainty principle.

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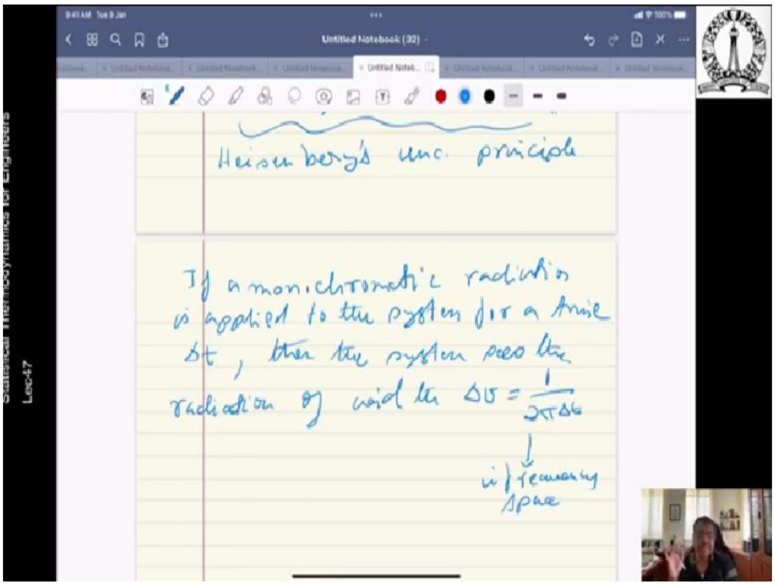
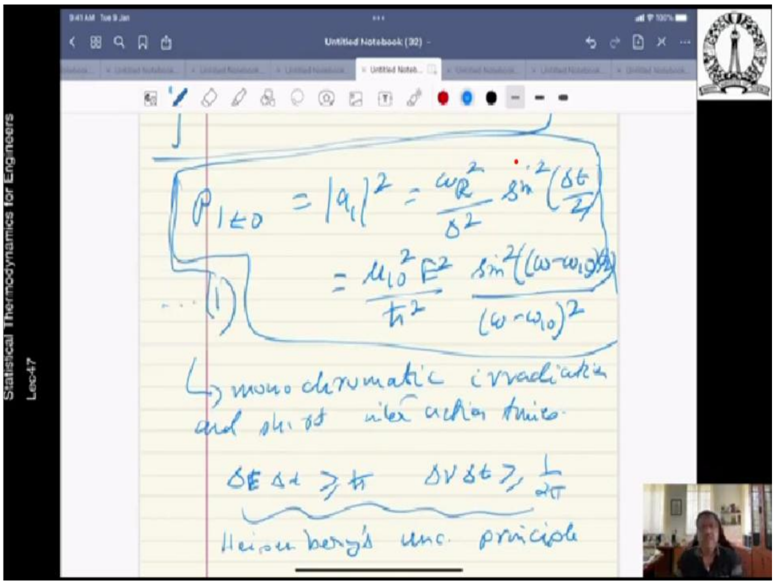


$\underbrace{\qquad\qquad}$ Heisenberg's unc. principle

If a monochromatic radiation is applied to the system for a time δt, then the system sees the radiation of width $\Delta\nu = \frac{1}{2\pi\delta t}$

$\downarrow$ in frequency space



$$\boxed{P_{1\leftarrow 0} = |a_1|^2 = \frac{\omega_R^2}{\delta^2}\sin^2\left(\frac{\delta t}{2}\right) = \frac{\mu_{10}^2 E^2}{\hbar^2}\frac{\sin^2((\omega-\omega_{10})t/2)}{(\omega-\omega_{10})^2}} \quad (1)$$

$\hookrightarrow$ monochromatic irradiation and short interaction times.

$\delta E\,\delta t \geq \hbar \qquad \delta\nu\,\delta t \geq \frac{1}{2\pi}$

$\underbrace{\qquad\qquad}$ Heisenberg's unc. principle

So, if a monochromatic radiation is really applied to a system, for a time delta t, the system sees the radiation of width. So, if a monochromatic chromatic radiation is applied to the system for a time delta t, then the system, sees the radiation of width, to the V, which is equal to 1 over 2 by delta in the frequency space. So, at nanosecond pulse of radiation, as an intrinsic width of about 1 60 megahertz in the frequency space. So, before we actually use this equation of the probability probabilistic equation, if we use this situation, let us, put this as 1 so that it is easier for us to do.

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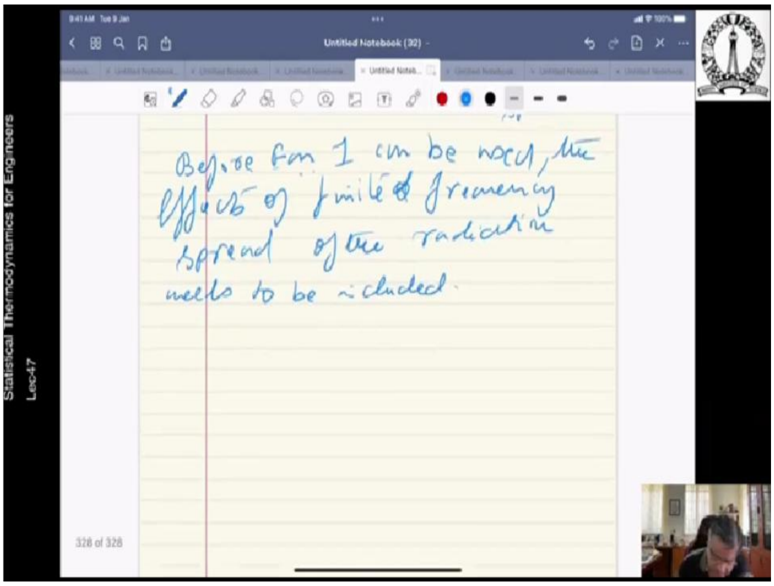
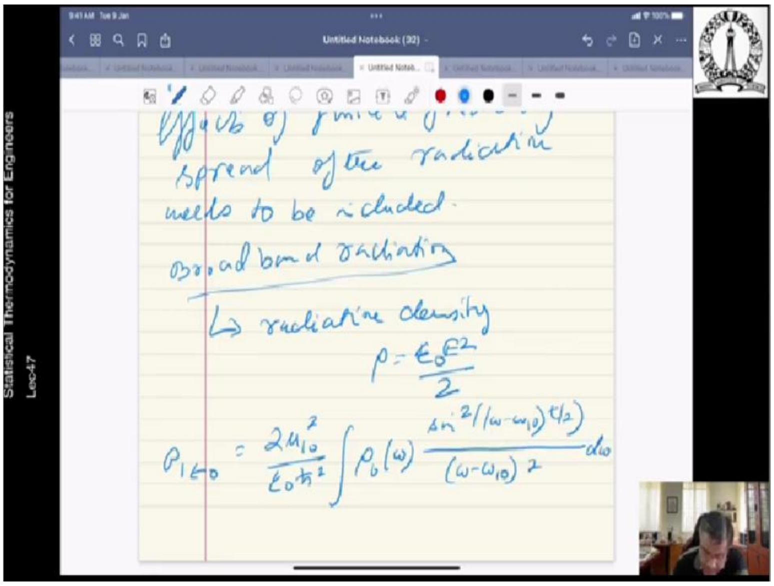


