# Statistical Thermodynamics for Engineers
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## Indian Institute of Science, Bengaluru
## Lecture 40
## Perturbation Analysis of the Schrodinger Wave Equation

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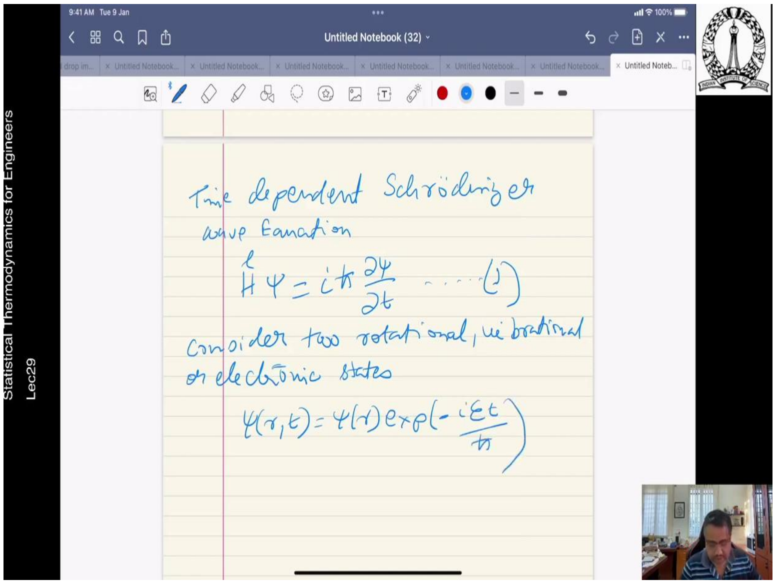
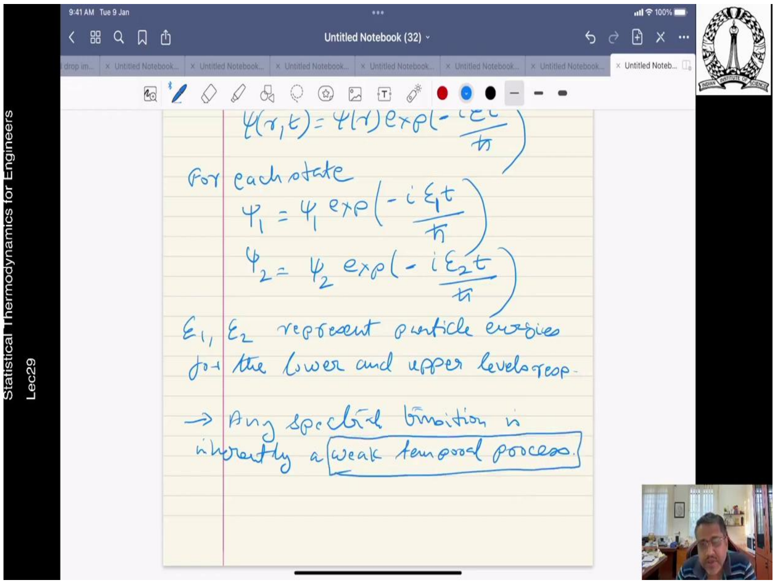


Time dependent Schrödinger wave Equation

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \ldots\ldots (1)$$

Consider two rotational, vibrational or electronic states

$$\psi(r,t) = \psi(r)\exp\left(-\frac{i\varepsilon t}{\hbar}\right)$$



$$\psi(r,t) = \psi(r)\exp\left(-\frac{i\varepsilon t}{\hbar}\right)$$

For each state

$$\psi_1 = \psi_1 \exp\left(-\frac{i\varepsilon_1 t}{\hbar}\right)$$

$$\psi_2 = \psi_2 \exp\left(-\frac{i\varepsilon_2 t}{\hbar}\right)$$

$\varepsilon_1, \varepsilon_2$ represent particle energies for the lower and upper levels resp.

→ Any spectral transition is inherently a $\boxed{\text{weak temporal process.}}$

So, welcome to lecture number 29 of the Statistical Thermodynamics for Engineers. So, we are going to now do the perturbation analysis of Schrodinger's wave equation. So, let us begin with the time dependent, time dependent Schrodinger, Schrodinger wave equation, equation, which is basically H, the Hamiltonian psi by d t. Now, we consider two rotational, vibrational or electronic states.

So, we find that the solution in this particular equation, say, if this is 1, the solution to this particular equation is given by, we already did this earlier if you recall. So, equation 5.38 in the book, r, t is equal to psi r exponential i divided by... So, that was the, now for each one of the state, for each state. So, let us take the state psi 1. So, this is the total psi and this is the r dependent psi.

So, minus i epsilon 1, 1 by h bar, psi 2, this is once again the r-dependent psi, the exponential minus i epsilon 2 t by h bar, where e 1 and e 2 present, represent particle energies or the lower and upper levels, upper levels, respectively. Now, here comes a key piece of assumption. So, assuming that any spectral transition is, so we assume what? Any spectral transition, is inherently a weak temporal process. Any spectral transition is inherently a weak temporal process. So, understand the word weak temporal process.

