ELEMENTS OF MODERN PHYSICS

Prof. Saurabh Basu
Department of Physics
IIT Guwahati

Lec 14: Time Dependent Perturbation Theory

So we will talk about time dependent perturbation theory and to distinguish it from the time independent perturbation theory that we have seen in details. Here in addition to removal of degeneracy either partial or complete removal of degeneracy. Here one can also get transition from one state to another. So in addition to removal of degeneracy, there could be transitions and this transition is purely, you know, facilitated by the time dependent term in the Hamiltonian. And so we'll start with the formalism part and then we'll talk about the harmonic perturbation that's harmonic in time.

We'll see how these transition probabilities are from one state to another. In particular, we will talk about a two-level system and in that connection, the spontaneous and stimulated emissions and absorptions as well. And we will draw a parallel with lasers where we talk about the Einstein's AB coefficients. Alright, so let us start with this formalism part and the formalism is this. that we now have a time dependent Hamiltonian or rather the perturbation term is time dependent.

And we have learned it earlier that Psi of t rather we have this the time independent problem is that you have a Psi which can be expanded in terms of this Cn and Phi n where Phi n is the basis and Cn are the complex coefficients. Now, when you go to the time dependent problems, the basis remains the same. But what you do is that you introduce a time dependence in the CNs. So this is what we have done. And we have said that this most convenient not to change the basis because every time then at each time there will be a new basis, which is not a convenient model to work with.

So, we will keep the basis the same, and there will be a Cn of t, which can be written as Cn at time t equal to 0, exponential minus Ent over h cross, and we also have phi n, okay. So, this was a, you know, stationary state ansatz, and then we, let us call this equation 1. Okay, so the time dependence, as I said, is carried by these coefficients, and that is how the time evolution of the state psi of t proceeds. So, we know that this problem is known,

that is H0 phi n, this is equal to En0 phi n, which is the unperturbed problem. So, this problem is known, okay, and this known problem, let us call it equation 2.

And so we have to solve this equation, which is I h cross d dt of psi of t. And now this is equal to h psi of t. And say this psi can be split into a time dependent, I mean, a time independent part, which is the unperturbed part of the Hamiltonian and say there is a lambda h prime. h prime t, which is explicitly dependent on time. So, we can put it into the Hamiltonian, and we have this d dt of psi of t. This is equal to h0 plus lambda h prime of t and psi of t, okay. So, now we have a time-dependent problem to solve, and the solutions, you know, will have to be done carefully, and we will still take the same ansatz that we have taken, that is, this ansatz equation 1.

$$\text{Formalism} \qquad\qquad |\psi\rangle = \sum_n C_n |\phi_n\rangle$$

$$|\psi(t)\rangle = \sum_n C_n(t) |\phi_n\rangle$$

$$= \sum_n C_n(0) e^{-iE_n t/\hbar} |\phi_n\rangle \qquad (1).$$

$$H_0 |\phi_n\rangle = E_n^0 |\phi_n\rangle \qquad\qquad : \text{ known} \qquad (2).$$

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$$

$$H = H_0 + \lambda H'(t)$$

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \left(H_0 + \lambda H'(t) \right) \psi(t). \qquad (3)$$

$$\rightarrow \text{ Convert This into an equation for } C_n(t).$$

So, if you take this ansatz and convert this equation to. an equation for Cn t instead of psi t. So, convert this into an equation for Cn t, okay, which is the same as the Schrodinger equation, just rewritten. in that form and that can be done when you, so you have a summation over n and i h cross d c n d t and plus E n 0 C n t, E n 0 is the, as we said, that is the eigenvalue of this unperturbed problem which is known. So, it is En0 psi Cn of t and. and this into exponential minus i E n 0 t over h cross and then there is a phi n and this is equal to E n 0 again and plus a lambda h prime of t and C n of t exponential minus i E n 0

t over h cross and phi n. So, this is nothing but the Schrodinger equation expressed in terms of not in terms of psi of t, but the coefficient C n of t is just the analogous of the Schrodinger equation. So what you can do is that you can take a scalar product with some, you know, phi m and cancel this exponential minus i Em 0 t by h cross. Why i E m? Because you take an overlap with this bra phi M. And when you do that, this phi m phi n will give you a delta m n. And then you have these exponential minus I E m 0 T by h cross.

And that can cancel from both sides, giving you this equation. Now, because of these Kronecker deltas that come in when you have a phi m phi n, this is equal to a delta m n, and then there is a sum over n. So, the sum really goes away, and you have a term which is like a dCm dt, which we will write as a Cm dot, okay. So, you get a dCm dt, which is nothing but Cm dot, which is equal to a lambda and a C n t exponential i E n 0 rather E m 0 minus E n 0 t over h cross and then you have to take the overlap of this phi m, I mean the h prime in between the phi m and the phi n which are the eigenstates of the problem.