Before Eqn 1 can be used, the effects of finite frequency spread of the radiation needs to be included.



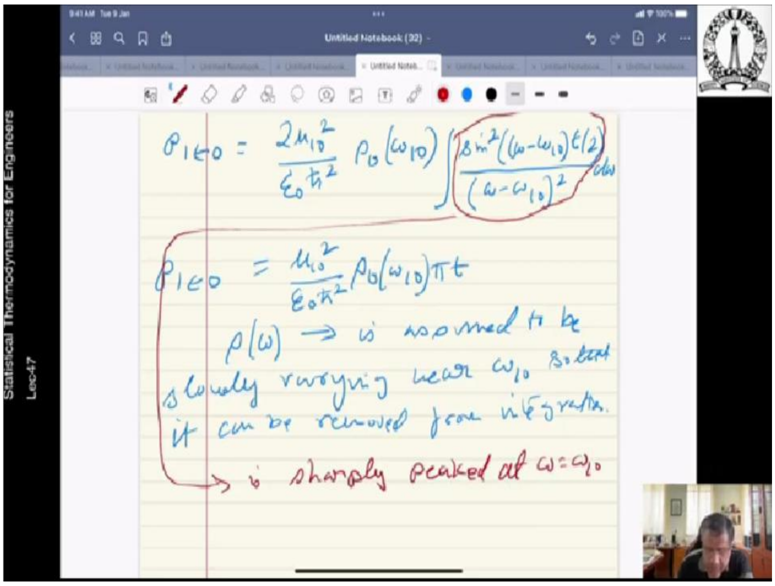
effects of finite frequency spread of the radiation needs to be included.

Broad band radiation

↳ radiation density

$$\rho = \frac{\epsilon_0 E^2}{2}$$

$$\rho_{1\leftarrow 0} = \frac{2\mu_{10}^2}{\epsilon_0 \hbar^2}\int \rho_0(\omega)\frac{\sin^2((\omega-\omega_{10})t/2)}{(\omega-\omega_{10})^2}\,d\omega$$



$$\rho_{1\leftarrow 0} = \frac{2\mu_{10}^2}{\epsilon_0 \hbar^2}\rho_0(\omega_{10})\int \frac{\sin^2((\omega-\omega_{10})t/2)}{(\omega-\omega_{10})^2}\,d\omega$$

$$\rho_{1\leftarrow 0} = \frac{\mu_{10}^2}{\epsilon_0 \hbar^2}\rho_0(\omega_{10})\pi t$$

$\rho(\omega) \rightarrow$ is assumed to be slowly varying near ω_{10} so that it can be removed from integration.

→ is sharply peaked at $\omega = \omega_{10}$

So, before, before equation 1 can be used, be used, the effects of finite frequency spread of the radiation must be included. So, if we consider the radiation applied to the system to be broadband rather than monochromatic, so let us assume that we have a broadband and radiation. And this broadband radiation has a radiation density, radiation density, which is a rho epsilon naught E square by 2.

So, the total transition probability therefore, will be given us P 01 equal to 2 mu 1 0 square by epsilon h bar square omega sin square is basically integrated over all frequencies d omega, which is therefore, P 10, is written as 2 mu 10 square epsilon naught h bar square omega 1 0. Integral square omega omega 1 0 by 2 whole square d omega. This ultimately gives rise P 1 0 as mu 1 naught square, divide by epsilon h bar square rho v omega 0.

This is, this omega, rho omega is assumed to be slowly vary slowly varying near omega 1 0, so that it can be removed, removed from integration. This is indeed the case because, sin square, if you look at sin square, this particular term, term that is marked here, this particular term is sharply picked and omega equal to omega 1 0.

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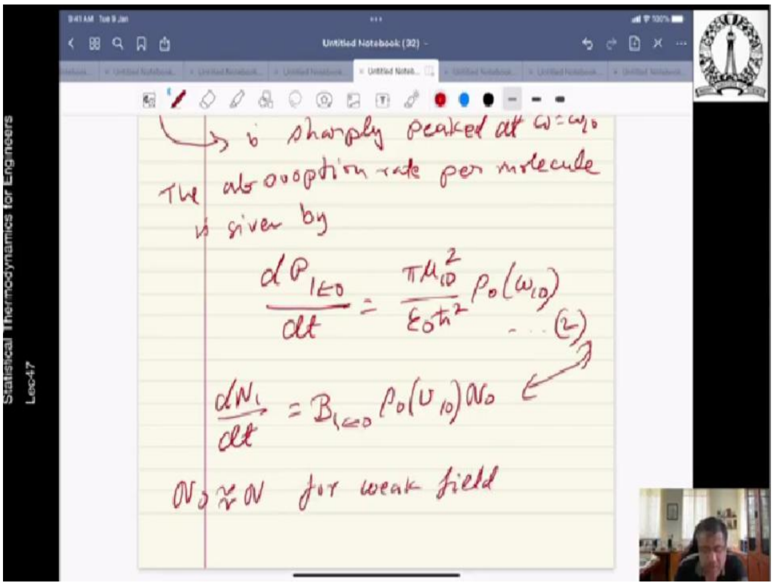

↳ is sharply peaked at $\omega = \omega_{10}$

The absorption rate per molecule is given by

$$\frac{dP_{1\leftarrow 0}}{dt} = \frac{\pi \mu_{10}^2}{\varepsilon_0 \hbar^2} \rho_0(\omega_{10}) \quad \cdots (2)$$

$$\frac{dN_1}{dt} = B_{1\leftarrow 0} \rho_0(\nu_{10}) N_0$$

$N_0 \simeq N$ for weak field

So, therefore the absorption rate per molecule is given by pi mu 1 0 square epsilon h bar square omega. This is absorption, sharply peaked. In order to derive an expression for the absorption coefficient in terms of the transition dipole moment, this equation, if we call this equation 2, say, this equation, needs to be compared with all the other equation now, needs to be compared with, remember the old equation that we had (())(7:33) system only 1, 0 rho V 0 N naught. So, recall so, that was the equation that we had per deal. So, as you can see, so the absorption, in order to write the absorption coefficient, this equation is now compared with this equation, with the assumption that N naught is almost equal to N or weak field. So, dividing my N basically gives a transition probability per molecule.

