The Statistical Thermodynamics for Engineers
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Lecture 56
Absorption and Emission of Radiation

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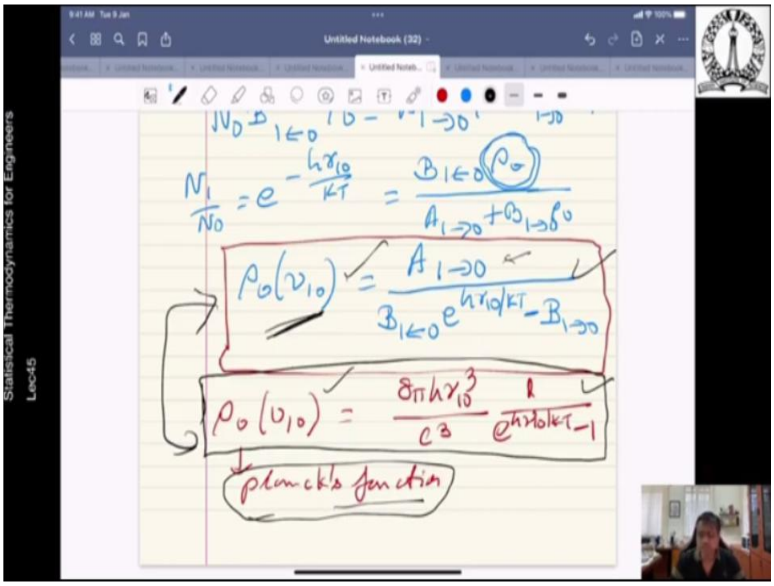

$$\frac{N_1}{N_0} = e^{-\frac{h\nu_{10}}{KT}} = \frac{B_{1\leftarrow 0}\rho_0}{A_{1\to 0} + B_{1\to 0}\rho_0}$$

$$\rho_0(\nu_{10}) = \frac{A_{1\to 0}}{B_{1\leftarrow 0}e^{h\nu_{10}/KT} - B_{1\to 0}}$$

$$\rho_0(\nu_{10}) = \frac{8\pi h\nu_{10}^3}{c^3}\frac{1}{e^{h\nu_{10}/KT}-1}$$

planck's function

So, welcome to lecture number 45, the Statistical Thermodynamics course. Now, as you can see that we wrote that from the two, two level energy system, we wrote that this was the expression when you take into account the spontaneous submission, the stimulated emission and the absorption. And we also have written the Planck's formula. And because this is the radiation density, so it looks like that if both of these two expressions, if they are valid, then it can be valid in only one way.

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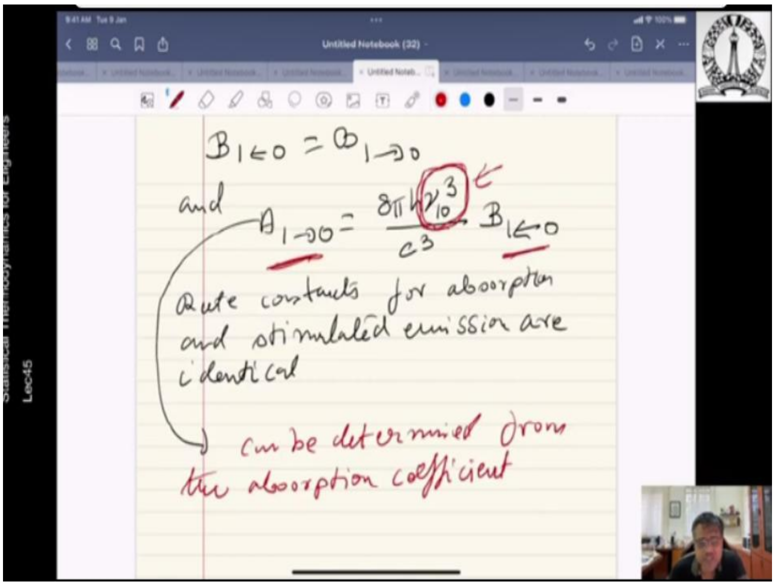
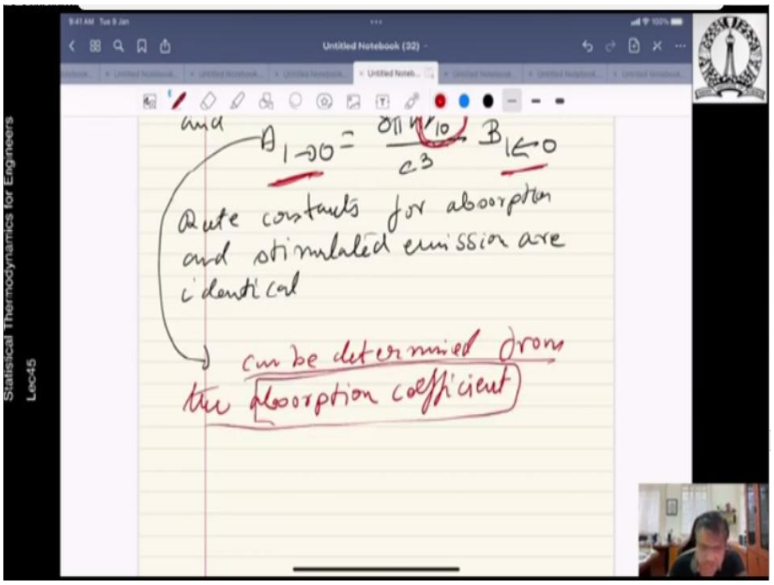


$B_{1\leftarrow 0} = B_{1\to 0}$

and $A_{1\to 0} = \frac{8\pi h \boxed{\nu_{10}^3}}{c^3} B_{1\leftarrow 0}$

Rate constants for absorption and stimulated emission are identical

can be determined from the absorption coefficient



and $A_{1\to 0} = \frac{8\pi h\nu_{10}}{c^3} B_{1\leftarrow 0}$

Rate constants for absorption and stimulated emission are identical

can be determined from the absorption coefficient

That means your B1 0 should be equal to B1 to 0 let me and A1 to 0 8 pi h B1 0. So, this essentially proves that the rate constants for absorption and innovated emission which are basically two very different physical processes are identical. And it also shows one other thing that the spontaneous emission coefficient, which is basically this guy, a spontaneous emission coefficient, can be determined from the absorption coefficient.

