Optical Spectroscopy and Microscopy

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Lecture – 12

Fundamentals of Optical Measurement and Instrumentation

Hello and welcome to the lecture series on optical spectroscopy and microscopy. In the last lecture, what we were actually looking at is the expression for the expansion coefficients ak or an in general and the way we got them is by using a time-dependent perturbation theory where we said hey look if the perturbation because of the light are interacting with the matter is small enough such that we can still write this whole state that the system is going to be thrown into in terms of the unperturbed energy eigenkets.

We may be able to write the superposition state the system is in currently as the linear combination of all of them and then did some juggling around with the terms and obtained an expression for an ek in general, actually to be precise we got the expression for first derivative of en or ek in an exact manner then we made an approximation and expanded the an in a power series in terms of lambda a coefficient to the perturbation Hamiltonian right. So then we gave some interpretation about the lambda.

How do we think about and how one can go about, what are the problems in this kind of an interpretation, but I kind of motivated you what is the nature of the lambda that you can satisfy yourself and then we wrote down specific, I mean equated the coefficients of the same powers of lambda, then obtained an expression for a series of coefficients of en.

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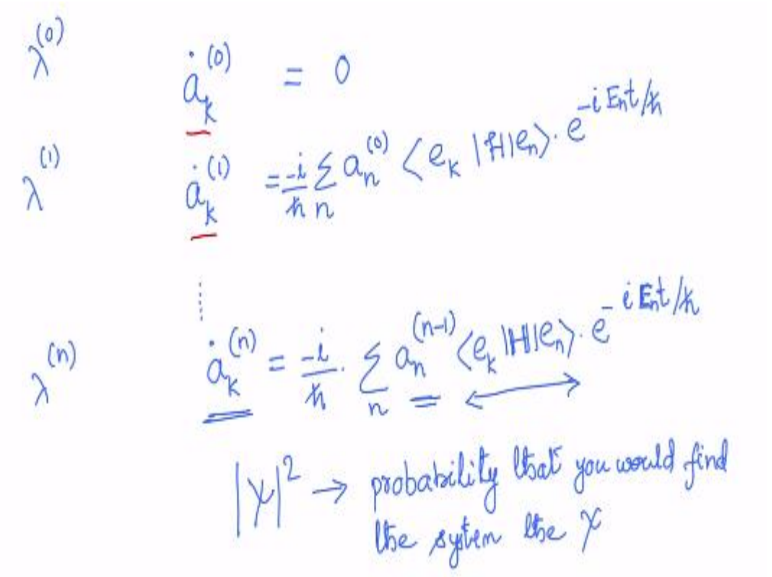

$\lambda^{(0)}$ $\quad \dot{a}_k^{(0)} = 0$

$\lambda^{(1)}$ $\quad \dot{a}_k^{(1)} = \frac{-i}{\hbar}\sum_n a_n^{(0)} \langle e_k|\hat{H}|e_n\rangle \cdot e^{-iE_nt/\hbar}$

$\vdots$

$\lambda^{(n)}$ $\quad \dot{a}_k^{(n)} = \frac{-i}{\hbar}\cdot\sum_n a_n^{(n-1)} \langle e_k|H|e_n\rangle \cdot e^{-iE_nt/\hbar}$

$|\chi|^2 \rightarrow$ probability that you would find the system the χ

So this is something similar to this right. So we have by equating the coefficients to the order of lambda, actually what we said is that we know the 0th order coefficient which is the ak dot corresponding to the 0th order that is here and the first order and in general the nth order okay. At that point, I told you that where we are heading to is we are trying to make use of the Born's principle and what it tells you is that if you take the modulus square of the state vector, then what it reflects or what it tells you is that the probability that you would find the system in the state chi right.