So this is the equation that we wanted to get at. And this equation is, you know, I mean, we are really doing first order in lambda. So lambda can be dropped because we just put that lambda to expand the perturbation Hamiltonian. But it was very clear that we are doing first-order perturbation theory because we have kept this term lambda, you know, the linear term in lambda. So, this lambda can be eliminated, and one can write this equation, you know, it is equal to i h cross cm dot.

So, do not miss this dot because this cm dot is equal to dcm dt. Okay, so make sure that the dot is bold such that one does not miss it. I drop this lambda for now, and then we have a n, and then there is a c n t, which we will write as exponential i omega m n t. Then we have this matrix element of H prime between the basis states of H0. So, this is an important equation that needs to be solved in order to solve the time-dependent problem. It has all the information, including the information about H prime that needs to be taken into account.

So, in the first order of the perturbation term, what you get is that the wave function has an evolution given by this equation. And this equation, even though you do not see a psi of t here, but it is exactly this carries the same information as psi of t in terms of this complex coefficients, which are C m dot of t, which is equal to sum over n and these coefficients and the matrix element of H prime between the eigenstates of H0. And then

there is this omega mn. So, this omega mn is nothing but Em0 minus En0, which are two unperturbed energies, divided by h cross.

So, you see that these h cross is absorbed in the step above and Em0 minus En0 divided by h cross becomes omega mn. And this has a solution. So, it is like dCm dt. And then one can actually write down an integral solution for this. Because we are now doing this problem in the first-order perturbation theory, we will simply put a sort of index 1.

So we will write this as Cm1. Because this 1 would simply indicate that we are really doing first-order perturbation theory. And for all practical purposes, we do not need to go beyond that. However, in some situations where the first-order correction, the splitting, or the transitions for some selection rules go to zero, then one may have to go to second order. But we really do not go into that.

So, your Cm1p, the solution of this equation is nothing but 1 by ih cross, the ih cross goes away and now I have these H prime, m k T prime and exponential I omega mn t prime and dt prime you see what we have done is that we can of course we can write it mn there is no problem I mean so it was just a dummy variable. So, now this integral, let us say, is from 0 to some t0. So, what is H prime mn? So, you have a phi m H prime phi n, which is nothing but equal to H prime mn.

So, that is a matrix element between these eigenstates m and n. This exponential term was always there. And what you have done is that you have integrated this equation in order to find Cm. And as I said, we have intentionally brought in this superscript 1 within brackets just to make sure that we are doing first-order perturbation theory. And a very important thing is that the perturbation is switched on from 0 to T0. So, H prime is switched on. That is, you apply this perturbation between some initial time, which can be 0 or even minus infinity, so that it is switched on at very large negative times, and then it is only switched on till a certain time.

So, this 0 to t0 makes sense. So, that is the one that we have in this particular case. Alright, so this is the equation that we need to you know worry about and how these equation is can be used and so basically if you really think about this that this this equation really gives you this the Cm 1 square gives you the this mod square of this, it gives you a transition probability from some initial state n to some final state m, okay? So, these are the states that are represented by the kets, okay?

So, we will have to calculate that. Alright, so let us specialize it for a particular case so that we can apply this formalism that we have learned. And so, what we do is write down this H prime mn is equal to some Amk. Let us not worry about this Amk to be the space part of this matrix element of H. So, that space part would of course lift the degeneracy, and that is what we have handled in the time-independent perturbation theory. Now, we are talking about the time-dependent one.

$$\sum_n \left[i\hbar \frac{dC_n(t)}{dt} + E_n^0 C_n(t) \right] e^{-iE_n^0 t/\hbar} |\phi_n\rangle = \sum_n \left[E_n^0 + \lambda H'(t) \right] C_n(t) e^{-iE_n^0 t/\hbar} |\phi_n\rangle$$

$$\langle \phi_m | \phi_n \rangle = \delta_{mn}$$

Take an overlap $\langle \phi_m |$

$$i\hbar \dot{C}_m(t) = \lambda \sum_n C_n(t) e^{i(E_m^0 - E_n^0)t/\hbar} \langle \phi_m | H' | \phi_n \rangle$$

$$\omega_{mn} = \frac{E_m^0 - E_n^0}{\hbar}$$

$\dot{C}_m = \frac{dC_m}{dt}$

$$\boxed{i\hbar \dot{C}_m(t) = \sum_n C_n(t) e^{i\omega_{mn}t} \underbrace{\langle \phi_m | H' | \phi_n \rangle}}$$

$C_m^{(1)}$

$$C_m^{(1)}(t) = \frac{1}{i\hbar} \int_0^{t_0} H'_{mn}(t') \exp(i\omega_{mn}t') dt'$$

$\langle \phi_m | H' | \phi_n \rangle = H'_{mn}$

H' is switched on between $0 \to t_0$.

$\left| C_m^{(1)}(t) \right|^2 \to$ transition probability from some initial state $|n\rangle \to |m\rangle$.