So, what you would note this particular factor, this is very important. It is this the relation between your spontaneous emission and your absorption. So, they are linked by this particular factor, which is cube. So, this plays a very role between the two, very role in the competition between the induced and the spontaneous emission processes. So, this is important. And we can see that the, how this can be determined from the absorption coefficient also. So, that is all very good.

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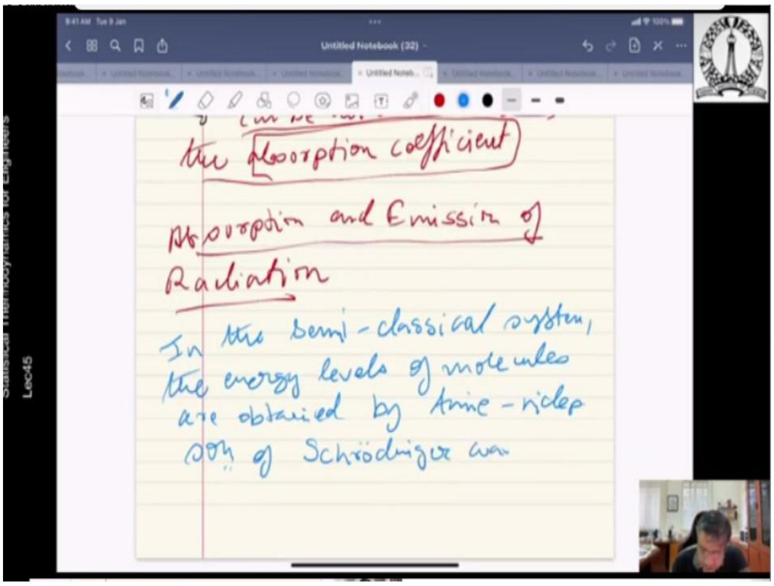

the absorption coefficient

Absorption and Emission of Radiation

In the semi-classical system, the energy levels of molecules are obtained by time-indep soln of Schrödinger wa

Now, let us look at absorption and emission of radiation. What are those? Absorption and emission of radiation. So, the interaction of electromagnetic radiation with matter can be described by a simple semi-classical model that we already know. So, this is obtained by the time independent solution of Schrodinger wave equation. In the semi-classical treatment, the energy levels of the molecules are obtained by the solution. So, let us write it, in the semi-classical system, the energy levels of molecules are obtained, by the time independent solution of Schrodinger wave equation.

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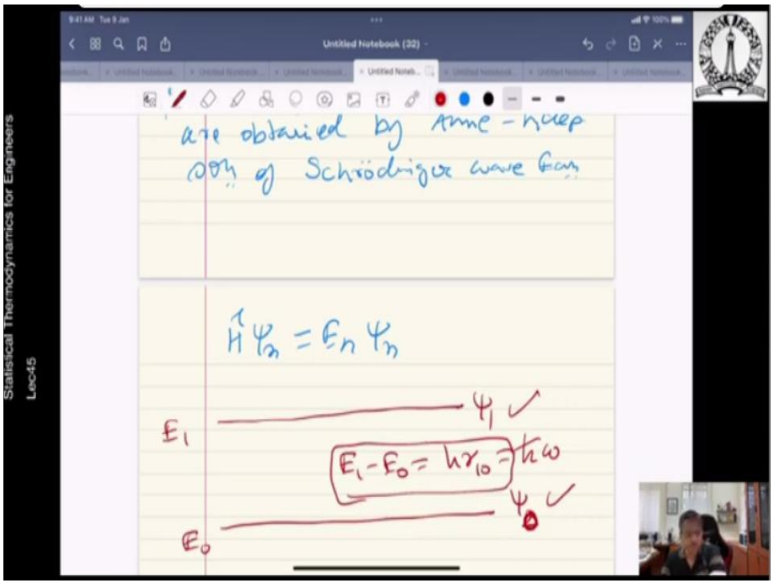

are obtained by time-indep soln of Schrödinger wave Eqn

$$\hat{H}\psi_n = E_n\psi_n$$

$$\boxed{E_1 - E_0 = h\nu_{10}} = \hbar\omega$$

So, that means essentially this. So, where while the electromagnetic radiation is treated in a classical fashion, while the electromagnetic radiation is treated classically. So, if we consider a two-level system, two level system. So, let us look at a simple two-level system once again. So, E1 minus E naught. So, this is a two-level system which is characterized by the two wave functions, upper and the lower wave functions.

The electromagnetic radiation that fulfils the Bohr condition is this, it is precisely tuned to the two energy levels. It is also given as, this is applied to the system to induce a transition from the lower state to the upper state. So, the molecules consist of nuclei and electrons that positions ri, possessive charges qi. So, we all know about this.

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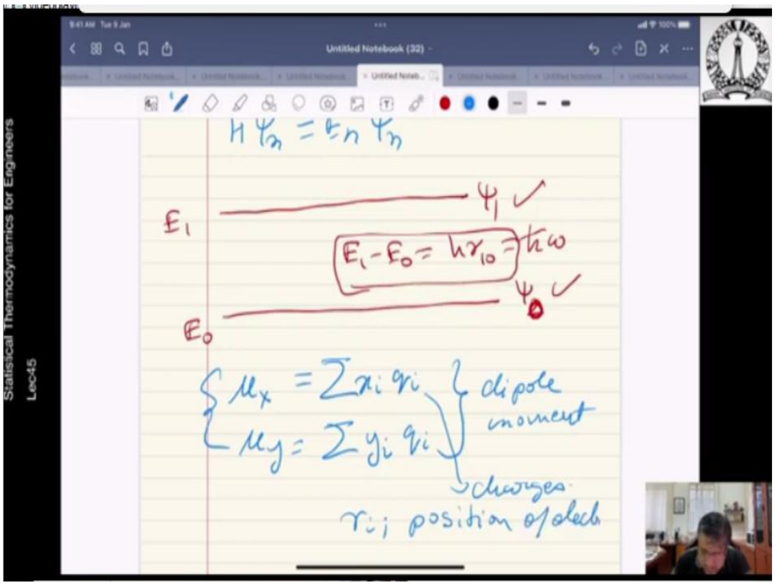