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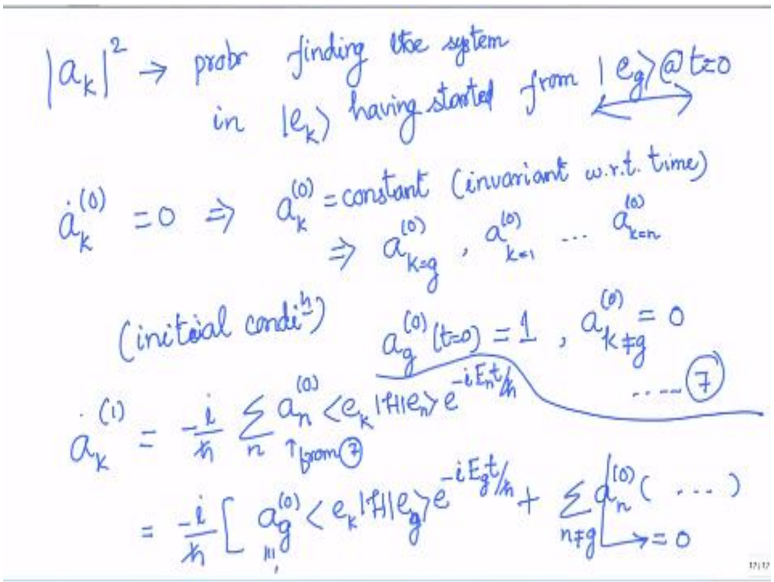

$|a_k|^2 \rightarrow$ probr finding the system in $|e_k\rangle$ having started from $|e_g\rangle$ @ $t=0$

$\dot{a}_k^{(0)} = 0 \Rightarrow a_k^{(0)} =$ constant (invariant w.r.t. time)

$\Rightarrow a_{k=g}^{(0)}, \; a_{k=1}^{(0)} \; \ldots \; a_{k=n}^{(0)}$

(initial condiⁿ) $\quad a_g^{(0)}(t=0) = 1, \; a_{k\neq g}^{(0)} = 0 \quad \ldots\ldots (7)$

$\dot{a}_k^{(1)} = -\frac{i}{\hbar}\sum_n \underset{\uparrow \text{from } (7)}{a_n^{(0)}} \langle e_k|\hat{H}|e_n\rangle e^{-iE_nt/\hbar}$

$= \frac{-i}{\hbar}\left[a_g^{(0)} \langle e_k|\hat{H}|e_g\rangle e^{-iE_gt/\hbar} + \sum_{n\neq g} \underbrace{a_n^{(0)}}_{=0}(\ldots) \right]$

Using that you can actually extend the idea and say that if we have a superposition state chi represented from a linear combination of various different eigenkets with the coefficients of ak, then what you are talking about here is that we are specifically talking about a kind of an operator or called as a projection operator and when you put in those projection operators, what we will see is that we can actually get the ak square being representative of the probability.

Now, I have not mathematically proven that this is the case and what I am going to do now is that things like this you remember we also had a similar issue with this expression right, the parentheses I asked you to work it out at home, so those kind of mathematical equations where I have just stated the answer and not necessarily proved, we will do the at the end of the lecture series and annexure or appendix to this lecture series where we will take up each one of these problems and then mathematically work out just for the want of time because we need to be concise in this lecture series.

So that people who are interested in the results can actually concentrate on the results, not necessarily having to know how we are getting them. The bottom line being we are after ak the modulus of the ak square, ak being here dependent on time. Now how do we get that? So we get that by simply looking at these expressions. The first 0th order coefficient, let us write down and see what does it tell you.

The 0th order coefficient tells you that ak dot to the 0th order is 0 implying, remember the ak dot is the first derivative with respect to time which it means that ak to the zeroth order is a constant it is invariant with respect to time. Since it is a derivative with respect to time and it is 0, then we are saying it is invariant with respect to time, what does it mean? So the ak values for the 0th order correction basically tells you invariant with respect to time.

This implies that whatever the value that we have whatever the ak has here is valid now which is valid before we turned on the perturbation, after we turned on the perturbation, and during the perturbation which is essentially telling you that is why it is time invariant, which means you can interpret that as reflective of the initial conditions right. It should also be obeying time t = 0 right. I mean if it were to be valid even after we turned on the perturbation, that is what it means by saying there is no time dependence.