So, we will only talk about a harmonic term, say for example like this. So, this is an example so that we can apply the first-order perturbation time-dependent perturbation theory that we have learned, okay. So, this is your H prime mn, sorry, this has to be n. And so, Amn, some matrix element which, you know, Amn is, of course, phi m H prime phi n, but only the space part. Okay, so this is what we start with. So, we have a CM1 t, the one that we have written down, and we can take this n state to be equal to the original state.

So, let us just say that your n state is a ground state, okay? So, this is n is equal to 0, say. So, you assume that it is a ground state of the system, and then what you have is that it is a 1 over i h cross a m n and 0 to t 0 d t prime and exponential i omega m n and the t prime.

And what we do is that we replace this sine by its exponential forms, which are exponential i omega t prime minus exponential. See, why am I writing t prime? It is because you are putting it inside an integral. And so, we use a dummy variable so that we can integrate it from 0 to t or here we are talking about 0 to t0. So, it is a dummy variable that needs to be integrated over, and that is why we are not using t, but they mean the same thing. So, it is exponential minus omega i omega t prime and divided by 2 i, and that is basically the sine omega t part.

where we have used the sin theta is equal to exponential i theta minus exponential minus i theta divided by 2, okay, 2i, sorry, okay, because your exponential i theta is cos theta plus i sin theta. Anyway, so that is the thing that you have, and when you do this integral, you have a mn and with a minus 2 h cross and then you have a 0 to t0 and we have a dt prime and we have exponential i omega plus omega mn and minus this d prime and exponential I, well, I mean, this can be written in the reverse way such that there is a symmetry and omega and this is like omega mn minus omega and so on. So, that is the term that we have, and we can integrate this and what we get is this I a

m n divided by 2 h cross, and we have exponential I t naught, and we have omega m n plus omega. divided by omega mn plus omega minus exponential I minus exponential i t0 omega mn minus omega So, there is a minus 1 here, and then there is another minus 1 here, and then we have omega mn minus omega and this. So, what we have done is that we have simply integrated this, and exponential integration is very simple, and then you get these energy denominators appearing there. So, we can measure the probability of transition from some initial state n. You can take this initial state to be any state.

Example $\qquad H'_{mn}(t) = A_{mn} \cdot \sin \omega t$ $\qquad\qquad A_{mn} = \langle \phi_m | H' | \phi_n \rangle$

$$C_m^{(1)}(t) = \frac{1}{i\hbar} A_{mn} \int_0^{t_0} dt' \, e^{i\omega_{mn}t'} \left[\frac{e^{i\omega t'} - e^{-i\omega t'}}{2i} \right]$$

only the space part.

Say $|n\rangle = |0\rangle$ initial
$|m\rangle$: final state

$\sin\theta = \dfrac{e^{i\theta} - e^{-i\theta}}{2i}$

$$= -\frac{A_{mn}}{2\hbar} \int_0^{t_0} dt' \left[e^{i(\omega_{mn} + \omega)t'} - e^{i(\omega_{mn} - \omega)} \right]$$

$\sin\omega t$

$$= \frac{i A_{mn}}{2\hbar} \left[\frac{e^{i t_0(\omega_{mn} + \omega)} - 1}{\omega_{mn} + \omega} - \frac{e^{i t_0(\omega_{mn} - \omega)} - 1}{\omega_{mn} - \omega} \right]$$

—— $|m\rangle$

—— $|n\rangle$

So, it can be a ground state, and we have not used it, but we have kept it N to be the initial state. So, this is the initial state, and m is the final state. So, like these are two states and this is n and this is m and these mod square of the Cm1 will give you a transition probability from some initial state that is n to a final state that is m. Okay. So, these transitions are, of course, new for us because we have not seen them in the time-independent perturbation theory. Let us look at these denominators, and these denominators will tell us something.

So, let us, so inside the bracket, so denominator of the first term. And so, we have what happens when the denominator goes to 0, that is like the term, you know, blows up. So, if omega mn plus omega goes to 0, then what we have is that Em minus En divided by h cross. Plus omega equal to 0. And why we are looking at this blowing up of this term or these denominators goes to 0 is because this omega is a variable frequency, that variable frequency associated with the perturbation term.

So if the perturbation actually clicks or rather it resonates with the energy difference between the two states that we are considering, then there could be a transition because that is going to give you the largest, you know, transition probability. So if you tune your omega, the omega that you are applying as a perturbation, which is equal to the difference between the two energies, then of course you have a sort of large, you know, that ratio becomes very large because this thing goes to zero, your denominator goes to zero, and the transition probability is going to be very large. And that is what we want to see. So, this means that your Em is equal to En minus h cross omega. And so, of course, this means that Em is less than En.

So, that tells you that basically, you know, your H mn, the perturbation term, it takes away energy. And when it takes away energy, it is called absorption, okay. And if you look at the denominator of the second term, when it diverges, basically— So, you have an omega Mn minus omega that is equal to 0, and that gives you finally an Em equal to En plus h cross omega. So, your final state has energy larger than the initial state, and this is called an emission.