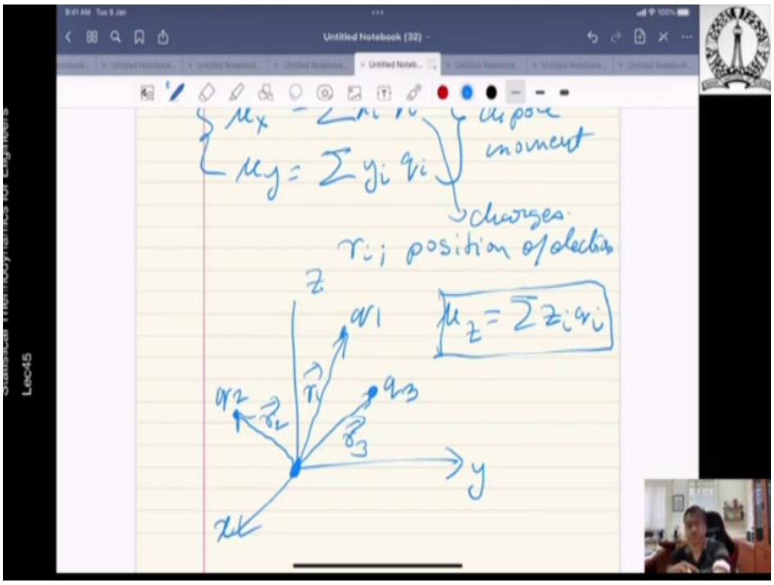
$H\psi_n = E_n\psi_n$

$\boxed{E_1 - E_0 = h\nu_{10}} = \hbar\omega$

$\mu_x = \sum x_i q_i$
$\mu_y = \sum y_i q_i$ } dipole moment

charges

r_i; position of elech



$\mu_y = \sum y_i q_i$ } dipole moment

charges

r_i; position of electron

$\boxed{\mu_z = \sum z_i q_i}$

So, if we have a Cartesian coordinate system, so the system will have, we can express that the system will have a net dipole moment in the, if we write it in a cartesian coordinate system to begin with, mu x summation xi qi. And there is mu y is written as yi qi. So, this is the dipole moment. This is the dipole moment which is, so the system will, can have a net dipole moment because it has got nuclei and electrons at different positions carrying charges qi. So, qi are the charges and ri is basically nothing but the position of the nuclei at the, position of electrons.

So, these electrons are basically are what are distributed in this particular way. So, it is like this, y, z, x like that. So, there maybe q3, q1, there may something like q2 somewhere. These are the kind of position vectors r1, r3, this is definitely your r2. So, they are located at different place and then of course there is a mu z also which is summation of zi qi. So, this is also given. Where, x, y, xi, yi, zi, other coordinates of particle i relative to the center of mass of the molecule and these are the positions of the particles.

So, that interaction of radiation with material system is taken into account. We already know about this by addition of a time dependent perturbation. So, this is we already know, we have done it before. So, that is what we are going to do.

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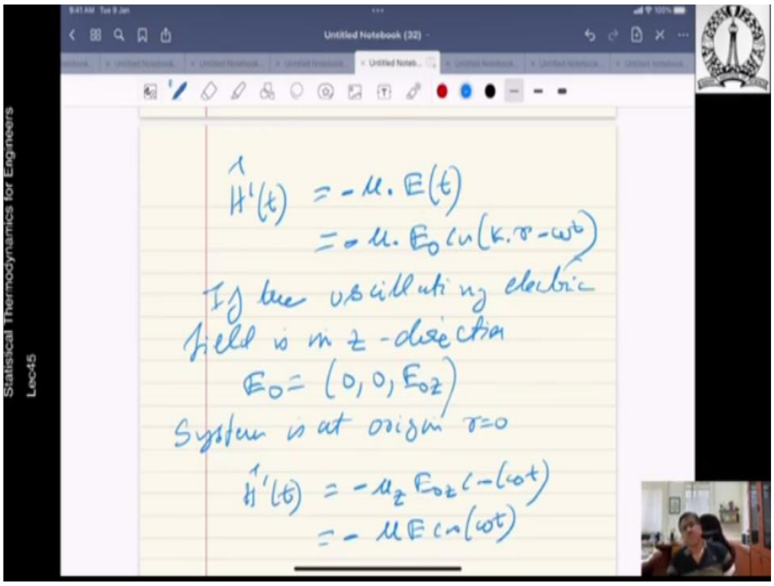

$$\hat{H}'(t) = -\mu \cdot E(t)$$

$$= -\mu \cdot E_0 \cos(k \cdot r - \omega t)$$

If the oscillating electric field is in z-direction

$$E_0 = (0, 0, E_{0z})$$

System is at origin $r = 0$

$$\hat{H}'(t) = -\mu_z E_{0z} \cos(-\omega t)$$

$$= -\mu E \cos(\omega t)$$

So, minus mu dot E t, and E is electromagnetic field basically, so dot k dot r minus omega t, So, if the oscillating electric field is in the z direction, and the system is at the origin, oscillating say if the oscillating electric field is in z direction, which means that your E naught is equal to 0 comma 0 oz, this and the system is at the origin and system is at origin are equal to 0. And the wavelength is basically greater than the dimensions of the system to avoid having different electric field strengths of different parts of the power.

So, the wavelength is greater than the dimensions of the system so to say. So, H hat prime is equal to minus mu z E oz of omega t. In other words, this is like mu E cost omega t. So, the transition probability is therefore obtained by solving the time dependent Schrodinger wave equation.