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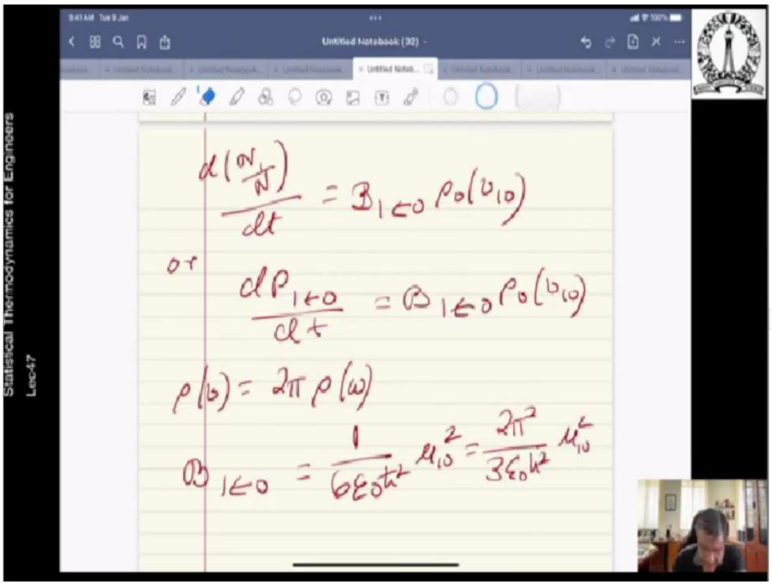


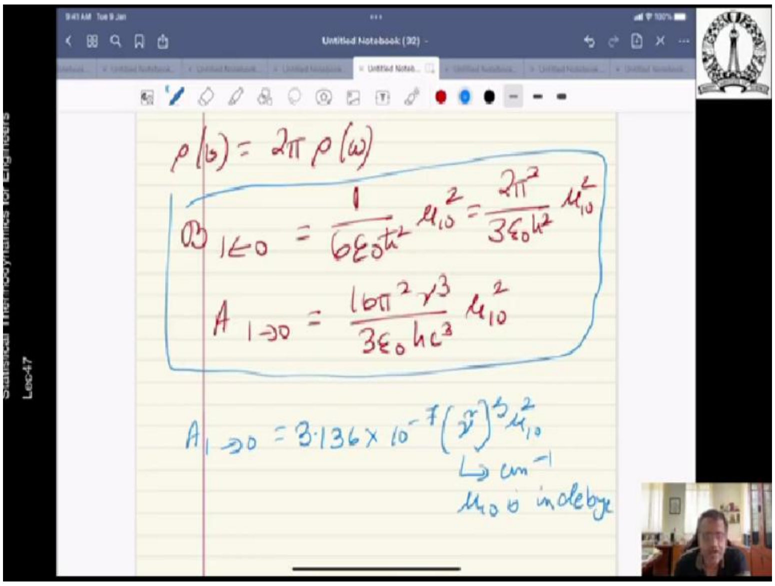
$$\frac{d\left(\frac{N_1}{N}\right)}{dt} = B_{1\leftarrow 0}\,\rho_0(\nu_{10})$$

or

$$\frac{dP_{1\leftarrow 0}}{dt} = B_{1\leftarrow 0}\,\rho_0(\nu_{10})$$

$$\rho(\nu) = 2\pi\,\rho(\omega)$$

$$B_{1\leftarrow 0} = \frac{1}{6\varepsilon_0\hbar^2}\mu_{10}^2 = \frac{2\pi^2}{3\varepsilon_0 h^2}\mu_{10}^2$$



$$\rho(\nu) = 2\pi\,\rho(\omega)$$

$$\boxed{\begin{aligned} B_{1\leftarrow 0} &= \frac{1}{6\varepsilon_0\hbar^2}\mu_{10}^2 = \frac{2\pi^2}{3\varepsilon_0 h^2}\mu_{10}^2 \\ A_{1\to 0} &= \frac{16\pi^2\nu^3}{3\varepsilon_0 h c^3}\mu_{10}^2 \end{aligned}}$$

$$A_{1\to 0} = 3.136\times 10^{-7}(\tilde{\nu})^3\mu_{10}^2$$

↳ cm^{-1}

μ_{10} is in debye

So, d N1 by N dt is equal to B 1 0 rho v 1 0 or d P1 0 divided by dt is equal to B 1 0 rho v, this. Here there is a factor of 3 which is missing, in this particular equation, in equation 2, because, this has been derived from isotropic radiation traveling in x, y, and z directions, whereas equation 2 that you see over here has been derived using a plane wave, traveling in the z direction only. Since only the z component of the isotropic radiation is effective in inducing a transition.

So, also noting this and also noting that rho V is equal to 2 pi rho omega. V 1 0 therefore becomes 1 over 6 epsilon h bar square mu 1 naught square, which is equal to 2 pi square 3 epsilon naught h square mu 1 naught square and A 1 to 0 is 16 pi square gamma cube, 3 epsilon naught h C cube mu 1 naught square. So, these two equations now are the key results because they relate to observe microscopic transitions to the microscopic transition dipole moment of an atom or a molecule.

So, we normally, if we substitute the numbers, A 1 0 will be actually equal to 3.136 into 10 to the power minus 7 cube mu 1 naught square, this is in centimetre inverse and mu 1 naught is indebye. Although, these equations are essentially correct, one factor that we have ignored over here is the possibility of relaxation. So, these things relax. Collision or spontaneous radiative lifetime of the upper state has been ignored so far. So, we have neglected collisions and spontaneous continuous radiated lifetime of upper state per state.