Denominator of 1st term.
$$\omega_{mn} + \omega = 0$$
$$\frac{E_m - E_n}{\hbar} + \omega = 0$$
$$E_m = E_n - \hbar\omega.$$

$E_m < E_n.$

H_{mn}' takes away energy $\rightarrow$ Absorption

Denominator of 2nd term
$$\omega_{mn} - \omega = 0$$
$$E_m = E_n + \hbar\omega.$$

$\rightarrow$ Emission

Emission is coming down from a higher state to a lower state, or rather, M is greater than N, and the reverse actually happens when you have absorption. So, this picture that we have is only for the emission part, and when you have the absorption, then you have these lying above this thing. That's also possible. This, you know, the two terms actually have both these possibilities. And so we'll mainly be interested in this emission term, but at the same time, the absorption term can also be considered.

So let's look at the second term and see what happens. So we are interested in the second term. which means that we talk about the conventional picture where E m is greater than E n, and we are going to talk about the emission spectrum. So, this is equal to minus I a m n divided by 2 h cross and rewriting it again, it is I t 0 omega m n minus omega minus 1 divided by omega m n minus omega, okay. So, this is the term that we have.

and we can do just a little bit of mathematical manipulation and can write it as amn divided by h cross and we have this exponential. So, what I do is that we take out this exponential and or rather we take out half of this exponential such that we can write it in a symmetric fashion. So, it is This is what I take a common here. So it's exponential i t0 by 2 omega mn minus omega.

This, if it is taken as common, then we can write it. So basically, there is a minus i there. And then there's a 2 h cross there, which will cancel out because there's a 2 i there and a sine of 2. you know, these T0 and omega mn minus omega and this divided by omega mn minus omega and so on, okay. So, these two terms, now this 2 will cancel with 2 and this minus i will cancel with i and we are left with these terms which is Amn by h, this half

I T 0 by 2 omega m n minus omega and this sign term which is there. So, this is your that C M 1 term only for the emission. So, the second term of C M 1 T and what we want is that we want to take the mod square of that to get the transition probability. and this is equal to amn mod square by h cross mod square. This term will not be there because you are taking a mod square.

So, this exponential i and there will be exponential minus i coming from the c star and will not give you anything. And then finally, we have a sine square. Now, writing this, let me just write this as alpha and we have an alpha t0 by 2. and divided by some alpha square okay. So, you can write you know this beta equal to alpha t 0 by 2.

So, you can write a beta equal to some alpha t 0 by 2 Anyway, these are constants. I mean, alpha is these omega mn minus omega in the sense that for a given frequency of the perturbation, of course, omega is constant, omega mn is constant and so on. So, we have a form which is the transition probability for emission or the emission probability, but we are just trying to, you know, simplify it so that we can bring it to a form that we can interpret the result. Okay.

Second term. $E_m > E_n$: Emission.

$$c_m^{(1)}(t) = -\frac{i A_{mn}}{2\hbar} \left[\frac{e^{it_0(\omega_{mn}-\omega)} - 1}{\omega_{mn} - \omega} \right]$$

$$= \frac{i A_{mn}}{2\hbar} \left[e^{\frac{it_0(\omega_{mn}-\omega)}{2}} \right] \left[\frac{2i \sin\left\{ \frac{t_0}{2}(\omega_{mn}-\omega)\right\}}{\underbrace{\omega_{mn} - \omega}_{\alpha}} \right]$$

$$\boxed{\left| c_m^{(1)}(t) \right|^2 = \left| \frac{A_{mn}}{\hbar} \right|^2 \frac{\sin^2 \alpha \frac{t_0}{2}}{\alpha^2}}$$

$$\beta = \frac{\alpha t_0}{2}.$$

So, use this beta there, and what we have is that we have a CM1 T square only the emission part is equal to AMN by h cross mod square of that. sin square beta divided by beta square and a constant which is coming because of this alpha to beta transformation, which is T square by 4, and anyway, that is a constant. So, what is important for us is this

