Optical Spectroscopy and Microscopy
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Lecture – 10
Fundamentals of Optical Measurements and Instrumentation

Hello and welcome to the lecture series on optical spectroscopy and microscopy. In the last class, we were actually developing a framework based on time dependent perturbation theory to understand how the light interacts with the matter. In brief, what we said was that we are going to take a system that can interact with light and then if you want to see how it is going to behave the first thing we are going to do is that we are going to write down its unperturbed, meaning before the light were to be shown on that system, whatever the energy states that the system can have, the molecule of the atom or in general a chromophore can have.

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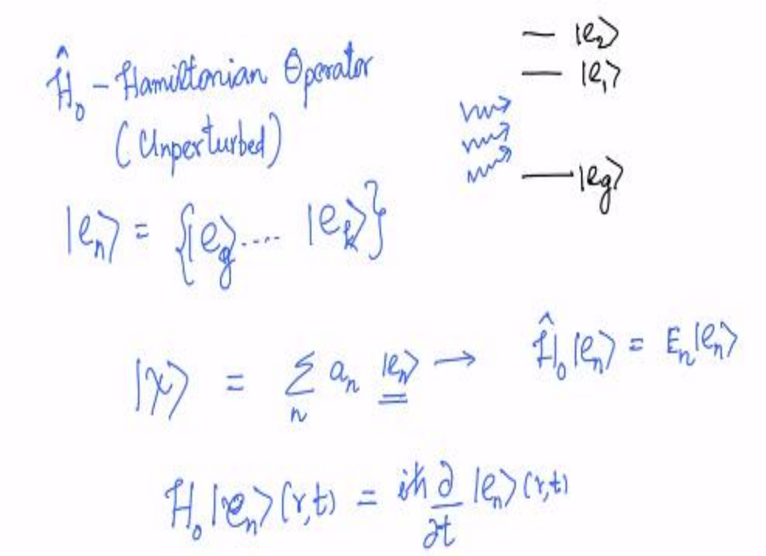

So we said okay let us take a system of energy eigen kets and we will represent the system in general as en where the e corresponds to different energy eigenstates, these are eigenstates of the Hamiltonian operator H0 specifically and the H0 not is the Hamiltonian operator of the system that we are studying when there is no light okay. It is called the unperturbed a Hamiltonian operator, so before the perturbation, unperturbed Hamiltonian.

So this is just before we started, these were the eigenstates the e's ranging from in general en set of eigenkets ranging from e1 all the way even eg the ground state all the way to some ek, we call them as the energy eigen states of the unperturbed system. So the idea here is that we are going to say the new energy eigen kets, the new energy states available for the molecule or for the system that we are studying can be described in terms of a linear combination of the existing, I mean the unperturbed energy eigenstates that is the perturbation is such that it is going to change the state of the system.

But the changed states we can write down still in terms of the original unperturbed energy eigenstates or in general after the perturbation if you have to represent the superpositions, if you have to represent the state of the system as a superposition, we talked about the superposition principle from Dirac's formalism, right. So now, this superposition would be some kind of a linear combination of these energy eigenstates okay.

Now, what we realize is that these energy eigenstates the ens that we are talking about these energy eigenstates of the unperturbed Hamiltonian that means that I would be able to write this as something like the operator H0 the Hamiltonian operator operating on the e0 will give you the energy out as an eigenvalue of the system. So now, this has one more restriction. Since these describe the state of the system, they have to also obey the Schrodinger's equation.

So, the Schrodinger's equation is given by it is in en, these ens are actually function of space and time and is given by ih cross the dou by dou t of en prime of r and t, space and time. So now this is a restriction because these describe the stationary states or this represents a state of a system, right. So Schrodinger said that if it were to describe a state of system, then it has to obey this relationship that puts in a restriction on the kind of solutions that the kind of forms that the en can take alright.