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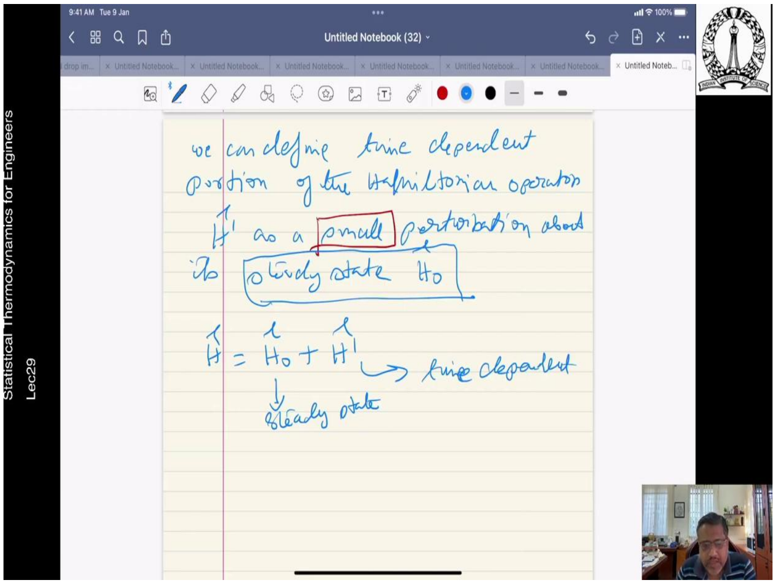
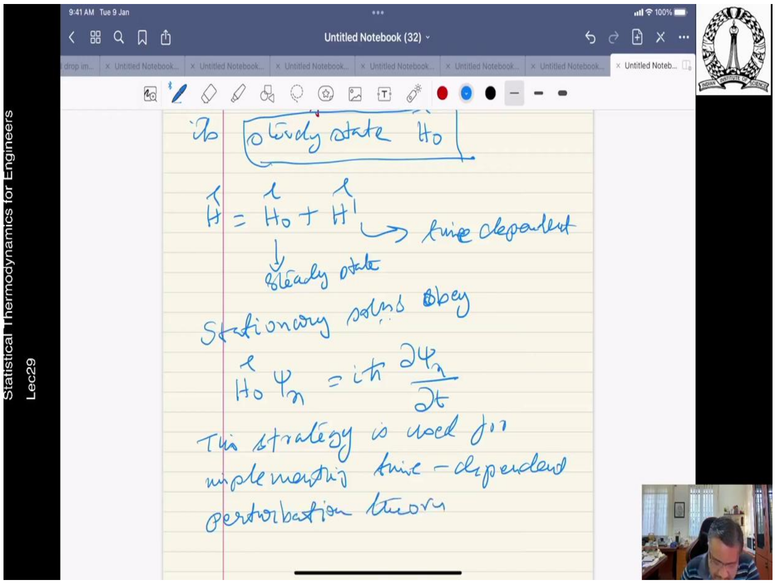


we can define time dependent portion of the Hamiltonian operator $\hat{H}'$ as a $\boxed{\text{small}}$ perturbation about its $\boxed{\text{steady state } \hat{H}_0}$

$$\hat{H} = \underset{\downarrow \text{ steady state}}{\hat{H}_0} + \hat{H}' \hookrightarrow \text{time dependent}$$



To $\boxed{\text{steady state } H_0}$

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{steady state}} + \hat{H}' \rightarrow \text{time dependent}$$

Stationary solns obey

$$\hat{H}_0 \Psi_n = i\hbar \frac{\partial \Psi_n}{\partial t}$$

This strategy is used for implementing time-dependent perturbation theory

So, therefore what we do based on this assumption is that we can define, a time dependent portion, not the Hamiltonian operator H hat prime as a small perturbation, the key word here is small, small perturbation about its steady state manifestation, which can be written as H naught hat. So, it is essentially like your fluid mechanics the linear stability type analysis that we there is a perturbation component which is time dependent and it is acting on the steady state manifestation which is H naught.

So, that means H bar is equal to H naught plus H prime. So, that is the total solution. So, this is the steady state, and this is the corresponding time dependent. So, the stationary solutions, so the stationary solutions obey solutions obey H naught n is equal to I h bar. So, this is the same strategy, this is the strategy that is used when implementing our time dependent, this strategy is the essential tactic. This strategy is used for, I think, for implementing the time dependent, time dependent perturbation theory.

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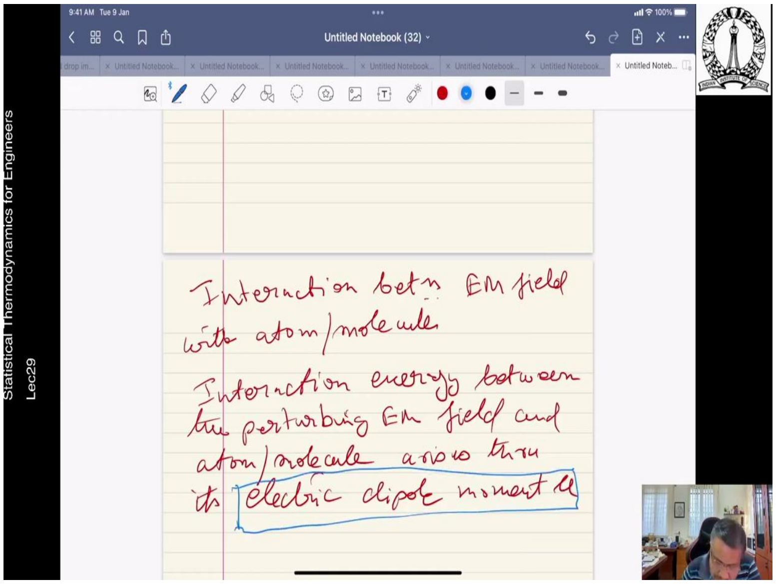

Interaction betn EM field with atom/molecule

Interaction energy between the perturbing EM field and atom/molecule arises thru its $\boxed{\text{electric dipole moment } \mu}$

So, so for our application the interaction energy, so what happens for our application, that interaction happens between the upper, there is an electromagnetic field and the atom of the molecule. So, there is, so if we write it, there is interaction between, between the perturbing, there is a, there is a EM field, EM field with atom slash molecule. Now, that is interaction energy between this, the interaction energy between the perturbing EM field, electromagnetic field and atom or slash molecule arises through, arises through its electric dipole moment, electric dipole moment mu.