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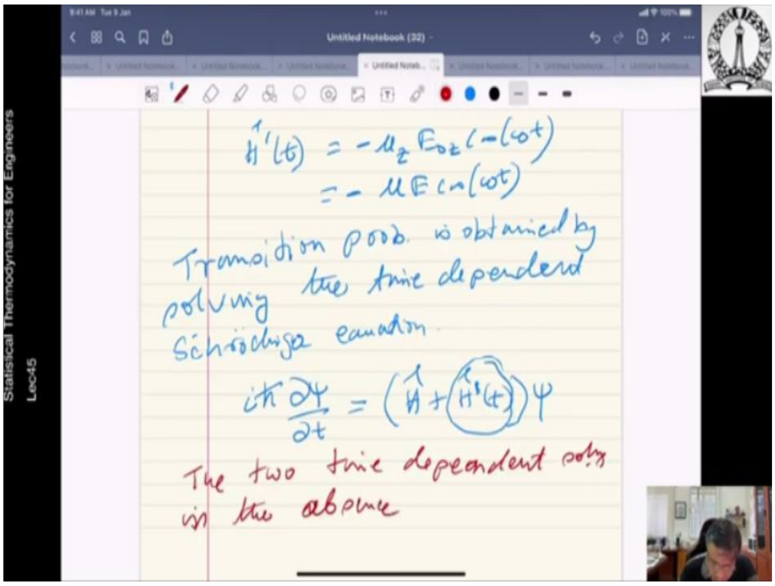
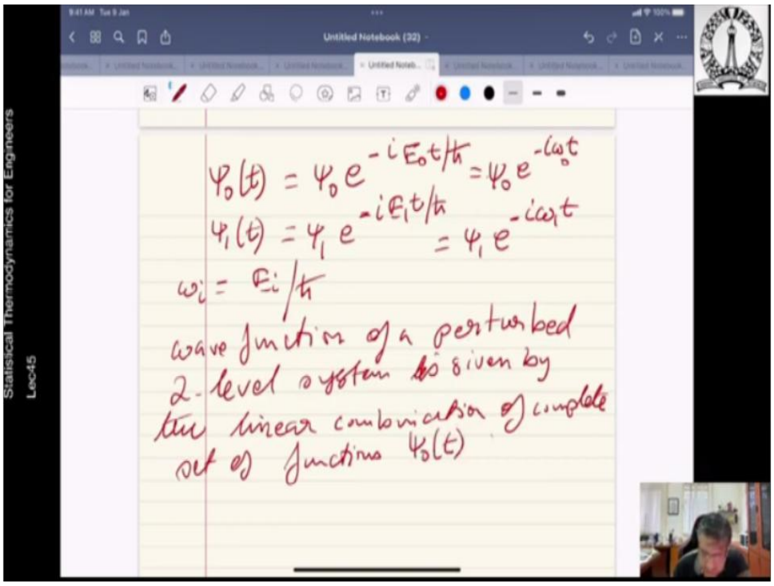


$$\hat{H}'(t) = -\mu_z E_{0z} \cos(\omega t)$$
$$= -\mu E \cos(\omega t)$$

Transition prob. is obtained by solving the time dependent Schrödinger equation.

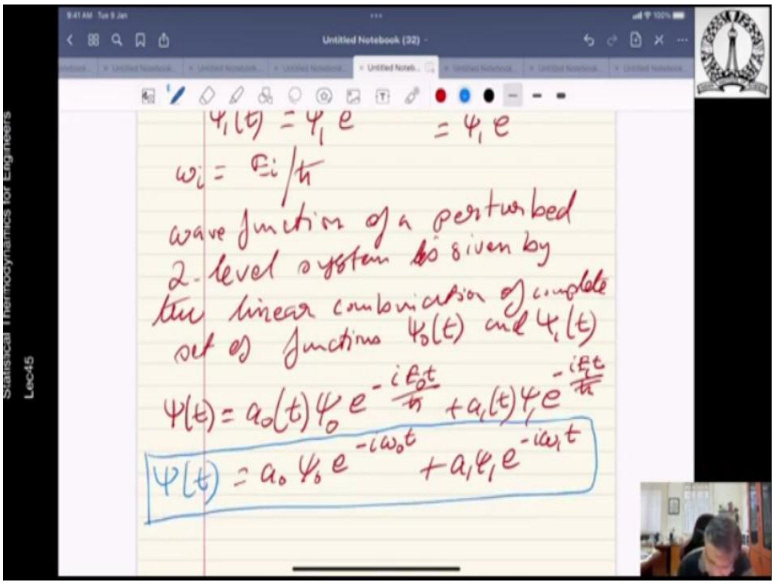
$$i\hbar \frac{\partial \psi}{\partial t} = \left(\hat{H} + \boxed{\hat{H}'(t)}\right)\psi$$

The two time dependent soln in the above



$$\psi_0(t) = \psi_0 e^{-iE_0 t/\hbar} = \psi_0 e^{-i\omega_0 t}$$
$$\psi_1(t) = \psi_1 e^{-iE_1 t/\hbar} = \psi_1 e^{-i\omega_1 t}$$
$$\omega_i = E_i/\hbar$$

wave function of a perturbed 2-level system is given by the linear combination of complete set of functions $\psi_0(t)$