It should also be valid before we turn on the perturbation. So you could interpret that as the initial conditions right, so what are the initial condition here, what does it tell you? It tells you that the ak to the zeroth order we can split it down as remember ak = g and a all of them to zeroth order right, please remember that, k =1 so on and so forth and we have written down as in general k equal to some n or m or it is infinite number of eigenkets so can actually go till k = infinity, many numbers okay.

So what it tells you is that at = 0, we know at which state we are starting in. For example if you are talking about a system at room temperature and we are talking about systems with a certain amount of energy e, from I mean energy gap delta e, then we can actually think of calculating or estimating how much of the population is present in each of the states determined by the thermal equilibrium.

Now if you take them to be these energy eigenstates correspond to the electronic energy levels, then you will see that they are dominantly present in the ground state or to say that it is safe to assume the initial condition to be such that ak for k = g is basically ag, the coefficient corresponding to the ground state at t = 0, at time t = 0 the initial condition we know has to be 1 because you remember ak square, a modulus ak square represents the probability of finding the system.

And I am here telling you that ag which is the coefficient of eg the energy eigenkets of the ground state the coefficient of that is equal to 1 and all other coefficients where k not equal to g to the 0th order is 0. Now that is our beginning state. The moment you have a way of writing down this ag to the 0th order, then the first order can be estimated, remember this expression is recursive in the sense that in order for you to know the nth term, you need to know the n-1 term because you have the nth order coefficient here.

We write that nth order coefficient in terms of n-1 th order and some additional terms here alright. So what it allows you to do now is we can actually go back and say okay, now I am going to look at this term. Now since I know this, aks, various different aks, can I actually write down this? So let us see what it means? We use this relationship, so this let us go back and find out whatever equation number is here, until here it is 5 and 6, I am going to call this as 7.

We have set of equations here, but all of them I am going to call that as equation number 7 and these ones I am going to call it as 6 okay, 6 is the equation for the general expression and 7 is for the 0th order term and then equating it to the initial condition whatever we have it okay, so with respect to time we call this as the initial condition right yes. So now what we are going to do is that we are going to evaluate it for ak to the first order that is given by either you can use this general expression equation number 6 or the equation that we have tick marked it here.

Which is -i by h cross summation of an to the 0th order and this matrix element e to the power –iEnT h cross right. So we write it as -i h cross summation over n an to the 0th order ek perturbation Hamiltonian H en that is correct and e to the power –iEnT divided by h cross okay. Now this is my equation 7. So from equation 7, we know this is from equation 7, we can actually substitute an of 0. So when we do that, you will see it comes to -i h cross. Now since all the aks where it is not equal to the ground state is 0.

So if you write down this expression you can actually write down as a ground state, now we know this is equal to 1 okay, so I am just still pulling it out where I have set the n = g right. I am writing it as the one of the terms is this ek Hamiltonian en becomes eg e to the power –iEn please notice the subscript n here, in a bit we are going to write this out more precisely, so this is eg I have absorbed the k in here because k was common all throughout.

So we will write down the expression for eg in a minute, Egt by h cross + all the other terms where n not equal to g, right, da da da okay. So now we know from equation 7, this is equal to 0. So the whole term, this whole term goes to 0 while this is equal to 1.