term: sin square beta by beta square. This is called a sinc function. It's like a sine x by x square of that.
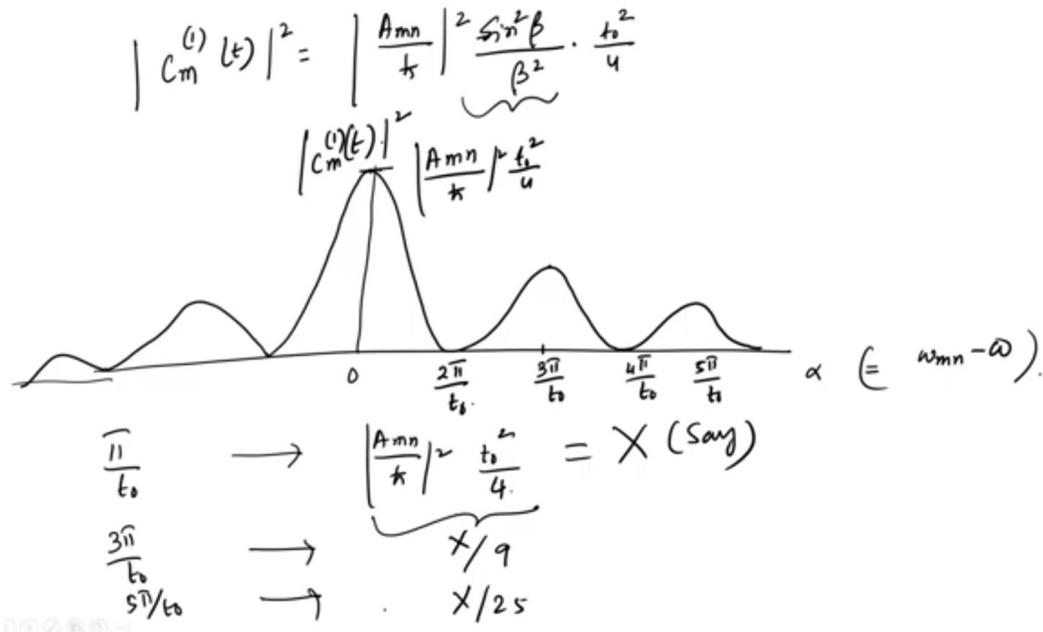
So, it's like sine square x by x square. And you can actually plot this function. I'll do a freehand plot. But you can do it on a computer, and it will be like there will be a central peak which is maximum, and then the subsequent peaks will be smaller and smaller and smaller and so on. Well, it's symmetric.

Do not mind too much about this, you know, details of the drawing, but it's, of course, symmetric. So, this is your CM1 tsquare mod square of that being plotted. And this is as a function of alpha. Which is nothing but omega mn minus omega. So, that is being plotted as a function of that.

And of course, you can also call it as it is basically, so what we plot is sin square beta by beta square. And this peak value, this peak value is equal to a mn. by h cross square into t square by 4. That's when the sine square beta by beta square equals 1. And this will happen at the 0, will happen at 2 pi over t 0.

I mean, so this alpha equal to 0 and this will happen at, you know, this is like 3 pi over t 0. And we have 4 pi over T0 and symmetrically on the other side as well. And all these are like 5 pi over T0. This is in terms of alpha. So, pi over T0 that corresponds to a value which is a m n by h cross squared.

and T0 square over pi square, okay, T0 square over 4, sorry, not pi square, that is 4. And similarly, the 3 pi by T0, this will be this term and divided by 9, this whole thing divided by 9 and 5 pi by T0 will correspond to this whole thing. I mean, so let us call this quantity to be equal to say x, say. So, this X by 9 and X by 25 and so on so forth.

$$\left| C_m^{(1)}(t) \right|^2 = \left| \frac{A_{mn}}{\hbar} \right|^2 \frac{\sin^2\beta}{\beta^2} \cdot \frac{t_0^2}{4}$$

$$\left| c_m^{(1)}(t) \right|^2 \qquad \left| \frac{A_{mn}}{\hbar} \right|^2 \frac{t_0^2}{4}$$

$$\alpha \left(= \omega_{mn} - \omega \right).$$

$$\frac{\pi}{t_0} \longrightarrow \left| \frac{A_{mn}}{\hbar} \right|^2 \frac{t_0^2}{4} = X \; (\text{Say})$$

$$\frac{3\pi}{t_0} \longrightarrow X/9$$

$$\frac{5\pi}{t_0} \longrightarrow X/25$$

So, these are the values that go down as you move away from the central maxima. So, the physically it means that if your perturbation term has a frequency that matches exactly with the level spacing, the energy difference between the two levels. then there is a large emission probability that is there for alpha equal to 0, which corresponds to omega mn equal to omega. As you go away on either of the sides, that is, you make omega to be larger or omega to be smaller, you see that the intensity of this emission spectrum or the probability of emission decreases very quickly.

At times, 2 pi by T0, it just has a zero. So, there is no emission happening. That happens because of the sine squared beta by beta squared. And at 3 pi by T0, it has a value which is one-ninth of the value seen at alpha equal to 0. And then it becomes one-twenty-fifth of the value seen at these,

5 pi by T0, and so on and so forth. So, this conclusively shows that it really goes down quickly and so on. All right. So, this is, in a nutshell, what perturbation theory is, and we can write down or rather get a little closer to what experimentalists would do or would like you to do, because this is just a transition probability.

It has to be multiplied by the energy density of radiation and speed of light and various things in order to actually transform it into intensity because the intensity of light is what you measure in experiment or rather you see that on the screen or on a spectrograph. So, that is an important quantity and this can be actually, you know, one can get a sort of one-

to-one correspondence if you think that. So, once we get this intensity of these or rather this transition probability for this radiation or rather this emission transition, then the intensity of EM wave This is given by I equal to half epsilon 0 C, epsilon 0 is the permittivity of free space and some E 0 square which is associated with the electric field and C is the speed of light. So, if you want to write this as say CM 1 T, this can be written in terms of all these quantities which are

say half and then you have this amn mod square and these I divided by epsilon 0 c h cross square and these you know sine square. I will simply write it as sine square beta by beta square now you know with this T0 square over 4. So, this is the same thing expressed in terms of intensity and so on. So, this intensity can be replaced by the speed of light and the energy density of radiation. So, this quantity is nothing but the energy density of radiation between a frequency omega and omega plus d omega.