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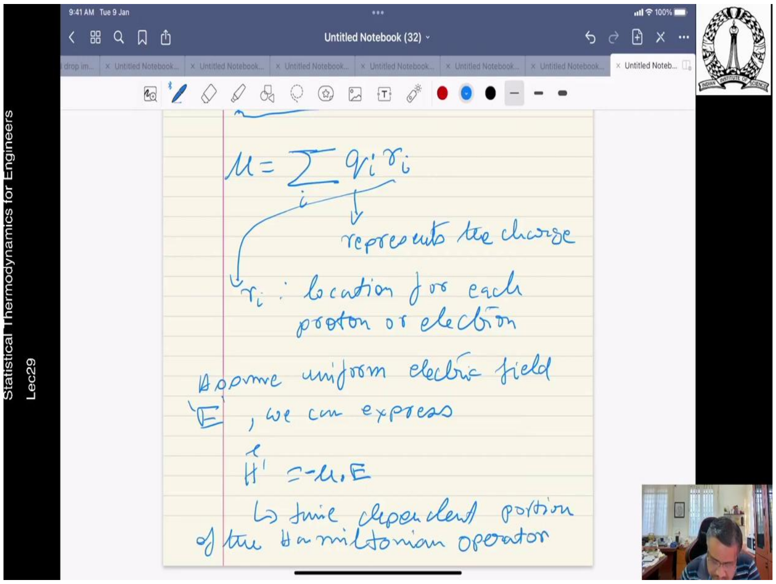

$$\mu = \sum_i q_i r_i$$

$q_i$ → represents the charge

$r_i$ : location for each proton or electron

Assume uniform electric field 'E', we can express

$$H' = -\mu . E$$

↳ time dependent portion of the Hamiltonian operator

So, in other words, mu will be equal to summation i, q i. So, q i, what does q i actually means, q i represents the charge, and what is r i? r i represents the location, the location for each proton or electron. So, r i is the location. So, it is basically the charge and the location. So, that is what is being summed over all charges and all locations. So, if you assume a uniform, assume uniform electric field, electric field E, we can express, express the Hamiltonian, Perturbed Hamiltonian or the time independent portion of the Hamiltonian operators H prime equal to minus mu dot E. So, this is once again the time dependent portion, dependent portion of the operator, portion of the Hamiltonian operator.

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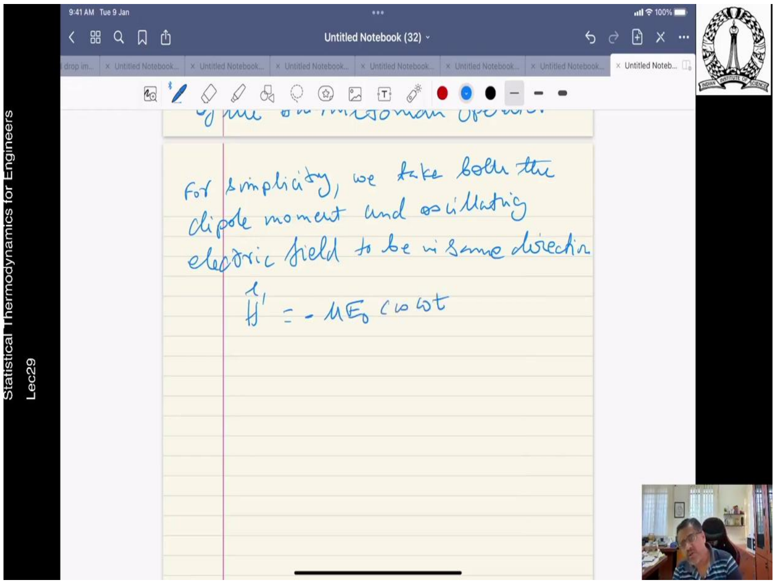
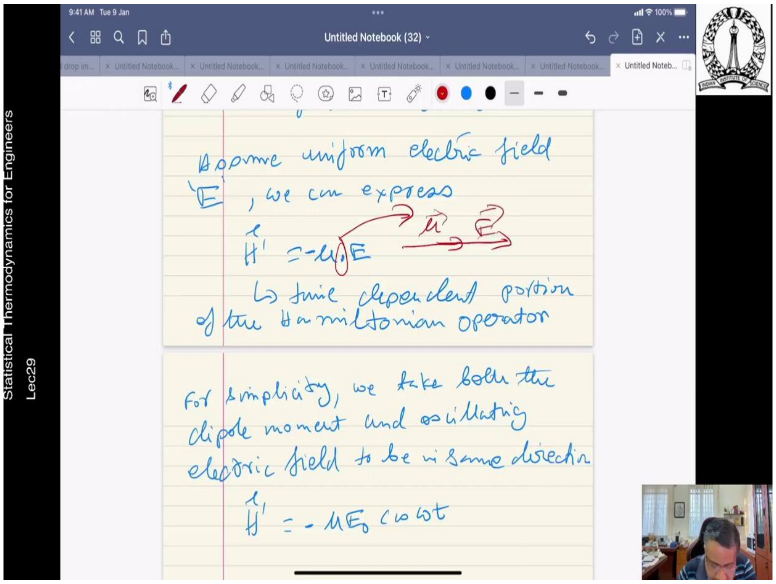