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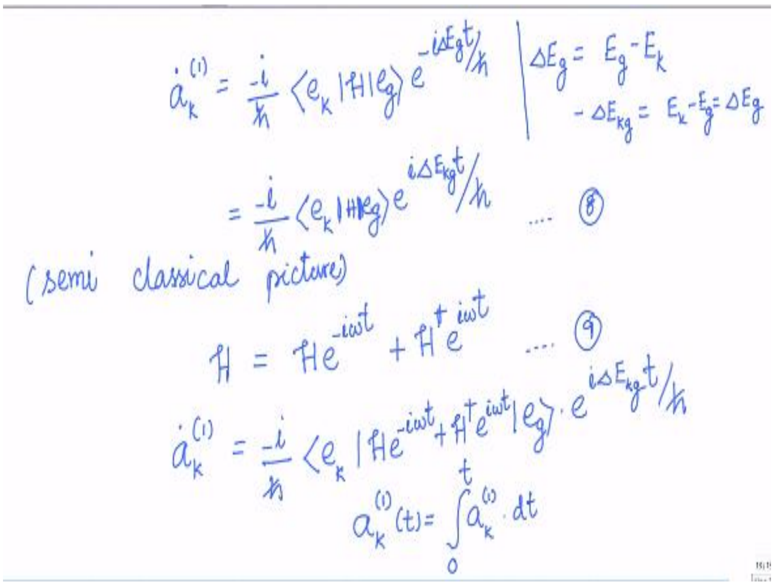

$$\dot{a}_k^{(1)} = \frac{-i}{\hbar}\langle e_k|\mathcal{H}|e_g\rangle e^{-i\Delta E_g t/\hbar} \quad \Big| \quad \Delta E_g = E_g - E_k$$

$$-\Delta E_{kg} = E_k - E_g = \Delta E_g$$

$$= \frac{-i}{\hbar}\langle e_k|\mathcal{H}|e_g\rangle e^{i\Delta E_{kg} t/\hbar} \quad \ldots ⑧$$

(semi classical picture)

$$\mathcal{H} = \mathcal{H}e^{-i\omega t} + \mathcal{H}^{\dagger}e^{i\omega t} \quad \ldots ⑨$$

$$\dot{a}_k^{(1)} = \frac{-i}{\hbar}\langle e_k|\mathcal{H}e^{-i\omega t} + \mathcal{H}^{\dagger}e^{i\omega t}|e_g\rangle \cdot e^{i\Delta E_{kg} t/\hbar}$$

$$a_k^{(1)}(t) = \int_0^t \dot{a}_k^{(1)} \cdot dt$$

In other words, we can actually use that information and write this whole expression as ak dot to the first order is given by -i h cross ek perturbation Hamiltonian eg e to the power -i we wrote Eg right, what is this Eg, EgT by h cross where our Eg essentially is a difference term you remember that corresponds to Ek - Eg, it is important to remember the sign. So let us go and crosscheck what is it, it is actually Eg - Ek its delta n we have written here and delta n is En - Ek, so sorry delta En so until here we have written delta En and there is a small mistake.

So this should be actually delta, delta, and so then if we do that our delta Eg is basically Eg - Ek where delta Eg is given by Eg - Ek and we know the ground state is of low energy, so it is convenient to write it in terms of minus delta Ekg being equal to Ek - Eg which is equal to delta Eg alright. So now using this, we could write this expression as -i h cross ek Hamiltonian eg e to the power i delta EkgT by h cross, please notice the minus sign has been absorbed here because of the transformation that we have done.

So what we have is this expression, then representing the change in ak with respect to time, alright. So I am going to rewrite it neatly. So on change in ak with respect to time, so the real term if you want to actually relate to is that we want to know, so this reflects as you know the ak is related to the probability that we will find the system in a state k having started from state g okay at the start of the interaction and how is it changing with respect to time is what the ak dot is actually representing to the first order correction okay that is what this one is about.

So now what you are going to do now is that we are actually going to calculate the ak itself, not just necessarily the rate, but ak itself. So if you have to do that what we need to do is we need to integrate this ak over time okay and in order to do that we need the H, the Hamiltonian is time dependent that is the whole idea here. So since the Hamiltonian is time dependent, we need to be able to have a form for this Hamiltonian, otherwise it will just be a general expression of not much use.

So there, we are going to make a next step equating the perturbation Hamiltonian picking up a function that is suiting or more close to what we think is our disturbance or other perturbation by letting the light interact with the matter. So since it is an electromagnetic wave and at least for the first approximation what we are going to do is we are going to treat the light here as a wave here right. It is a classical picture that we are going, so it is called as a semi classical picture later in the course.