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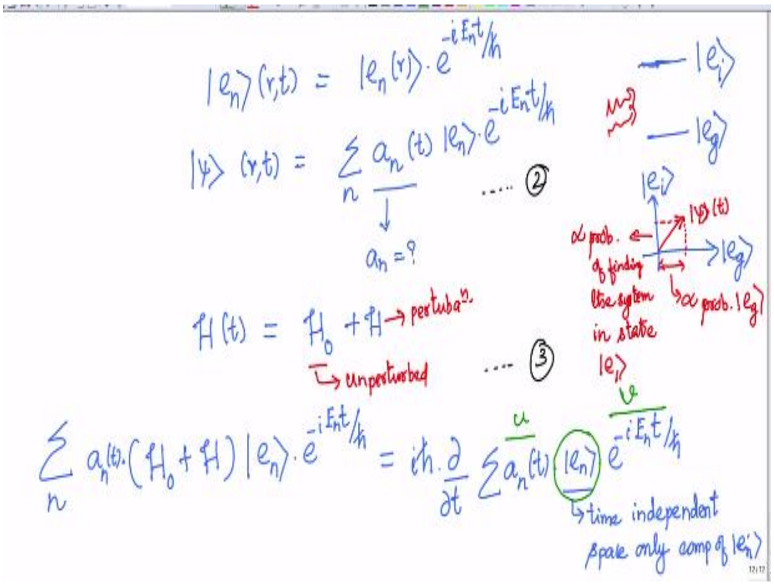

So one of the general solutions for the en that satisfies the above equation is of the form the en in general dependent on space and time can be written as a space only component, alright. So, I am going to write it as en just space only component en of r times e to the power minus iEnt by h cross. Now the h cross here, we have seen the h cross before and En is the energy and t is the time.

Now if we use this in our superposition, then we can write the psi itself r, t as summation of an, summation is over all the eigen kets or the eigenstates of the unperturbed system, an these coefficients time en e to the space only components times Ent over h cross. Now as we will see since this superposition state in the last class what we have seen is that this is a superposition state that describes the time evolution of the system, which means this should be holding true even at time t = 0 alright.

So if this were to be holding through even at time t = 0, then these ans essentially are going to tell you the distribution of the population at time t = 0, alright. From that time onwards, things start changing, which means this coefficients an themselves have a time dependent behavior right. So, I showed this in a simple 2-level system. If you think of 2-level system alright, we have a ground state and an excited state here right represented by e1.

So then this 2-level system can be thought of as 2-dimensional system where one of the dimensions happens to be the eigen ket of the ground state and the other is that of the excited state. Now what we are saying is that we are going to represent the change state as an arrow that is described by a linear combination of these two basis vectors and what we are actually asking is, this actually evolves as a function of time, now this is a function of time this vector per se.

Now what we are saying is this is our ki and that is changing as a function of time, essentially what we are trying to do here is to take the projection, right. This will tell you it is related to, right, so this projection reflects is proportional to the probability of we finding the system in the ground state and this in turn is proportional to the probability of we finding the system in the excited state, system in state e1. Now this is probability of finding the state in state eg. Now since this is changing as a function of time, you would see that the ans themselves are going to be varying as a function of time.

So now at t = 0, you would if we are talking about a purely electronic system and then you will see that almost all of the population is at the ground state, so what you would have is the ag = 1, ag while the an for all n's that is not g will be equal to 0. From that point onwards, it is actually moving or changing to represent how the population is changing over a period of time. So, the question now boils down then to evaluating this ans, if we know the ans, then we would be able to write down the system time evolution okay, so that is the goal.

So can we find out the ans? The answer is yes we can find out. The way we do that is we make use of some of the principles of the vector space that we saw using the polarization and so on and the principles of quantum mechanics that we use to describe the uncertainties before. So, what we do? The first thing is that we realize that the new Hamiltonian, the time dependent Hamiltonian that is operational alright from the time point where we start to shine the light in general can be written as H0 times h okay.

Now it is the fact that we can write like this is an important assertion here, we could actually write it like this is very very important because what we are saying here is that you would be cleanly able to separate out the perturbation as and the new perturbation that is because of the light that you are shining in as an addition to the unperturbed system, right. So remember these are the unperturbed Hamiltonian H0 and this H is the perturbation itself. Now, if you can write it down as H0 + H and it is no wonder, I mean this again is describing the state of the system.

So it should obey the Schrodinger equation too which means we should be able to combine this equation, the equation for the new Hamiltonian along with the superposition state psi and make use of the fact that the psi is a superposition of eigen kets, energy eigen kets of the unperturbed Hamiltonian. So in short, we can write the equation let us call this as equation number 1 okay. We can write the equation number 1 making use of 2 and 3 as follows, alright. Our Hamiltonian is given by H0 + H operating on psi right.