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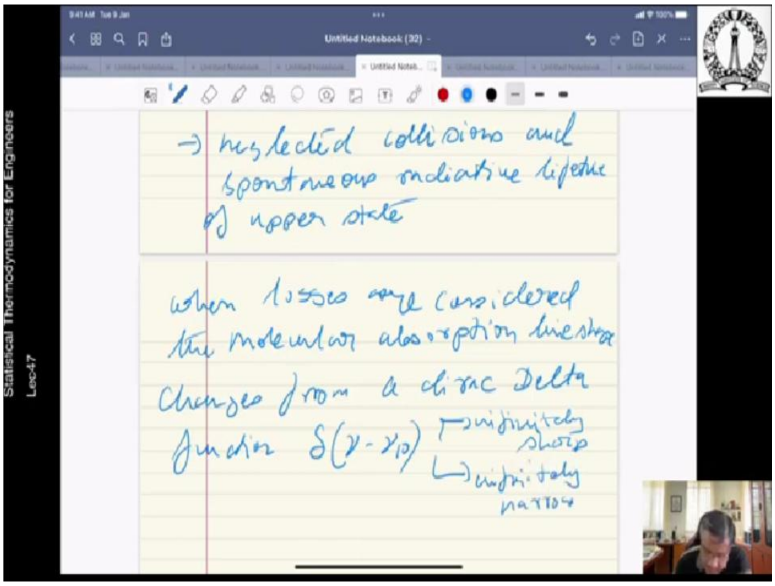
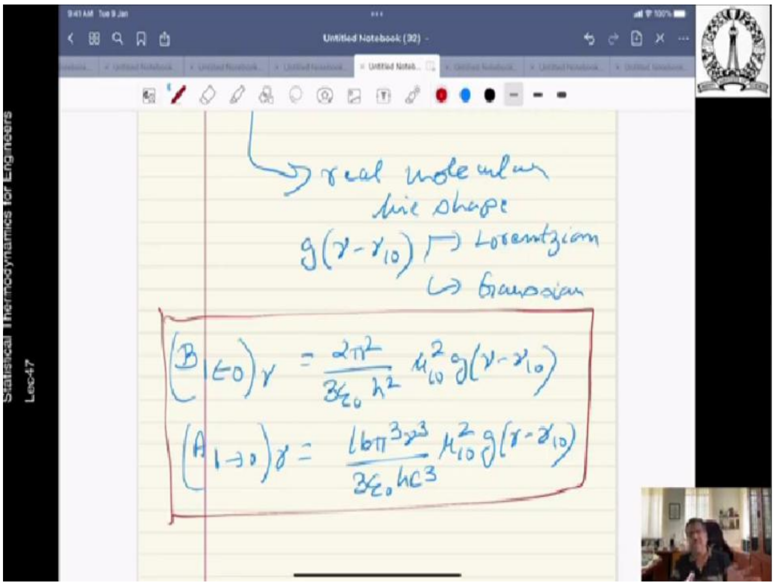


→ neglected collisions and spontaneous radiative lifetime of upper state

when losses are considered the molecular absorption lineshape changes from a dirac Delta function $\delta(\nu-\nu_{10})$ → infinitely sharp ↳ infinitely narrow



→ real molecular line shape

$g(\nu-\nu_{10}) \rightarrow$ Lorentzian

↳ Gaussian

$$(B_{1\leftarrow 0})_\nu = \frac{2\pi^2}{3\epsilon_0 h^2}\mu_{10}^2 g(\nu-\nu_{10})$$

$$(A_{1\rightarrow 0})_\nu = \frac{16\pi^3\nu^3}{3\epsilon_0 hc^3}\mu_{10}^2 g(\nu-\nu_{10})$$

So, when these losses are considered, when the losses are considered, the molecular absorption line shape, shape changes from Dirac delta function, is delta naught which is basically infinite, infinitely sharp and infinitely narrow. So, this is the Dirac delta function to a real molecular line shape so this converts to a real molecular line shape. So, this molecular line shape is called, it is given as g, which can be either a Lorentzian or a Gaussian. This is of uni, finite width and height.

As a result, the equations can be rewritten now. So, 2 pi square, 3 epsilon naught square, mu 1 naught g square cube is the first one, and then A 1 to 0 gamma 16 pi cube, gamma cube divided by 3 epsilon naught, hC cube mu 1 naught square g minus mu 1. So, these were the two expressions that you get in which, these are the actual absorption coefficients and the initial coefficients.

So, so basically if you integrate it across all frequencies, you will get just the coefficient P. So, so these are all have dimensions of minus 1 and this has the dimension of having second inverse, sorry, not minus 1. So, also note that the, that the 2 levels 1 and 0 are assumed to be non-degenerate. The usual cases are degenerate, atomic and molecular levels are a little bit more complicated. So, the energy levels are considered to be degenerate.

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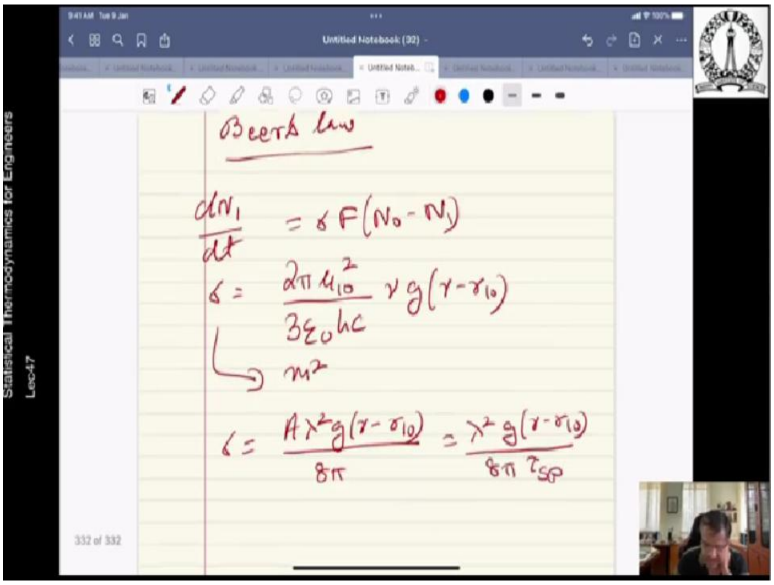