For simplicity, we take both the dipole moment and oscillating electric field to be in same direction

$\hat{H}' = -\mu E_0 \cos\omega t$



Assume uniform electric field 'E', we can express

$\hat{H}' = -\mu \cdot E \quad \vec{\mu} \rightarrow \vec{E}$

↳ time dependent portion of the Hamiltonian operator

For simplicity, we take both the dipole moment and oscillating electric field to be in same direction

$\hat{H}' = -\mu E_0 \cos\omega t$

So, if we take that both the dipole moment for simplicity comma take both the dipole moment and oscillating electric field and oscillating electric field to be in the same direction. So, in other words bar mu naught cross omega t. So, that means the dot product now because of cos, it is a dot product. So, this was the dot product. So, that both the vectors are basically in the same direction.

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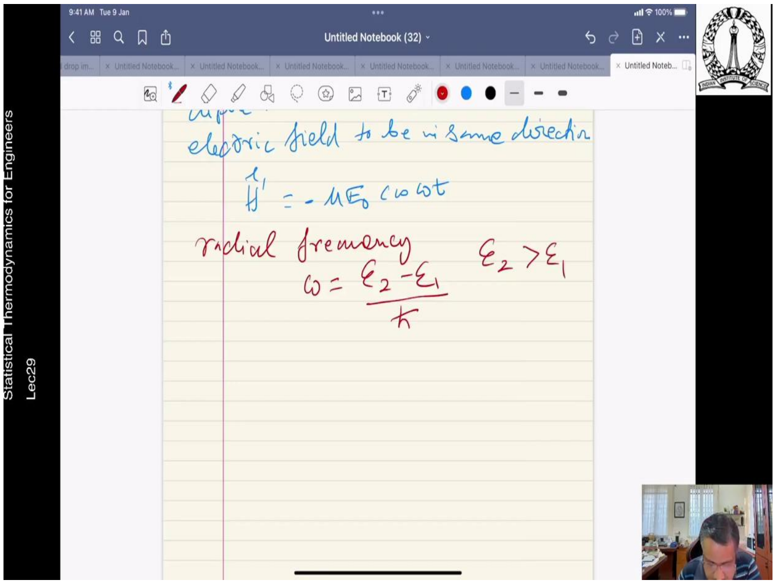
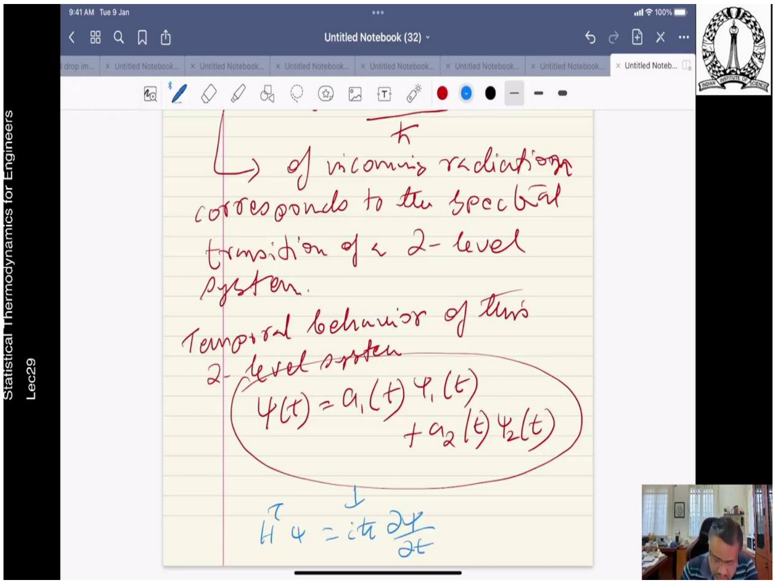


electric field to be in same direction

$\overset{t}{H}' = -\mu E_0 \cos \omega t$

radial frequency

$\omega = \frac{\varepsilon_2 - \varepsilon_1}{\hbar}$ $\varepsilon_2 > \varepsilon_1$



$\hookrightarrow$ of incoming radiation corresponds to the spectral transition of a 2-level system.

Temporal behavior of this 2-level system

$$\boxed{\psi(t) = a_1(t)\psi_1(t) + a_2(t)\psi_2(t)}$$

$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$

This is the cos omega t where the radial frequency, so the radial frequency, frequency is written as omega equal to e 2 minus e 1 divided by h bar. Remember that e 2 is higher energy level, greater than e 1. So, the radial frequency of the incoming radiation corresponds to the spectral transition for a 2-level system. So, the radial frequency of the incoming radiation, incoming radiation in this case the imposed electromagnetic field or the imposed electric field, the rate incoming radiation corresponds, corresponds to the spectral transition, the spectral transition of a 2-level system..

So, that is what it is, as required, if you have to investigate what is the transition probability. So, remember a transition probability is what we are after. So, if we now want to investigate this 2-level system as a dynamic perturbation about its stationary solution, so what we are supposed to investigate? The temporal behavior, behavior of this 2-level system. We have psi is equal to a 1 t psi 1 t plus a 2 t psi 2 t. So, now what happens, now that we have done this, now you substitute, you substitute, we substitute this into the equation that we wrote just a few minutes ago.