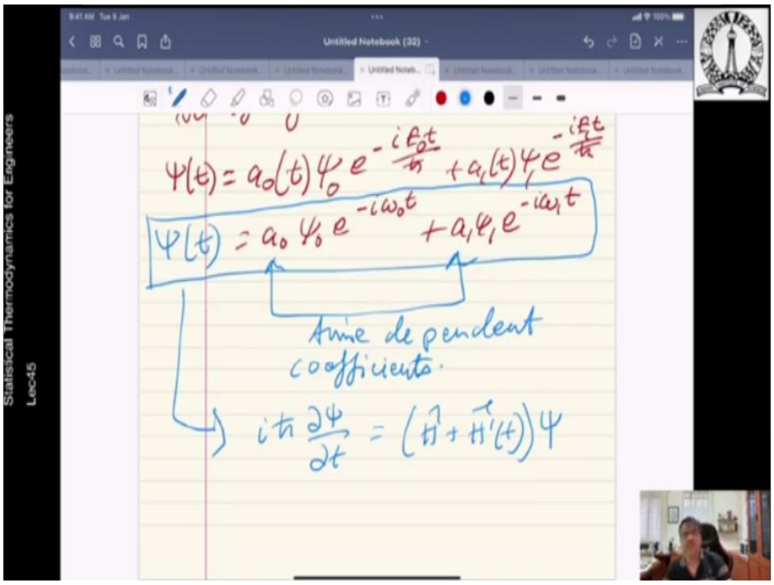
$\psi_1(t) = \psi_1 e \quad = \psi_1 e$

$\omega_i = E_i/\hbar$

wave function of a perturbed 2-level system is given by the linear combination of complete set of functions $\psi_0(t)$ and $\psi_1(t)$

$$\psi(t) = a_0(t)\psi_0 e^{-\frac{iE_0t}{\hbar}} + a_1(t)\psi_1 e^{-\frac{iE_1t}{\hbar}}$$

$$\boxed{\psi(t) = a_0\psi_0 e^{-i\omega_0 t} + a_1\psi_1 e^{-i\omega_1 t}}$$



$$\psi(t) = a_0(t)\psi_0 e^{-\frac{iE_0t}{\hbar}} + a_1(t)\psi_1 e^{-\frac{iE_1t}{\hbar}}$$

$$\boxed{\psi(t) = a_0\psi_0 e^{-i\omega_0 t} + a_1\psi_1 e^{-i\omega_1 t}}$$

time dependent coefficients.

$$i\hbar\frac{\partial\psi}{\partial t} = (\hat{H}+\hat{H}'(t))\psi$$

So, the transition probability, probability is obtained by solving the time dependent, dependent Schrodinger equation which essentially translates to i h prime psi by d equal to H hat plus H hat prime t psi. So, in the absence of, in the absence of this part, the absence of the prime, the two time dependent solutions will be, in the absence of (())(11:10) is given as psi 0 t is equal to psi 0 E minus i E naught t by h bar, which is equal to i naught, e i omega naught t.

And then there is psi 1 t equal to psi 1 E1 t divided by h bar which is equal to psi 1 e minus i omega 1 t, where your omega i is basically Ei h bar. So, this is the time dependent solution of the time dependent wave function. Whereas, the other one was a time independent we can write it with that time independent wave function.

So, the wave function of a perturbed two-level system is given by a linear combination of complete set of functions psi naught t and psi 1 t. Correct. So, psi t is therefore given as a naught. So, this is a linear combination. So, and this is basically the time independent part. So, e minus i e naught t by h bar plus is a1 t given us. Again, this is the time pre-independent part minus i E1 t by h bar. So, in short, it can be written as a naught, just dropping the t now, psi naught e minus i omega naught t plus a1 psi 1 e minus i omega 1 into t.

So, this is the complete wave function. So, these are the time dependent coefficients. a naught a1, these are called the time dependent coefficients. So, substitution of this particular solution into the time dependent Schrodinger wave equation. So, you can substitute this now to i h bar time, this is the complete time dependent solution.

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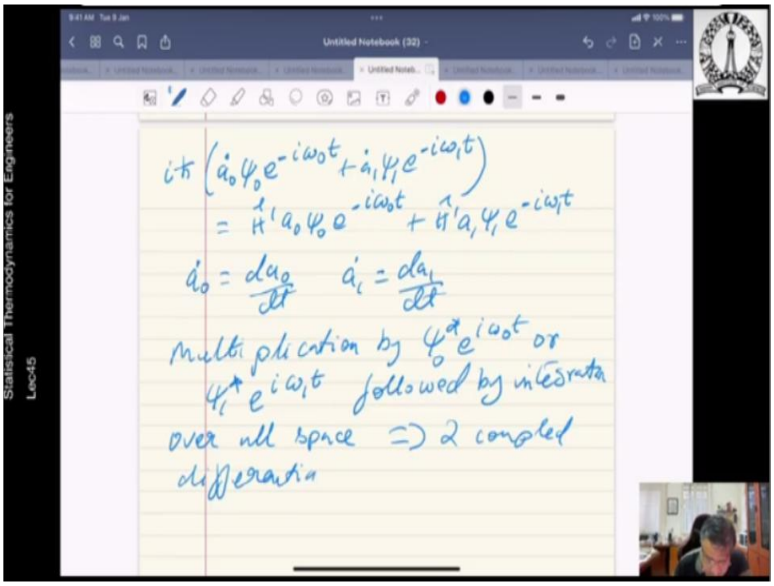
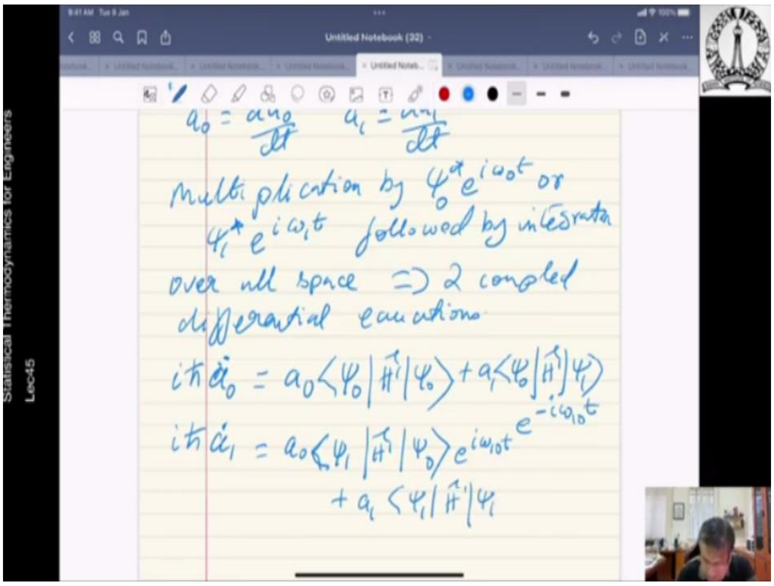


$$i\hbar\left(\dot{a}_0\psi_0 e^{-i\omega_0 t}+\dot{a}_1\psi_1 e^{-i\omega_1 t}\right)$$
$$=\hat{H}'a_0\psi_0 e^{-i\omega_0 t}+\hat{H}'a_1\psi_1 e^{-i\omega_1 t}$$
$$\dot{a}_0=\frac{da_0}{dt}\qquad \dot{a}_1=\frac{da_1}{dt}$$