Okay, so this transition probability ultimately leads me to this expression. Let us call it as gamma mn. You can write it as 2 epsilon 0ch cross square and we have this amn. and it is actually an average—you know, this average is required to account for all available frequencies. So, that you have this u omega and then this sine square, I will not open this thing, I will still write it as sine square beta by beta square and we have this T0 square by 4 that is coming in that can be pulled out and then we have this d omega and this is over all frequencies I mean 0 to infinity, okay.

So, that is really the transition probability. But nevertheless, I mean, if you do not want to do these transformations, your CM1 theoretically still conveys the same meaning apart from certain constants that you see appearing because of this, you know, all these transformations from one sort of variable to another where we brought in the intensity and then this intensity was, you know, later on written as in terms of the energy density and so on and so forth. Okay. So, let us go back and do a simpler problem. The simpler problem is just a two-level problem where, instead of m n, we will simply talk about 1 and 2. So, let us see what that comes to.

Intensity of the EM wave

$$I = \frac{1}{2} \epsilon_0 c \, E_0^2.$$

$$\left[C_m^{(1)}(t) \right]^2 = \frac{1}{2} \, |A_{mn}|^2 \, \frac{I}{\epsilon_0 c \hbar^2} \left[\frac{\sin^2 \beta}{\beta^2} \right] \frac{t_0^2}{4}.$$

$$I \rightarrow \underbrace{c \, u(\omega) d\omega}$$

$$\Gamma_{mn} = \frac{1}{2 \epsilon_0 c \hbar^2} \, \langle |A_{mn}| \rangle \int_0^\infty u(\omega) \, \frac{\sin^2 \beta}{\beta^2} \left(\frac{t_0^2}{4} \right) d\omega.$$

So, time-dependent perturbation theory for a two-level problem. So, we will call it time-dependent perturbation theory (TDPT) for two-level systems. So, let us say these levels are psi a and psi b, they were labeled as m and n, but now we just talk about a psi a and psi b. So, the C is equal to C a psi a plus some C b psi b and of course, this C a and C b are dependent on time for these time dependent cases. So, psi of t is nothing but C a exponential minus I a 0 t over h cross psi of a plus C b exponential minus E b 0 by t by h cross psi of b. So, that is the time-dependent thing, and we of course know that H0 psi a is equal to E a0 psi a and H0 psi b, which are the unperturbed eigenstates of the problem, E B0 psi b, with well-defined energies E0 b and E0 a.

And these well-defined energies help us to build up the wave function at subsequent times. And we can, you know, now we need to find C a t and C b t. And what you do is, if you put these ansatzs into the Schrödinger equation, let us call this ansatzs as 1. So, put this unsuds in H psi equal to i h cross del psi del t or d psi dt, what you get is that you get, you know, because you have two terms that you need to—your psi of t, there is a function of t which I left.

So, when you take a derivative for the right-hand side to be calculated, the derivative will involve two terms, both dependent on t. So, to apply the chain rule by taking a derivative of one, keeping the other constant, and then repeating the process in the reversed order. So what you get is two coupled equations, and these two coupled equations will tell you that, if you see some cancellation, I will not repeat some really trivial steps here. You can do it. I hope you understand what has been said. So you have this H, which has to be operated on psi.

So you write H of psi, this psi. And the right-hand side requires you to take a time derivative. And while taking the time derivative of these under-braced terms, there are two terms, and some of them will cancel, and you will have a Ca dot t. That is the equation of motion for Ca, which is nothing but the Schrödinger equation, equal to minus I by h cross t. Ca H prime aa. Now, the C a means really that you have C a at 0. and then, you know, the Cb or, you know, let us not specify this.

$$\text{TDPT for 2 level systems.}$$

$$H_0 |\psi_a\rangle = E_a^0 |\psi_a\rangle \\ H_0 |\psi_b\rangle = E_b^0 |\psi_b\rangle$$

$$|\psi_a\rangle \qquad |\psi_b\rangle.$$

$$|\psi\rangle = C_a |\psi_a\rangle + C_b |\psi_b\rangle.$$

$$|\psi(t)\rangle = \underbrace{C_a^{(t)} e^{-iE_a^0 t/\hbar}} |\psi_a\rangle + \underbrace{C_b^{(t)} e^{-iE_b^0 t/\hbar}} |\psi_b\rangle \quad (1).$$

$$\text{find } C_a(t), \; C_b(t).$$

$$\text{Put } \psi(t) \text{ in } \quad H\psi = \underbrace{i\hbar \frac{d\psi}{dt}}.$$

$$\dot{C}_a(t) = -\frac{i}{\hbar}\left[C_a \underbrace{H'_{aa}} + C_b H'_{ab}\, e^{-i(E_b - E_a)t/\hbar} \right] \Bigg\}\; \text{coupled}$$