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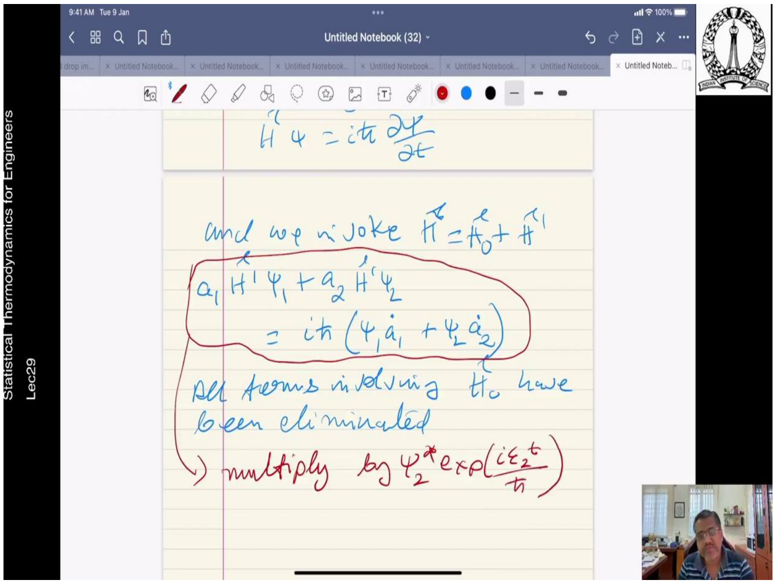


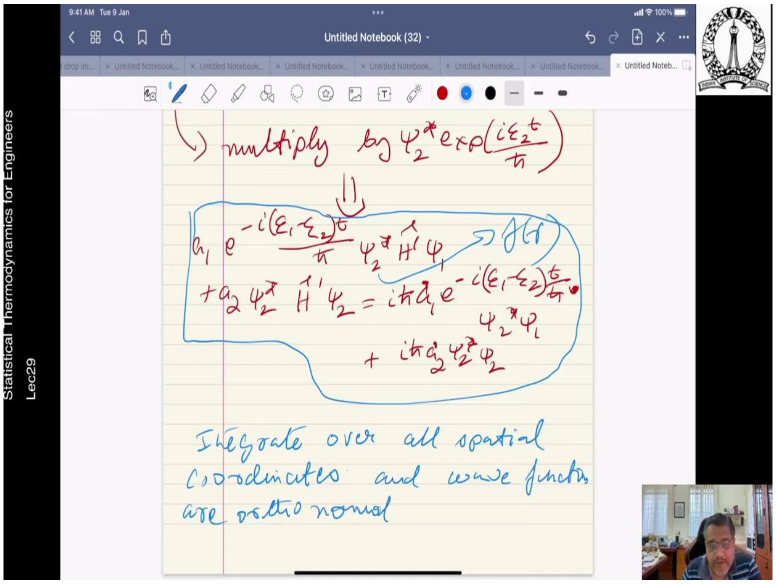
$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$$

and we invoke $\hat{H} = \hat{H}_0 + \hat{H}'$

$$a_1\hat{H}'\psi_1 + a_2\hat{H}'\psi_2 = i\hbar(\psi_1\dot{a}_1 + \psi_2\dot{a}_2)$$

All terms involving $\hat{H}_0$ have been eliminated

multiply by $\psi_2^* \exp\left(\frac{i\varepsilon_2 t}{\hbar}\right)$



↳ multiply by $\psi_2^* \exp\left(\frac{i\varepsilon_2 t}{\hbar}\right)$

$$\Downarrow$$

$$a_1 e^{-i(\varepsilon_1-\varepsilon_2)\frac{t}{\hbar}} \psi_2^* \hat{H}' \psi_1 + a_2 \psi_2^* \hat{H}' \psi_2 = i\hbar \dot{a}_1 e^{-i(\varepsilon_1-\varepsilon_2)\frac{t}{\hbar}} \psi_2^* \psi_1 + i\hbar \dot{a}_2 \psi_2^* \psi_2$$

$\to f(r)$

Integrate over all spatial coordinates and wave functions are orthonormal

We substitute this into your, into your total solution like this. Something like that and we invoke equation, and we invoke. a 1 H bar equal to a 2. So, all the terms involving, all terms involving, have been eliminated. So, now what happens is that we multiply, we multiply this equation, we multiply this equation, multiply by psi 2 star exponential i e 2 t h bar. So, now we, and then we substitute from equations from the biparts solutions that we have already, already got, psi 1 and psi 2.

So, therefore this gives a 1 e minus i e 1 e 2 t h bar psi 2 H bar psi 1 plus a 2 psi 2 star, so these are once again the r portion, that is really cursive function, psi 2 equal to h bar a 1 dot e minus i e 2 t by h bar psi 2 star psi 1 plus i h bar into a 2 bar psi 2 star psi 2. So, this is the two, this is what you get. Now, you integrate about all spatial coordinates. Now integrate, remember these three psis, integrate over all spatial coordinates, spatial coordinates and wave functions are orthonormal, remembering that the wave functions are orthonormal.