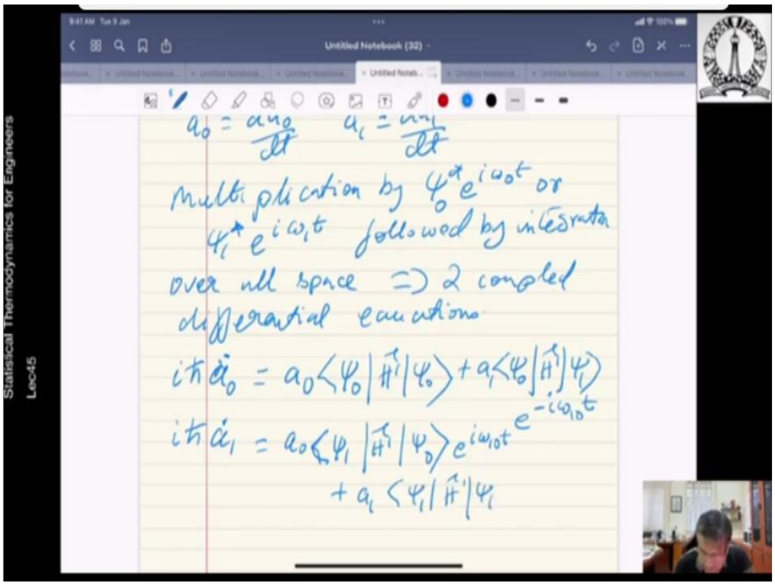
Multiplication by $\psi_0^* e^{i\omega_0 t}$ or $\psi_1^* e^{i\omega_1 t}$ followed by integratn over all space ⇒ 2 coupled differentia



$$\dot{a}_0=\frac{da_0}{dt}\qquad \dot{a}_1=\frac{da_1}{dt}$$

Multiplication by $\psi_0^* e^{i\omega_0 t}$ or $\psi_1^* e^{i\omega_1 t}$ followed by integratn over all space ⇒ 2 coupled differential equations

$$i\hbar\dot{a}_0=a_0\langle\psi_0|\hat{H}'|\psi_0\rangle+a_1\langle\psi_0|\hat{H}'|\psi_1\rangle e^{-i\omega_{10}t}$$
$$i\hbar\dot{a}_1=a_0\langle\psi_1|\hat{H}'|\psi_0\rangle e^{i\omega_{10}t}$$
$$+a_1\langle\psi_1|\hat{H}'|\psi_1$$



$a_0 = \frac{da_0}{dt} \quad a_1 = \frac{da_1}{dt}$

Multiplication by $\psi_0^* e^{i\omega_0 t}$ or $\psi_1^* e^{i\omega_1 t}$ followed by integration over all space $\Rightarrow$ 2 coupled differential equations

$$i\hbar \dot{a}_0 = a_0 \langle \psi_0 | \hat{H}' | \psi_0 \rangle + a_1 \langle \psi_0 | \hat{H}' | \psi_1 \rangle e^{-i\omega_{10} t}$$

$$i\hbar \dot{a}_1 = a_0 \langle \psi_1 | \hat{H}' | \psi_0 \rangle e^{i\omega_{10} t} + a_1 \langle \psi_1 | \hat{H}' | \psi_1$$

If you substitute this solution into that, this leads to the equation i h bar a naught, this is once again the time independent portion. Remember that is why I am the writing it in a1 bar. Dot means it is a differential with respect to time equal to H bar a naught i e minus i omega naught t. plus H bar a1 psi 1 e minus i omega 1.

So, a naught dot is equal to d a naught by dt, a1 dot is equal to d a1 by dt. So, that is the whole set that we have written. And so now what we are going to do, multiplication by, or by integration over all space. Let us do multiplication by, once again this is I will write it in italics, the conjugate or this is also the conjugate we followed by integration over all space, then gives basically two coupled needles, two coupled differential equations.

So, what are those differential equations, i h sorry, a naught dot equal to a naught plus a1 psi naught psi 1 then e t psi omega 1 0 into t. So, we will see what those bracketed terms actually means. Let me write down this first and then of course h bar a1 dot is equal to a naught psi 1 H i bar psi naught e i omega 1 0 into t plus a1 psi 1 H hat i. So, these are the two coupled differential solutions.

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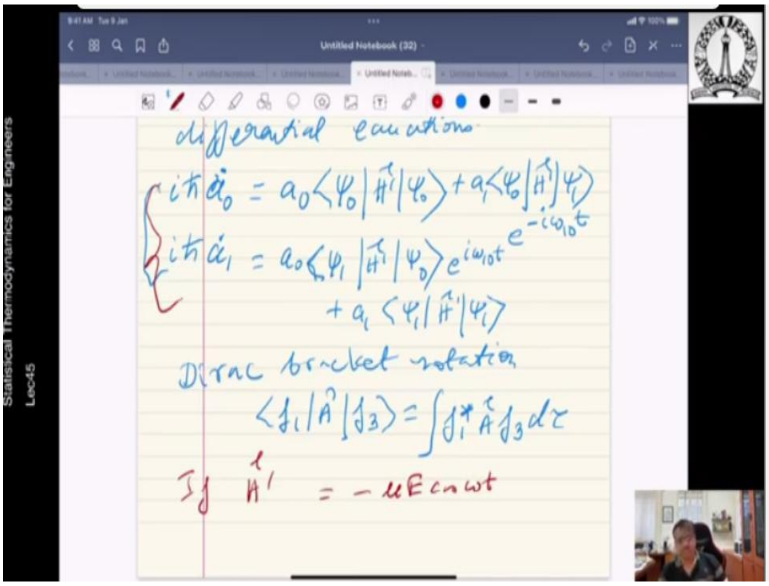

differential equations

$$i\hbar \dot{a}_0 = a_0 \langle \psi_0 | \hat{H}' | \psi_0 \rangle + a_1 \langle \psi_0 | \hat{H}' | \psi_1 \rangle e^{-i\omega_{10} t}$$

$$i\hbar \dot{a}_1 = a_0 \langle \psi_1 | \hat{H}' | \psi_0 \rangle e^{i\omega_{10} t} + a_1 \langle \psi_1 | \hat{H}' | \psi_1 \rangle$$