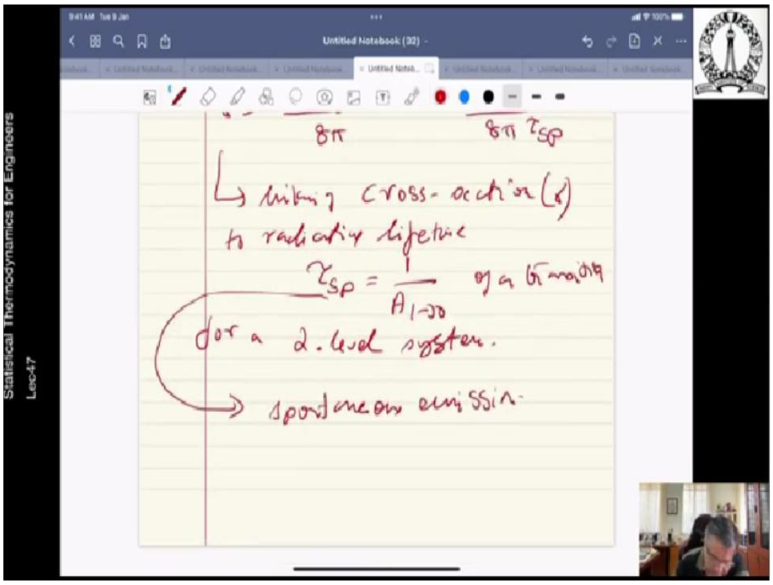
Beers law

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

$$\sigma = \frac{2\pi \mu_{10}^2}{3\varepsilon_0 hc} \nu g(\nu - \nu_{10})$$

$\hookrightarrow m^2$

$$\sigma = \frac{A\lambda^2 g(\nu - \nu_{10})}{8\pi} = \frac{\lambda^2 g(\nu - \nu_{10})}{8\pi \tau_{sp}}$$



$\hookrightarrow$ linking cross-section (σ) to radiative lifetime

$\tau_{sp} = \frac{1}{A_{1\to 0}}$ of a transition

for a 2-level system.

$\to$ spontaneous emission

So, now that we have taken this detour, now we can understand when we wrote in our Beer’s law, you recall your Beer's Law, we wrote that d N1 by dt was equal to sigma F N naught minus N1, where sigma was equal to 2 pi mu 1 naught square divided by 3 C gamma g v minus 1 0, which was in the, this had the dimension of meters square. This is the dimension of meters square.

The physical interpretation, we also say this is the effective area that the molecule presents to a flux of photons of flux or stream of photons of flux X. So, it is now therefore, therefore very convenient, very convenient so to say if we now cast this sigma, in this particular form, A square g gamma (())(15:55) 8 pi lambda square g 8 pi tau sp. So, which relates to the cross section of the cross section to the radiator.

So, this is basically linking the cross section which is basically what is sigma to radiative lifetime tau sp is equal to 1 over A 0 of a transition, or for a 2 level system. The subscript sp refers to spontaneous emission. So, this is spontaneous emission, this is an inverse of the lifetime. So, this can be related to real multi-level systems, by doing other methodologies. So, now let us look at that if a flux.

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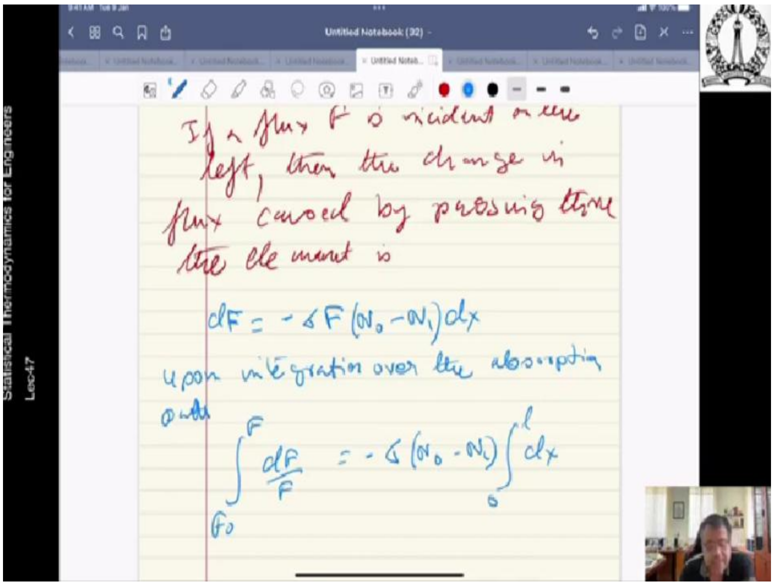
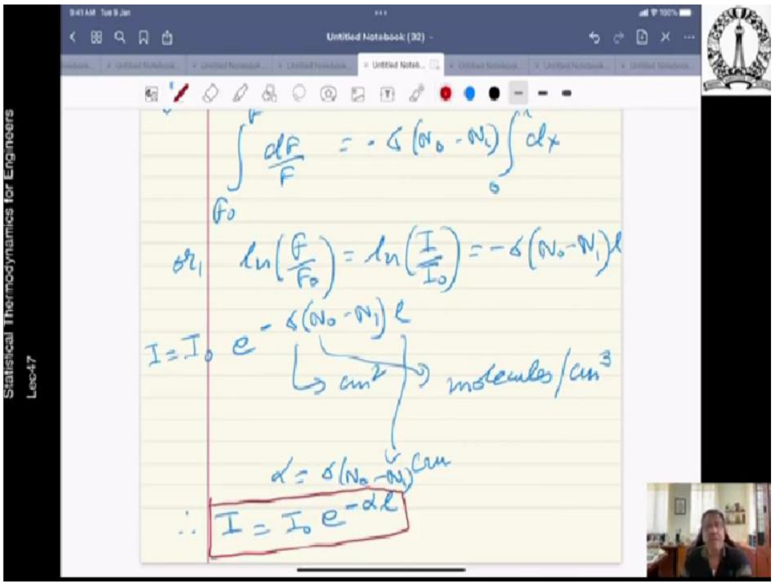