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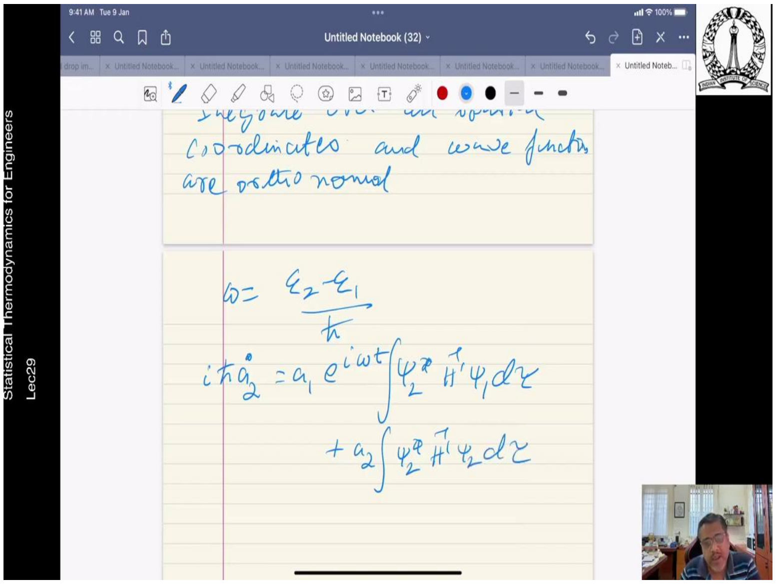
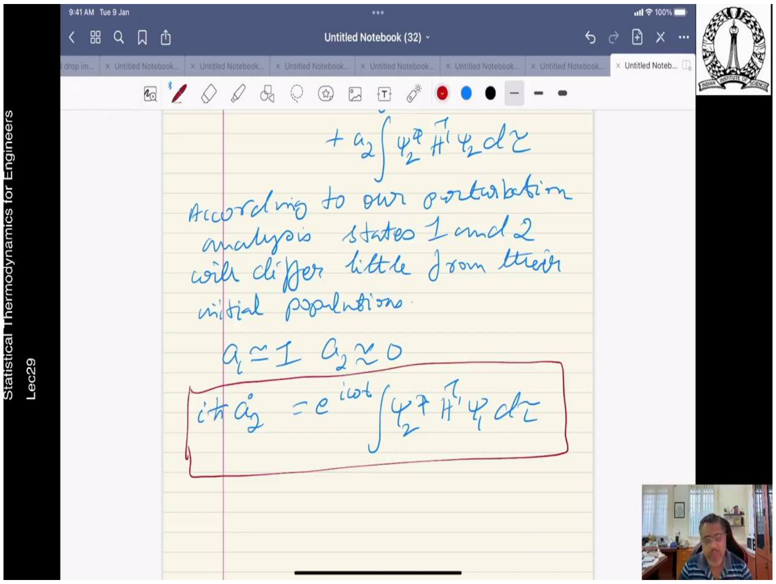


integrate over all spatial coordinates and wave functions are orthonormal

$$\omega = \frac{\varepsilon_2 - \varepsilon_1}{\hbar}$$

$$i\hbar \dot{a}_2 = a_1 e^{i\omega t}\int \psi_2^* \hat{H}' \psi_1 \, d\tau + a_2 \int \psi_2^* \hat{H}' \psi_2 \, d\tau$$



$$+ a_2 \int \psi_2^* \hat{H}' \psi_2 \, d\tau$$

According to our perturbation analysis states 1 and 2 will differ little from their initial populations.

$$a_1 \simeq 1 \quad a_2 \simeq 0$$

$$\boxed{i\hbar \dot{a}_2 = e^{i\omega t}\int \psi_2^* \hat{H}' \psi_1 \, d\tau}$$

So, and we also know that omega equal to psi 2 by psi 1 divided by h hat, or h bar. So, what you get is i h bar into a 2 bar is equal to a 1 e i omega t integral psi 2-star bar hat psi 1 tau plus a 2 psi 2 star. So, this is what you get. And according to our perturbation, so this is the total analysis that you get. So, according to our perturbation analysis, states 1 and 2 will differ little from their initial populations. So, according to our perturbation analysis, perturbation analysis, analysis, states 1 and 2 will differ little, from their initial populations, their initial populations. So, we have a 1 is almost equal to 1, a 2 almost equal to zero. So, i h bar a 2 dot equal to e i omega t psi 2 star, perturbed Hamiltonian psi 1 d tau. This is what you get.

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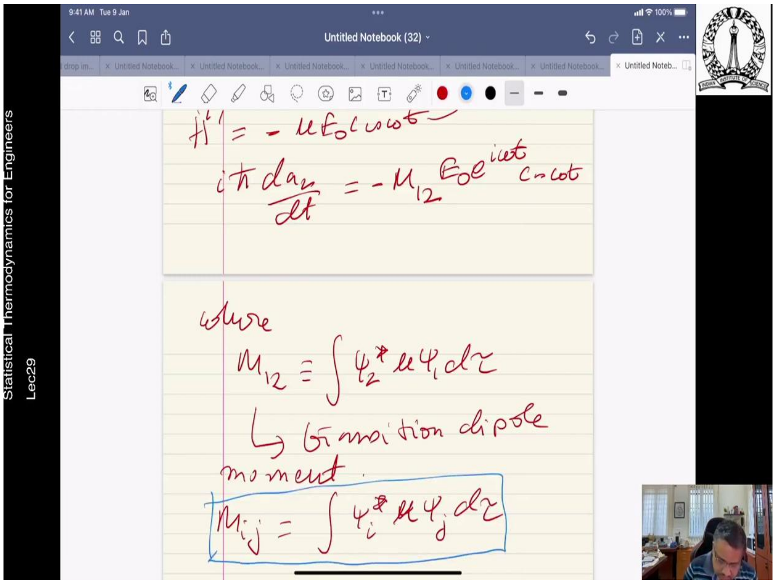

$\hat{H}' = -\mu E_0 \cos\omega t$

$i\hbar \frac{da_2}{dt} = -M_{12} E_0 e^{i\omega t} \cos\omega t$

where

$M_{12} = \int \psi_2^* \mu \psi_1 d\tau$

↳ transition dipole moment.