$$\dot{C}_b(t) = -\frac{i}{\hbar}\left[C_b \underbrace{H'_{bb}} + C_a H'_{ab}\, e^{-i(E_a - E_b)t/\hbar} \right]\; \text{equation.}$$

$$H'_{aa} = H'_{bb} = 0$$

So, this is Cb and H prime ab and exponential minus i Eb minus Ea by t by H cross, and the other term will become equal to Cb dot. This is equal to minus i by h cross Cb H prime bb Ca H prime ab exponential minus i Ea minus Eb t by h cross, and those are the two coupled equations that you need to solve. See this is important because the time derivative of C a requires the knowledge of C a and C b at time t equal to 0 and same that C b dot also requires the time evolution of or rather the you know the knowledge about C b and C a at time t equal to 0 and these energy terms are there which are between I mean like the energy differences, okay. Now, it is almost natural to assume that or it is easy to understand as well that the perturbation term will not have any matrix elements between the same states. So, these terms which connect the state to itself by H prime that is not happen because your H prime is explicitly dependent on time.

So, this term will have a time, meaning there is an omega associated with it; there is a frequency associated with it. So, these terms will only have matrix elements with the other state, meaning A will have a matrix element with B, and B will have a matrix

element with A. But these terms are usually equal to 0. So, there is no matrix element of H prime between the diagonal states or between the same states. So, this is equal to 0.

That, of course, simplifies this equation or the set of equations. It is like a C A dot. t, this is equal to minus i over h cross, Cb H prime ab exponential minus i e b minus e a t by h cross, and also you have a Cb dot. which is equal to minus I over h cross C A H prime B A exponential minus I E A minus E B T over h cross, okay. So, it simplifies the equation that there are no diagonal elements, and it is only the off-diagonal elements; nevertheless, it is coupled, basically.

So, if at t equal to 0, the system starts from the state A, which means at t equal to 0, say this is for an example. So, at t equal to 0, you have the system starting from psi A. That means C A 0 is equal to 1 and C B 0 equal to 0. Now, at time t, say the system is found in this, so this psi B will, if it is found in psi B, then it is equal to C B equal to Cb at time t equal to 1 and Cb at time, Ca at time t equal to 0, okay.

$$\dot{C_a}(t) = -\frac{i}{\hbar} C_b \, H'_{ab} \, e^{-i(E_b - E_a)t/\hbar}.$$

$$\dot{C_b}(t) = -\frac{i}{\hbar} C_a \, H'_{ba} \, e^{-i(E_a - E_b)t/\hbar}.$$

Say/ At $t=0$, $|\psi_a\rangle \rightarrow$ $C_a(0) = 1,$ $C_b(0) = 0.$

$t = t,$ $|\psi_b\rangle \rightarrow$ $C_b(t) = 1,$ $C_a(t) = 0.$

So, that tells you that the system has made the transition from one state to another, and if you are talking about the emission, then A is a lower state, a lower energy state, and the other one, B, is a higher energy state, okay. So, we need to, you know, kind of put these things in perspective and let us talk about this Einstein's AB coefficients and see that how all these things that we have learned from the first order time dependent perturbation theory and how it can be applied to these properties of laser. So, we will do a semi-classical picture and we will introduce these Einstein's coefficients. And we have this as a picture. So, we have this state as state 1 and this state as 2.

Or you can call it AB, whatever you want to call it. And let me now use color. So, let's use three colors, for example. So, there's a maroon color we have done. So, let's call that as A21.

We'll tell you what A21 is. So, these are these mn's, because we are talking about 2 and 1, so this is called, you know, the emission. This is one of the emissions; we will define it as spontaneous or stimulated. So, let us use another color, let us use, for example, blue, and this blue color would correspond to a B. 1, 2, or, sorry, this is 8, 1, 2, because this is defined as 1, 2. We will do that in just a while. So, 1, 2, and let us choose another color, maybe a green one, where we show it.

So, this is a B21. So, let us just define them now. So, these A's are A and B are Einstein's AB coefficients. These are called A and B coefficients. I repeat this A and B twice, but the ones we are using are called Einstein's A-B coefficients.

So, the A coefficient stands for spontaneous emission. So, it is spontaneously emitted, and when you write it like this, it actually means that A12—the target state or the final state is written first, and the initial state is written later, okay. And the B coefficient actually represents induced emission or absorption. Okay, so the transition probability for spontaneous emission is per unit time, basically.

This is equal to A12, and the transition probabilities for induced emission, again per unit time, this is equal to B12, but it also depends upon the energy density of radiation. So, we write it as B12 omega. So, the transition probability for induced absorption per unit time —this absorption and this is equal to b21 u omega okay.

So, at a steady state when all these upward and downward transitions are equal that is no more transition is happening. So, at steady state, you have N2 which is the occupancy of atoms in the state 2 that multiplied by A12 plus B12 U omega, this is equal to U omega as we have said that it is energy density of radiation. is equal to n1 b21 u omega. So, if you do this, if you just open this bracket, so it is a12 plus b12 u omega, this is equal to n1 by n2 b21 u omega.