Dirac bracket notation

$$\langle f_1 | \hat{A} | f_3 \rangle = \int f_1^* \hat{A} f_3 \, d\tau$$

If $\hat{H}' = -\mu E \cos \omega t$

Now, obviously we are going to ask what those, those bracketed terms actually mean. So, this is the Dirac notation, Dirac bracket notation; notation which tells you that this is f1 A hat, this is operator and f3, this is what we are trying to say. This is basically integral f1. This is the conjugate A f3 d tau, where tau is basically in the box the entire space.

So, no approximation has been made other than that there are two states, psi 1 and psi naught. So, the equations, these two equations that we see over here, they completely have come out. They have completely come out equivalent to the original Schrodinger equation, except now that we have taken a time perturbed solution and a time non-perturbed solution.

Now if, if H hat prime is taken as minus mu E cos omega t, the electric dipole approximation, then the time dependent perturbations H prime has all parity that it is the odd function of the spatial coordinates. In other words, H hat prime is a odd function. Since mu is equal to minus ez. So, the products psi 1, the mode of psi 1 square or psi naught square are even functions. So, the integrates are basically odd functions are also odd functions. So, as we know that all atomic and molecular states that have definite parities, even on odd with respect to the inversion of the space fixed coordinate system.

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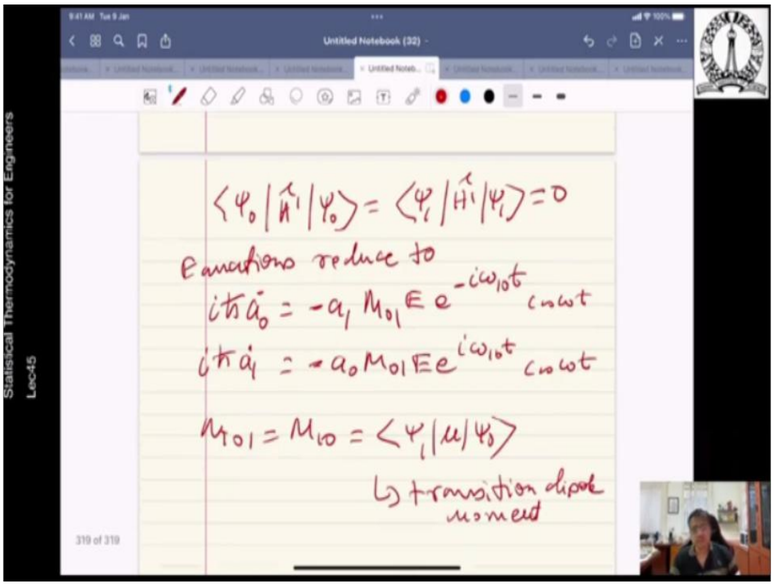

$$\langle \psi_0 | \hat{H}' | \psi_0 \rangle = \langle \psi_1 | \hat{H}' | \psi_1 \rangle = 0$$

Equations reduce to

$$i\hbar \dot{a}_0 = -a_1 M_{01} E e^{-i\omega_{10}t} \cos \omega t$$

$$i\hbar \dot{a}_1 = -a_0 M_{01} E e^{i\omega_{10}t} \cos \omega t$$

$$M_{01} = M_{10} = \langle \psi_1 | \mu | \psi_0 \rangle$$

↳ transition dipole moment

One can write, one can write, is equal to 0. So, therefore, using this the equations can be reduced to, the equations reduce to i h bar a naught dot minus a1 M 01 E i omega 1 0 t cos omega t. And then of course, i h prime a1 dot minus a naught M 01 E e exponential i omega 1 naught t cos omega t, where the integral M 01 as we know already is the same as the other one. It is like psi 1, mu psi naught. It is called the transition dipole moment. This we already have learned transition dipole. And it is the most critical factor in we already know in determining the selection rules and everything, it is a vector quantity. And, it is M 10 is a vector quantity.

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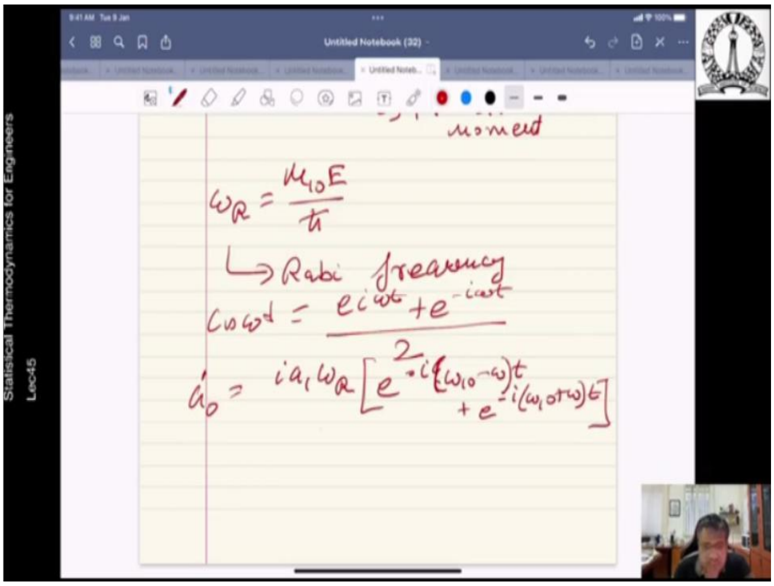