$\boxed{M_{ij} = \int \psi_i^* \mu \psi_j d\tau}$

So, now, if you now substitute the expression for H hat prime which is equal to minus mu E naught cos omega t, we substitute it here, substitute here, then what you get is i h bar da 2 by dt is equal to, I will write what the expression is, M 1 2 E naught e i omega t cos omega t. And what is M 1 2? Where M 1 2 is equal to psi 2-star mu psi 1 d tau. So, this is called, this is called the transition dipole moment, which in, in more general case, so we can write it in a more generic one, it is m i j, it is basically psi I mu psi j.

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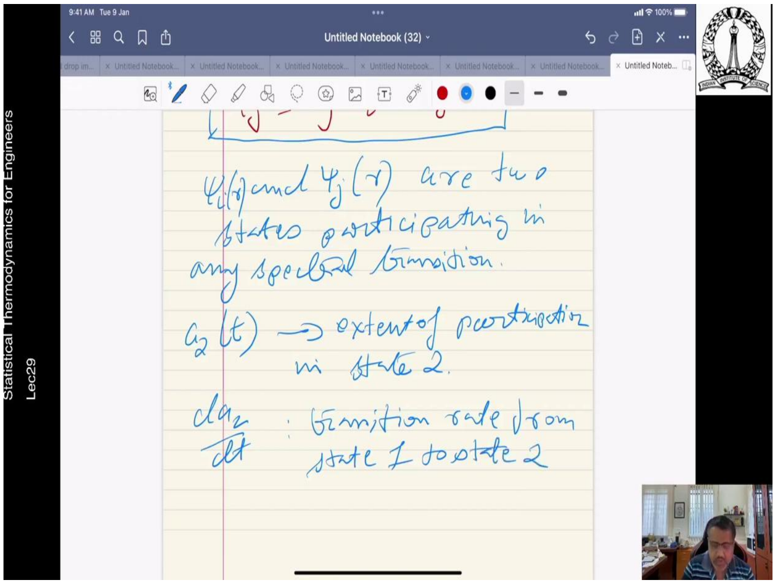
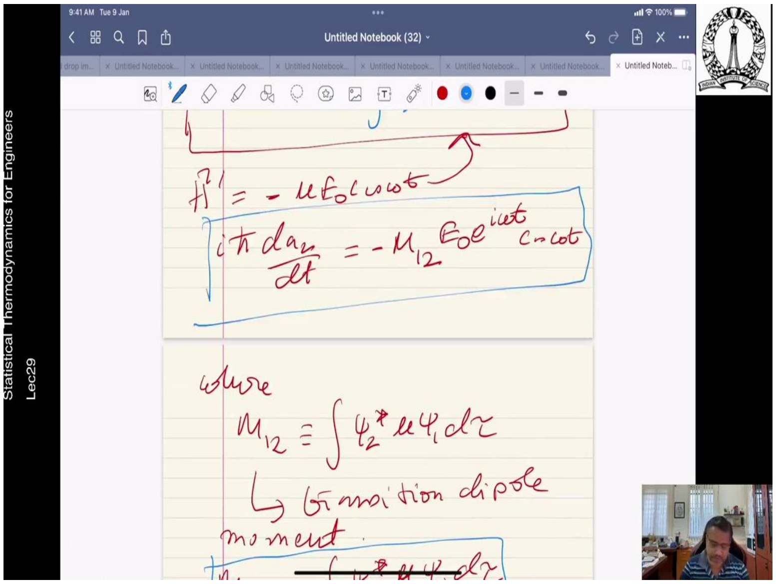


$\psi_i(r)$ and $\psi_j(r)$ are two states participating in any spectral transition.

$a_2(t) \rightarrow$ extent of participation in state 2.

$\frac{da_2}{dt}$ : transition rate from state 1 to state 2



$$\hat{H}' = -\mu E_0 \cos\omega t$$

$$i\hbar \frac{da_2}{dt} = -M_{12} E_0 e^{i\omega t} \cos\omega t$$

where

$$M_{12} \equiv \int \psi_2^* \mu \psi_1 \, d\tau$$

↳ transition dipole moment.

So, the two wave functions here, mu basically it is psi I and psi j r are, we identify the two states, two states participating, participating in any, any spectral transition. So, in essence, a 2 t, it represents, represents the extent of participation in, extent of participation, participation in state 2. Therefore, d a 2 by d t is interpreted as a transition rate, transition rate from State 1 to state 2. So, that is the transition rate. So, so this equation, if you look at this particular equation, which is this, so if you look at this equation, then this equation actually states that transition between two rotational, vibrational and electronic states is impossible if M 1 2 is 0.