Einstein's Coefficients.

$$A_{12} \quad B_{12} \quad B_{21}$$

$$|2\rangle$$

$$|1\rangle$$
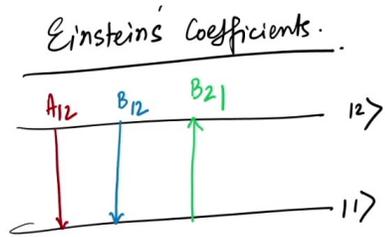
$A \& B$ are Einstein's $A \& B$ Coefficients.

A : Spontaneous emission.

B : induced emission/absorption.

Transition probability for spontaneous emission./time = A_{12}.

" " induced " / time = $B_{12} u_\omega$.

" " absorption / time = $B_{21} u_\omega$.

At steady state,

$$N_2 \left(A_{12} + B_{12} u_\omega \right) = N_1 \, B_{21} \, u_\omega.$$

$$A_{12} + B_{12} u_\omega = \frac{N_1}{N_2} \, B_{21} \, u_\omega$$

And so, your E2 minus E1 is basically the perturbation term, which is basically the frequency of the perturbation. So, h cross omega. Now, we also know from Boltzmann statistics that n1 by n2 is nothing but exponential of E2 minus E1 divided by So, the occupancies of these two states at a temperature T would be given by this, which is nothing but exponential h cross omega by kT. So, this ratio that you got here N1 by N2 at a temperature T is nothing but this exponential h cross omega by T. So, basically the transition rate that you get here is that, so minus dN2 by N2, it is like a beta T, which is like a radioactive decay with inverse of beta as the lifetime and so on.

So, that tells us that if you want to have a one to one correspondence and using the steady state equation, if you want to calculate the this U omega, then the U omega would look like this. So, b12 u omega this is equal to exponential h cross omega by kT b21 u omega and so u omega this is equal to a12 divided by exponential h cross omega by kT into b21 minus b12 and so on. So, that is the energy density of radiation and if you compare with the Planck's formula for the radiation intensity, I mean this energy density, then it looks like this h cross omega square by pi square c cube and divided by e to the power h cross omega by kT minus 1. So, this is Planck's law or Planck's law of blackbody radiation.

$$E_2 - E_1 = \hbar\omega$$

$$\frac{N_1}{N_2} = e^{(E_2-E_1)/k_B T} = e^{\hbar\omega/k_B T}$$

$$-\frac{dN_2}{N_2} = \beta t$$

$$A_{12} + B_{12} U_\omega = e^{\hbar\omega/k_B T} B_{21} U_\omega$$

$$U_\omega = \frac{A_{12}}{e^{\hbar\omega/k_B T} B_{21} - B_{12}}$$

Planck's law:
$$= \frac{\hbar\omega^2}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

So, you see that it is very easy to see that this and B12 is the same as B21, to remind you that B12 and B21 are these things which we have mentioned here. So, this B12 and B21 are these transition probabilities for induced emission and induced absorption. So, they are the same, and not only that, your A12. by B12 from this comparison gives you h cross omega cube divided by pi square c cube that tells you that A12 is equal to h cross omega cube by pi square c cube into B12.

$$B_{12} = B_{21}$$

3 cofficients.

$$\frac{A_{12}}{B_{12}} = \frac{\hbar\omega^3}{\pi^2 c^3}$$

$$A_{12} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{12}$$

There is really one Independent Einstein's coefficient.

So, there are three coefficients and two relations that you have. One relation is that two of them are exactly the same, and the other relation is that the third one, that is A12, has a relationship with either B12 or B21, which are the same, which means there is really one independent Einstein coefficient. So we have calculated the transition probability the

CM1 square and then have you know gone ahead and said simplified it for just a two level problem and then these transition probabilities have shown to have a sharply peak structure at resonance and as you move away from resonance the probability of transition, or the transition probability, drastically goes down.

And then using a semi-classical picture, we have calculated the Einstein's coefficients from the energy density, comparing it with the energy density of the blackbody radiation. And this sort of concludes. Of course, we have not done any example problems, which will be dealt with in the assignments or the tutorials. And so, we have introduced this time-dependent perturbation theory and have explained how, in addition to the removal of degeneracy, which was already done by the space part or the spatial part of the perturbation, this causes transitions between one state and another.

And that's an important thing. I mean, and these are related to the lasing action where there are, you know, the atoms are being either, you know, pulled up from one lower state to a higher state, which are induced absorption, or there could be two other processes, which are spontaneous emission. Induced emission. These coefficients can be calculated from all the CM 1 square mod square that we have started with and we have told how for a harmonic perturbation these transition probabilities look like. So we will stop here and we will continue with some more things, particularly these what are called as a Clebsch-Gordon coefficients, etc., which need to be done and explained. It is a little complicated if one has not done it before, but I hope I will be able to explain how it works.

Thank you. Thank you.