If a flux F is incident on the left, then the change in flux caused by passing thru the element is

$$dF = -\sigma F (N_0 - N_1)\, dx$$

upon integration over the absorption path

$$\int_{F_0}^{F} \frac{dF}{F} = -\sigma (N_0 - N_1) \int_0^l dx$$



$$\int_{F_0}^{F} \frac{dF}{F} = -\sigma (N_0 - N_1) \int_0^l dx$$

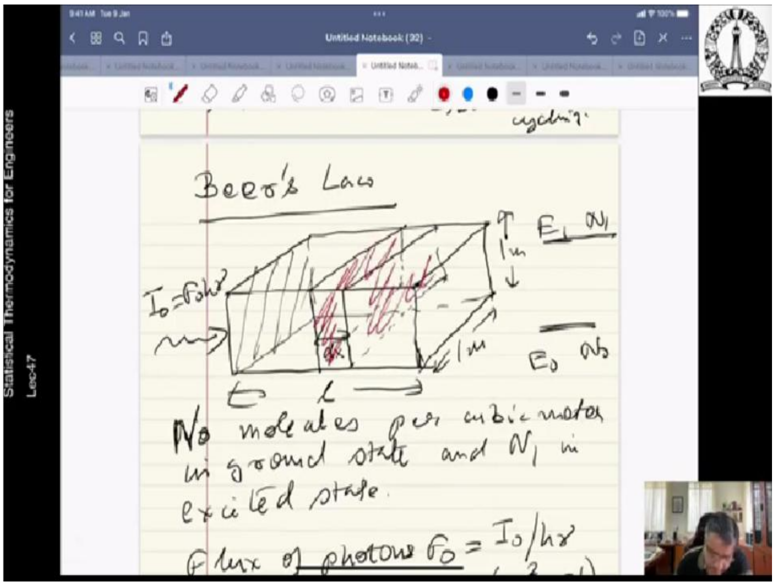
or, $\ln\left(\frac{F}{F_0}\right) = \ln\left(\frac{I}{I_0}\right) = -\sigma (N_0 - N_1) l$

$$I = I_0\, e^{-\sigma (N_0 - N_1) l}$$

$\sigma \to cm^2$, $(N_0 - N_1) \to$ molecules/cm^3

$\alpha = \sigma (N_0 - N_1)\ cm$

$$\therefore \boxed{I = I_0\, e^{-\alpha l}}$$



Beer's Law

N_0 molecules per cubic meter in ground state and N_1 in excited state.

Flux of photons $F_0 = I_0/h\nu$

So, let us look at if a flux, F is incident on the left of the element thickness dx. This was the thickness dx, if you recall. This was the thickness dx, that is what we did earlier. The thickness dx on the left, with a smaller element of thickness dx, with a cross-sectional area of 1 meter square. Then the change in flux caused by passing through the element is given as dF equal to minus sigma F N naught minus N1 dx. Integrating over the absorption part, this becomes if F naught f, df by minus N1 0 to L dx.

Or ln F by F naught is equal to ln I naught is equal to minus sigma N naught minus N1 l dot Or in other words, it can be written as I, I is equal to I dot exponential minus sigma N naught minus N1 l, which is, which is called the Beer's law. Actually, it is written in a slightly different form ins several textbooks.

So, your sigma of course is reported in centimetre square. N is in molecules per CC centimetre cube and l is in centimetre, rather than the corresponding SI units. So, if we consider alpha is equal to sigma N naught minus N1, therefore, I will be written as I naught, it need to be part of minus alpha l. So, this will be the expression. So, this sets the stage now that we have seen this is what we Beer Lambert’s law is.

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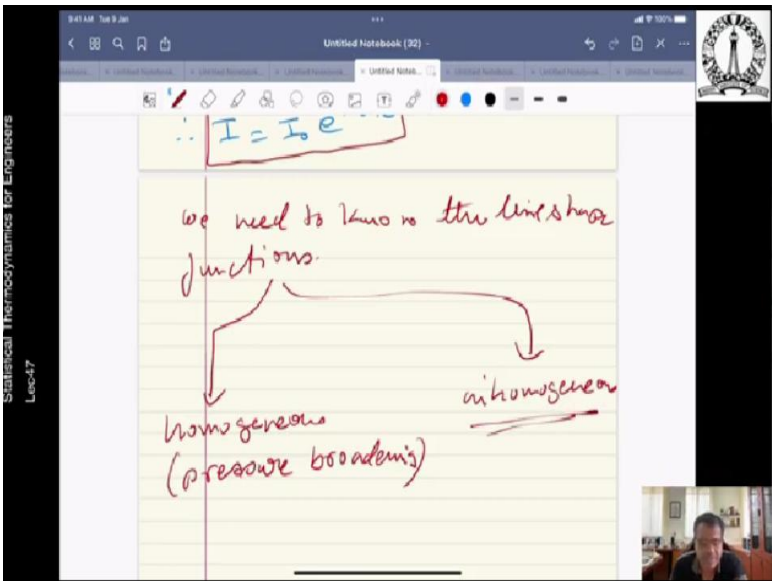
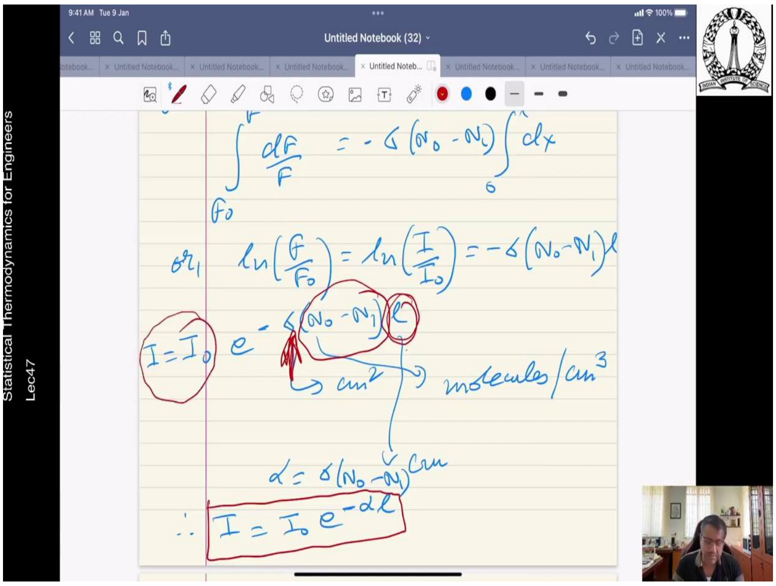


$\therefore \boxed{I = I_0 e}$

we need to know the lineshape functions.

homogeneous (pressure broadening)

inhomogeneous



$$\int_{F_0}^{F} \frac{dF}{F} = -\sigma(N_0 - N_1)\int_0^{x} dx$$

or, $\ln\left(\frac{F}{F_0}\right) = \ln\left(\frac{I}{I_0}\right) = -\sigma(N_0 - N_1)l$

$$\boxed{I = I_0}\, e^{-\underset{\hookrightarrow cm^2}{\sigma}\underset{\hookrightarrow molecules/cm^3}{(N_0 - N_1)}\,l}$$

$$\alpha = \sigma(N_0 - N_1)\ cm$$

$$\therefore \boxed{I = I_0 e^{-\alpha l}}$$

Now, on a spectrum of a real molecule, we need to know the line shape functions. We need to know the line shape functions. So, Beer Lambert law, as you can see it serves different purpose. It allows you to calculate the concentration. So, long as you know what this guy is all about. And you know the length. So, as you can see it is dependent on the length. So, more the length, more is the sensitivity of this particular parameter. So, it is easy to measure experimenting.