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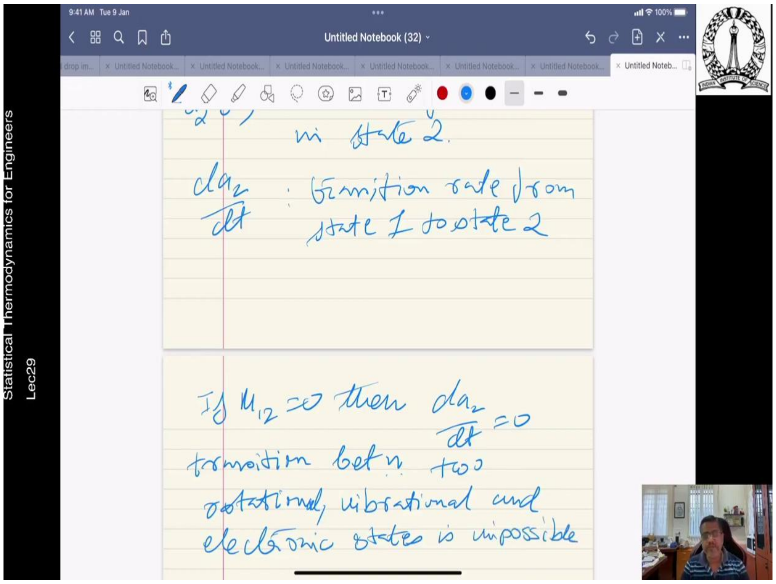
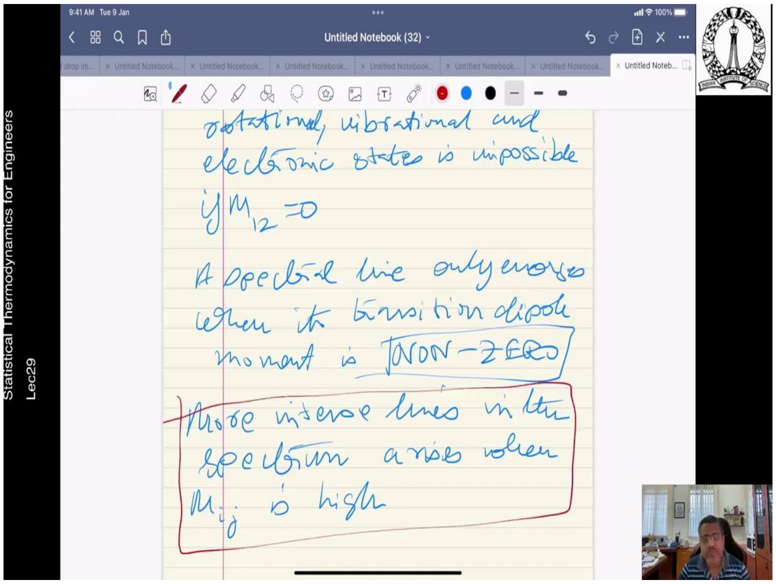


in state 2.

$\frac{da_2}{dt}$ : transition rate from state 1 to state 2

If $M_{12} = 0$ then $\frac{da_2}{dt} = 0$

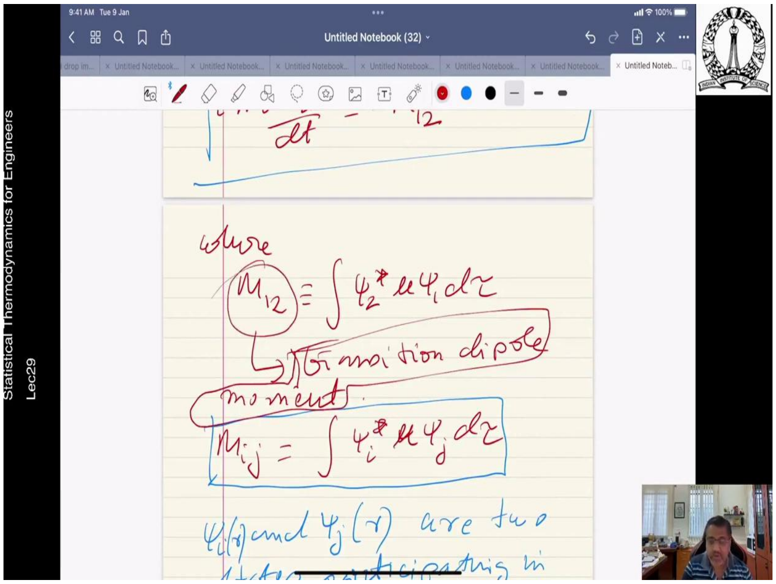
transition betn two rotational, vibrational and electronic states is impossible



rotational, vibrational and electronic states is impossible if $M_{12} = 0$

A spectral line only emerges when its transition dipole moment is $\boxed{\text{NON-ZERO}}$

More intense lines in the spectrum arises when $M_{ij}$ is high



where

$$M_{12} = \int \psi_2^* \mu \psi_1 \, d\tau$$

→ transition dipole moment

$$\boxed{M_{ij} = \int \psi_i^* \mu \psi_j \, d\tau}$$

$\psi_i(r)$ and $\psi_j(r)$ are two states participating in

So, if M 1 2 is equal to 0, then, then d a 2 by d t is also equal to 0. So, that means transition, transition between, between two, two rotational, rotational, vibrational and electronic states is impossible if M 1 2 is equal to 0, which other way means if the transition dipole moment is 0. So, spectral line only emerges, a spectral line only emerges, only emerges when its transition, transition dipole moment is non-zero.

So, generally, you will find more intense lines in the spectrum, the more intense lines in the spectrum, spectrum arises, arises when, when M i j is high. So, of course, so you need to evaluate the transition dipole moment, but of course this evaluation does not require the determination of all possible transition dipole moment. So, mathematical symmetry of any wave function is also used. And so, these rules can be, the selection rules can be expressed in terms of the allowed changes and characteristics quantum numbers. But this is how the situation happens.

So, we can say that the transition dipole moment is the most important thing which determines which are the allowable transitions. This has to be non-zero for us to have an allowable transition. So, next lecture, we will see that how the selection rules can be cast in terms of simple changes in this, in the quantum numbers, and by using the properties of the different mathematical functions from these quantum numbers actually emerged. So, that is what we are going to do in the next class. So, this is end of, end of basically your Lecture 29.