So we could write the electromagnetic radiation as an oscillating electric field so in which case the perturbation Hamiltonian H can be conveniently written as the H e to the power -i omega t, it is also called as a harmonic perturbation because the perturbation changes in its amplitude with a frequency of omega plus for the ease of mathematical convenience and the ease of proceeding forward with the derivation, we would write this perturbation Hamiltonian as a sum of two Hamiltonians that is basically this is called as a Hermitian adjoint of the Hamiltonian operator.

Basically you would like to express this as complex conjugates you will see why it is pretty convenient here, comes in handy. So you could write this as sum of this e power i especially two different complex numbers operated by, I mean multiplied by Hamiltonian operator and its Hermitian adjoint. So we would substitute. We can substitute this into the above equation. So let us just call it equation 8 and the description of the Hamiltonian itself as equation 9.

Substituting 9 into 8, we obtain ak dot to the first order is given by -i h cross ek Hamiltonian e -i omega t + Hermitian adjoint ei omega t eg times e to the power i delta Ekg h cross. Please make sure that I am not missing any terms here. So just write it properly, it is e to the power i delta Ekg t by h cross alright. So, now you can see this is a linear operation we can actually write it into 2 different terms and then go ahead and integrate or in other words we can actually we can estimate the ak dot first order correction to the first order as ak as a function of time right.

It is changing as a function of time as this integral 0 to t ak of dt and substituting this the whole expression and then integrating it over, what we will see.

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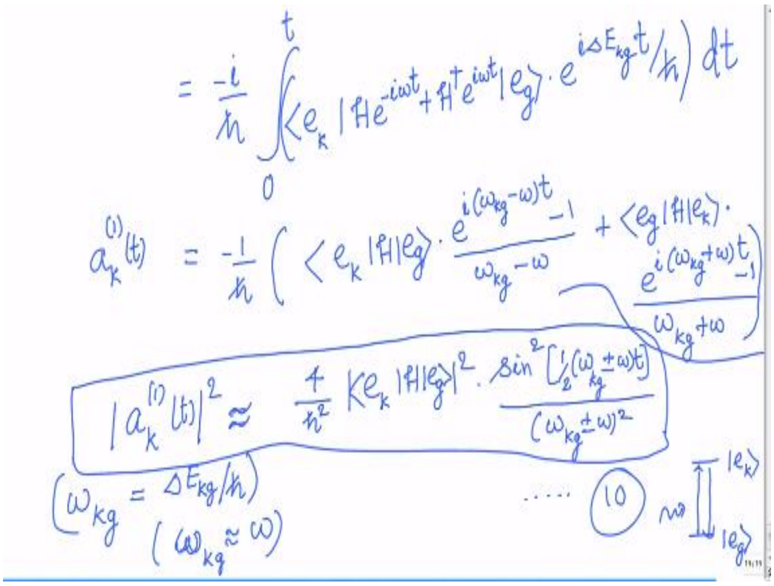

$$= \frac{-i}{\hbar}\int_0^t \left(\langle e_k | H e^{-i\omega t} + H^\dagger e^{i\omega t} | e_g\rangle \cdot e^{i\Delta E_{kg} t/\hbar}\right) dt$$

$$a_k^{(1)}(t) = \frac{-1}{\hbar}\left(\langle e_k|H|e_g\rangle \cdot \frac{e^{i(\omega_{kg}-\omega)t}-1}{\omega_{kg}-\omega} + \langle e_g|H|e_k\rangle \cdot \frac{e^{i(\omega_{kg}+\omega)t}-1}{\omega_{kg}+\omega}\right)$$

$$\boxed{|a_k^{(1)}(t)|^2 \approx \frac{4}{\hbar^2}|\langle e_k|H|e_g\rangle|^2 \cdot \frac{\sin^2[\frac{1}{2}(\omega_{kg}\pm\omega)t]}{(\omega_{kg}\pm\omega)^2}}$$

$(\omega_{kg} = \Delta E_{kg}/\hbar)$

$(\omega_{kg} \approx \omega)$

..... ⑩

So substituting this and if you actually do the integral, then what we can actually see is integral the integral goes as -i h cross integral 0 to t, I have dt which would mean, please go ahead and calculate what you will see is that it will work out to -1 by h cross times two terms, term number 1, ek the Hamiltonian eg times e i omega kg - omega t – 1 divided by omega kg - omega + eg the Hamiltonian ek times e to the power i omega kg + omega t - 1 divided by omega kg + omega.