So, but in real life we still need to know the real spectrum of a molecule. So, the line shape functions basically falls into 1 or 2 of the general categories. One is homogeneous and the other one is inhomogeneous. Well, that did not require much of a guessing. The homogenous line shape of occurs when all molecules have identical line shape functions.

For example, if an atomic or molecule absorber in the gas station is subjected to high pressure, then all molecules in the system are found to have an identical pressure brought on line shape for a particular transition. Pressure broadening of a transition is therefore, same to be homogeneous broadening, if this is one example is therefore pressure broadening. We will see more of these a little later.

On the other hand, if the molecule is dissolve in a liquid and then the disorder inherent infrastructure of the liquid provides different environments. So, the absorption spectrum is made up of different spectrum, different molecular environments. So, this is therefore called in homogenously broadened.

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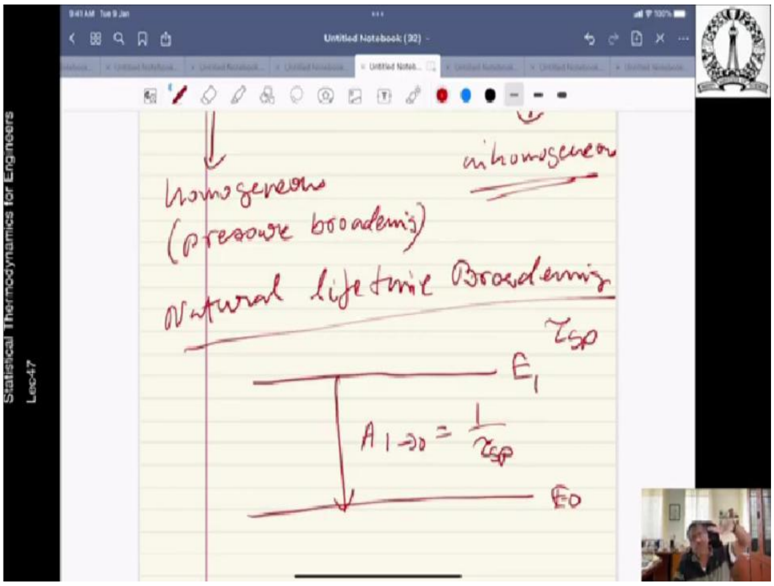


homogeneous (pressure broadening)

inhomogeneous

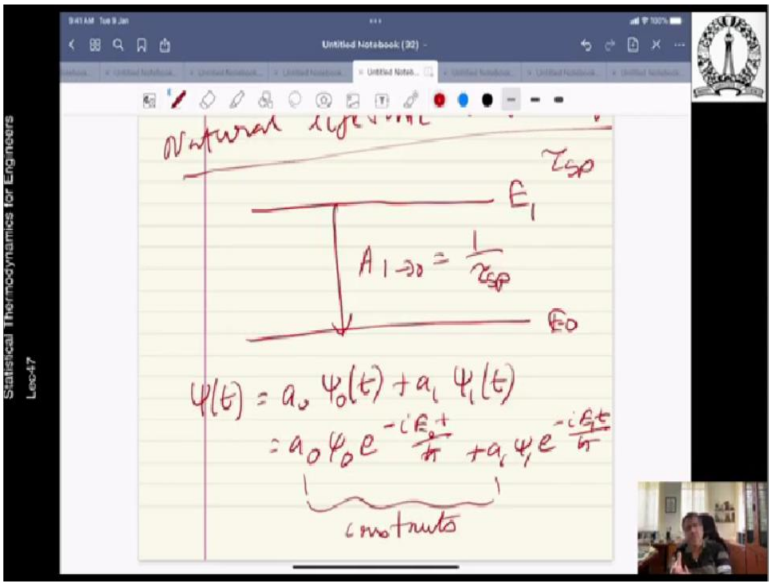
Natural lifetime Broadening

τ_{sp}

E_1

$A_{1\to 0} = \frac{1}{\tau_{sp}}$

E_0



Natural lifetime

τ_{sp}

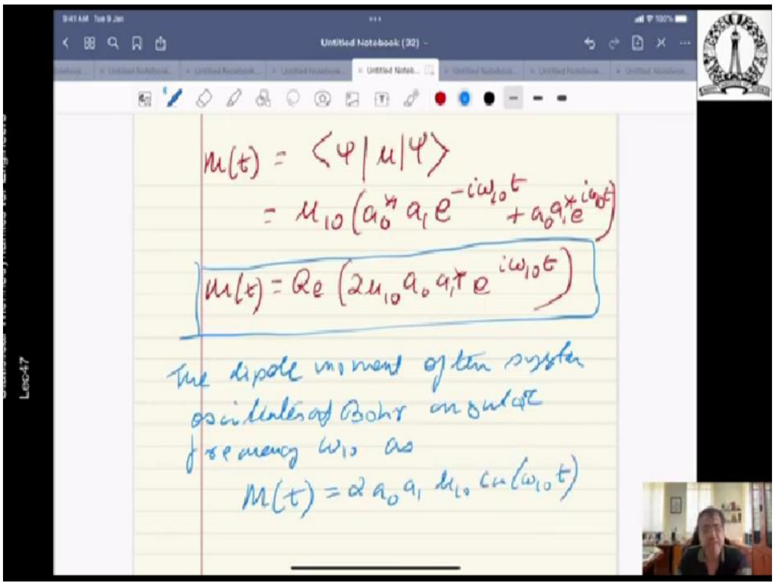
E_1

$A_{1\to 0} = \frac{1}{\tau_{sp}}$

E_0

$$\psi(t) = a_0\psi_0(t) + a_1\psi_1(t)$$

$$= \underbrace{a_0\psi_0 e^{-\frac{iE_0t}{\hbar}} + a_1\psi_1 e^{-\frac{iE_1t}{\hbar}}}_{\text{constants}}$$