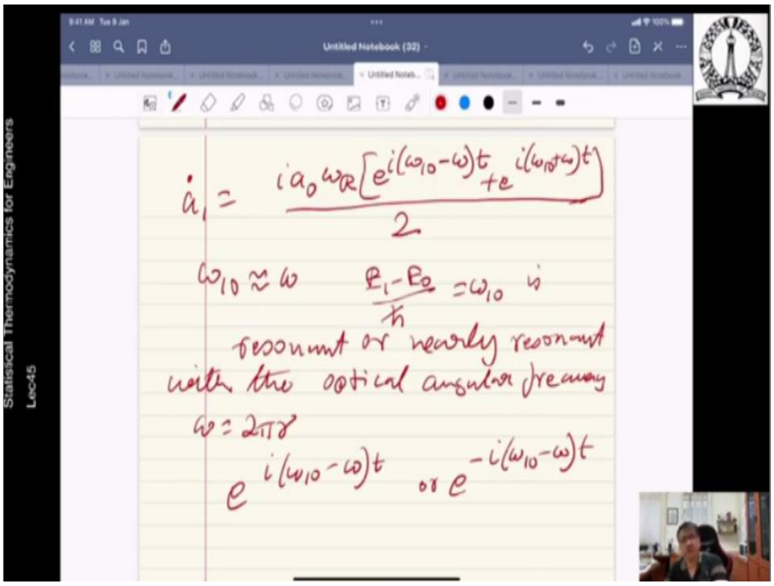
moment

$$\omega_R = \frac{M_{10} E}{\hbar}$$

↳ Rabi frequency

$$\cos \omega t = \frac{e^{i\omega t} + e^{-i\omega t}}{2}$$

$$\dot{a}_0 = i a_1 \omega_R \left[e^{-i(\omega_{10}-\omega)t} + e^{-i(\omega_{10}+\omega)t} \right]$$



$$\dot{a}_1 = \frac{i a_0 \omega_R \left[e^{i(\omega_{10}-\omega)t} + e^{i(\omega_{10}+\omega)t} \right]}{2}$$

$\omega_{10} \approx \omega$ $\quad \frac{E_1 - E_0}{\hbar} = \omega_{10}$ is resonant or nearly resonant with the optical angular frequency $\omega = 2\pi\nu$

$e^{i(\omega_{10}-\omega)t}$ or $e^{-i(\omega_{10}-\omega)t}$

So, it is convenient to define omega R as M 10 into E by h bar. This is also known as the Rabi frequency, after II Rabi. We also know that most omega t is equal to e i omega t plus e i minus exponential form. So, therefore, the two equations for the rate constants of the a naught dot and a1 dot is then written as a naught dot is i a1 omega R e minus i omega 1 0 minus omega into t plus e exponential it is omega 1 0 plus of mega t and this is divided by 2. Similarly, a1 dot written as i a naught omega R e i omega 1 0 minus omega t plus e i omega 1 0 plus omega into t.

So, we close the bracket and then you divide it by 2. So, the physical meaning for the Rabi frequency will be, would be clear. So, these are the two, a1 and a2 or d a1 by dt and d a naught by dt. So, at this stage, only approximation that we can make is omega 1 0 is almost the same as omega since, the system with both frequency omega 1 0 is nearly or is resonant or nearly resonant with the optical angular frequency of 2 pi.

So, we basically what we are trying to say is E1 minus E naught by h bar, which is equal to omega 1 naught is resonant or nearly resonant with the optical angular frequency omega equal to 2 pi r. So, the terms therefore, the terms which is represented as e i omega 1 0 minus omega into t or E minus i omega 1 0 minus omega into t, they represent slowly varying functions of time compared to the rapidly oscillating non-resonant ones.

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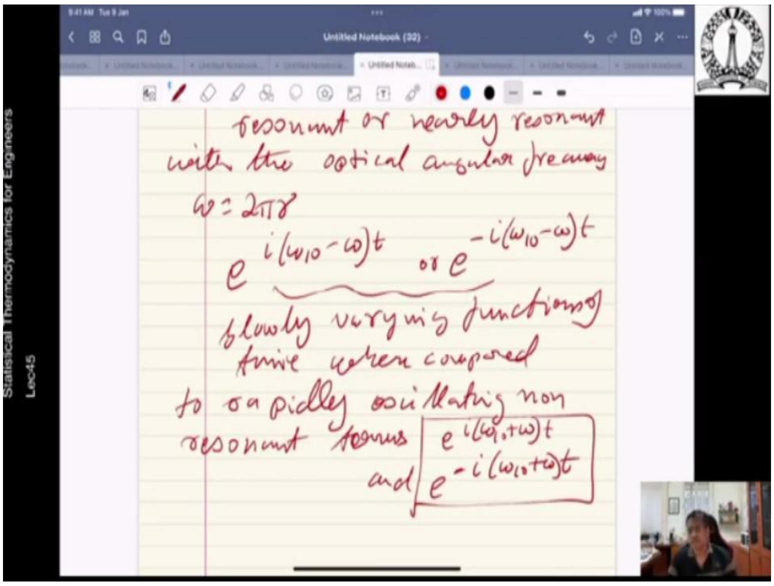

resonant or nearly resonant with the optical angular frequency $\omega = 2\pi\nu$

$$\underbrace{e^{i(\omega_{10}-\omega)t} \text{ or } e^{-i(\omega_{10}-\omega)t}}$$

slowly varying functions of time when compared to rapidly oscillating non resonant terms

$$\boxed{\begin{matrix} e^{i(\omega_{10}+\omega)t} \\ \text{and} \quad e^{-i(\omega_{10}+\omega)t} \end{matrix}}$$

So, this represents the slow, slowly varying functions of time when compared to rapidly oscillating non-resonant terms e i omega 1 0 plus omega t and e minus i omega 1 0 plus omega into t. So, we will see in the next lecture that how this approximation and where does it lead to. So, we will cover this as the next class. Thank you.