Now this is the expression for ak to the first order as a function of t. So now the real quantity of interest that we actually are looking for is modulus ak t the square of that and we can actually go ahead and calculate. There will be again many terms and we are going to neglect some of the cross terms and the approximation because what we are really interested in is a special situation where this omega kg I have to define that first, where omega kg is nothing but you remember our delta Ekg by h cross.

So I have because there are many such things and we are going to have omega cross, so it is easier to represent them as an angular frequency, so I am actually doing that, so that is what is happening here. It is actually delta Ekg by h cross. The condition that we are actually interested in is for omega kg is approximately or pretty close to omega okay. In that scenario, we could actually neglect some of the cross terms. So let us make an approximation here. So let us write it down as approximation.

Please go ahead and verify yourself 4 by h cross square times ek Hamiltonian eg modulus square is very very important term, please keep a note of it, and times sin square half omega kg + actually there will be 2 terms we can write it in a concise form using a plus minus notation so let me rewrite it here as half and omega kg + - omega t divided by omega kg + - omega whole square. So this is a very important result. It illustrates quite a few points, alright.

So let us call that as equation number 10 and a big nice box and it illustrates quite a few points. Number one first and foremost is that you realize the ak t it goes as modulus square of this term, it is called as a matrix element, modulus square of the matrix element because basically the Hamiltonian operator that the perturbation Hamiltonian operating on the ground state puts you in the system in a superposition state and from that superposition state we are actually pulling out what fraction of that superposition state corresponds to ek, a state k.

This is the state we are interested in asking if the system has gone to that state k with energy ek alright. So you start with a ground state eg okay and because of the light and the matter interaction captured by this Hamiltonian, the system is thrown into some kind of superposition state and then what we are doing is we are taking the scalar product with ek and the modulus square of it right, keeping in terms with what we have described in terms of Born’s interpretation and all that.

It tells you that now I am going to look for from the resulting superposition state what fraction of it is actually ek. If there is a higher fraction, then we say that the transition has happened from eg to ek, then this system has moved from eg to ek. Interestingly since it is a modulus square, we will quickly see it is insensitive to the fact whether the system goes from eg to ek or ek to eg, both of them will give you the same number.

The rate of transition given by this ek of t will be exactly same because you see the only places the ek and eg omega k and the k and g terms are coming in are in this matrix element which is under the modulus square and then here again omega kg alright. So we will dissect out this term a little bit more and then show you that in one case where it is absorption, one will be positive and other will be negative.

So basically they corresponds to absorption and emission process and all we are seeing is that upon shining the light, you have equal probability of taking the system from ground state to the excited state as that of taking the system from the excited state to the ground state. Then why do we have this notion that we see the molecule absorbs or the system absorbs the light on its interaction that we will soon see is predominantly because of the fact, when it is dominantly because of the fact that the population distribution of the molecules are to start with present exclusively in the ground state.

A large fraction is in the ground state, as a result you tend to see net absorption because there is not nothing much there in the excited state at all for it to come back. If it were to be there, then the probability that the light will take it from the excited state to the ground state is exactly same as that of the ground state of the excited state or in other words what we are saying is that by doing this framework or by going through this description, what we have inadvertently landed on is the fact that the light that causes the absorption can also cause an emission.

This we will call it as a stimulated emission because it happens in the presence of the electromagnetic radiation. We will expand on this a little bit more and then bring it to a closure of doing an experiment with an absorption spectrometer and what would we get in such a result and how do we equate that to this terms and parameters that we have put in, alright. I will see in the next class.