$$\mu(t) = \langle\psi|\mu|\psi\rangle$$

$$= \mu_{10}\left(a_0^* a_1 e^{-i\omega_{10}t} + a_0 a_1^* e^{i\omega_{10}t}\right)$$

$$\boxed{\mu(t) = Re\left(2\mu_{10} a_0 a_1^* e^{i\omega_{10}t}\right)}$$

The dipole moment of the system oscillates at Bohr angular frequency ω_{10} as

$$M(t) = 2 a_0 a_1 \mu_{10} \cos(\omega_{10}t)$$

So, let us look at natural lifetime broadening. So, what is natural lifetime broadening? Consider once again a 2-level system, with an intrinsic lifetime of about tau sp. This is E1, this is E naught. So, this is the 1 0, it is 1 over tau sp describes the state of the 2-level system in the absence of electromagnetic. So, let us once you do that, the wave function that describes the state of the system, is given as psi t equal to a naught, this is also, we have done it before. Again, do it here, bring it here.

So, this is now given as, writing it in terms of the time independent portion of the wave function. Which one, these are simply constants. Should the system be excited into a super positioned state, the dipole moment of the system is therefore, given by this is once again the high dependent portion, this is equal to 1, 0 a0 star a1 omega naught t plus a naught a1 star e i, So, it is the real part 2, 1, 0 a0, a1 star M t.

So, this is your omega t, assuming space fixed moments both ban. So, the dipole moment of the system oscillates at the Bohr angular frequency. The dipole moment of the system oscillates at Bohr angular frequency, 1 naught as M t equal to 2 a naught a1 mu 1 naught cos omega 1. So, these are chosen to be real numbers.

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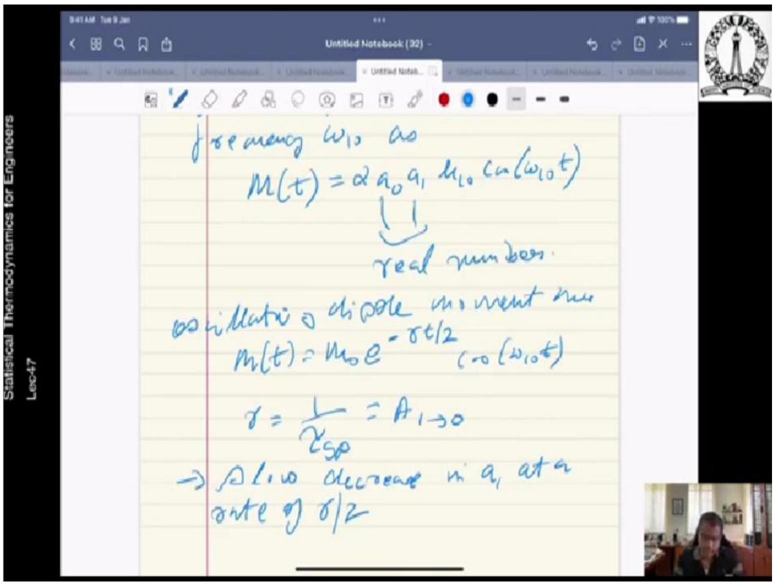


frequency ω_{10} as

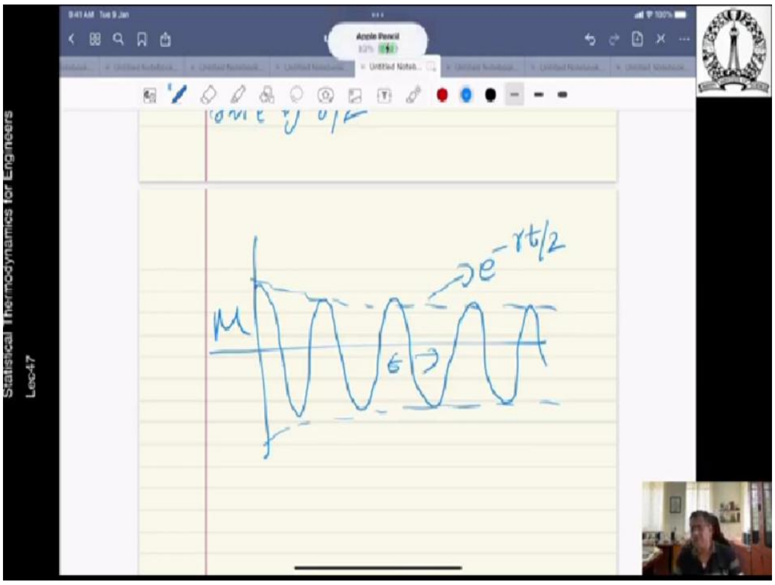
$$M(t) = 2\,\underbrace{a_0 a_1}_{\text{real numbers.}}\,\mu_{10} \cos(\omega_{10} t)$$

oscillating dipole moment now

$$M(t) = M_0 e^{-\gamma t/2} \cos(\omega_{10} t)$$

$$\gamma = \frac{1}{\tau_{sp}} = A_{1\to 0}$$

→ Also decrease in a_1 at a rate of $\gamma/2$



Now, if the population in the excited state decreases slowly in time relative to the reciprocal due spontaneous emission, then the amplitude of the oscillation will also decrease. This corresponds to a slow decrease in a1 at a rate of gamma by 2, where gamma a 1 over the relaxation time for the spontaneous emission, which is nothing but a.

So, in other words, we can write the oscillating dipole moment now is M t equal to M naught minus gamma t by 2 omega 1 0 into t, where this is nothing but 1 over tau sp is equal to A 1 0. This corresponds to a slow decrease in A1 at a rate pi by 2. So, this is what the dipole moment now looks like. So, it just kind of tries to, it is an envelope along which, it kind of goes down.

So, it is like this, this slowly coming down. So, this is basically envelope, which is e minus gamma t by 2. This is M, and this is time. This is how the dipole moment actually comes down. So, in the next class we will see how this dipole, what are the different line shape that are possible, like the Lorenzen and the Gaussian that we already mentioned and how they depend on this dipole moment, transition dipole moment. Thank you.