So the psi here is the linear combination, so I could in principle take this Hamiltonian operator inside the summation, is a linear operation so what I can do is, do this an, remember these are function of t evolving over or changing as a function of t operating on en times e to the power minus iEnt by h cross, that is the left hand side of the equation number 1. We know that is equal to that minus it is ih cross dou by dou t of this summation an of t en e to the power minus iEnt by h cross.

Now, please remember this is a time independent, this en is time independent space only component of the energy eigenvector en or en prime if you want to distinguish, right. Which means when you are taking the partial derivative, this will have 2 terms, one corresponding to this is of the form u times v, so that is your u and that is your v while this en because of the time independence stands out as a constant. So, let us do this differentiation and I am going to move to the next page and just carry on only the right hand side alright. So, let us go to the new page.

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$$= \sum_n i\hbar\left[\dot{a}_n(t)\,|e_n\rangle e^{-iE_nt/\hbar} + a_n(t)|e_n\rangle\, e^{-iE_nt/\hbar}\left(-\frac{iE_nt}{\hbar}\right)\right]$$

$$\sum_n a_n(t)\left[H_0|e_n\rangle e^{-iE_nt/\hbar} + H|e_n\rangle e^{-iE_nt/\hbar}\right] = \sum_n i\hbar\, e^{-iE_nt/\hbar}\left[\dot{a}_n(t) - a_n\frac{iE_nt}{\hbar}\right]|e_n\rangle$$

$$\langle e_i|e_j\rangle = \delta_{ij} \quad \begin{matrix} =1 & i=j \\ =0 & i\neq j \end{matrix} \quad \ldots\ldots (4)$$

$\times \langle e_k|$

$$\sum_n a_n(t)\left[\langle e_k|H_0|e_n\rangle e^{-iE_nt/\hbar} + \langle e_k|H|e_n\rangle e^{-iE_nt/\hbar}\right] = \sum_n i\hbar\, e^{-iE_nt/\hbar}\left[\dot{a}_n(t) - a_n\frac{iE_nt}{\hbar}\right]\langle e_k|e_n\rangle$$

$1 = \langle e_k|e_{n=k}\rangle$

The right hand side of the previous equation is given by ih cross dou by dou t of the first thing would be dou by dou t of an of t, so we will abbreviate it as an dot of t times en, the rest everything remains just the same which is iEnt by h cross plus the derivative of the second term. Now we keep these things an of t en it is dou by dou t of this term, the v term, it is an exponential, so we are going to get this form h cross multiplied by minus iEnt divided by h cross okay.

So now, what we can do is that we can do the same thing for the left hand side, what we make use of is that you will see that there are 2 terms, one corresponding to H0 operating on en of this whole expression and the other corresponding to the perturbation Hamiltonian. So what we will do is we will now concentrate on the left hand side of this equation. So if you write it, we will split them into 2 terms.

So an of time t operating on H0 en e to the power minus iEnt by h cross, alright so just make sure we are not missing anything, + the perturbation Hamiltonian en e to the power iEnt by h cross = ih cross times e to the power minus iEnt by h cross times, taking the exponential term as a common that we have is an dot of t derivative of an, actually you have a minus coming in from here, so that is minus an times iEnt by h cross. So there will be a term here, I am just writing it down which is basically your eigen ket en.

There is the summation term here which we missed, so we need to summate this whole thing across n alright. So now if you notice this term right, it is summation of n, so an of t H0 e to the power n this term is would be exactly same as that of this term, alright, because when the Hamiltonian operates on this en this being the eigen ket is going to give you the eigenvalue. So what you will have is, if you notice here that as I was telling you that the Hamiltonian H0 is the unperturbed Hamiltonian.

It is operating on an eigen ket and then the perturbation Hamiltonian is operating on another eigen ket and the goal here is for us to actually figure out what this ans are and one important step that we need to take following this to obtain the expression for an is make use of the fact that the energy eigen kets or the basis sets that we have used have the property of orthogonality that is the property where we know that we can write it as en, in general eiej, basically you are taking a product of the corresponding or any bra vector i with a ket vector ej.

Then it has this property because it forms the basis and we require this to be the property which is Kronecker delta ij which says it will be equal to 1 only and only if i equal to j and be equal to 0 if i not equal to j. So what we will do is that both the left and the right hand side we are going to multiply with a bra vector ek alright. We are going to left multiply with the bra vector ek the entire equation.

So one can write down this then as summation an of t ek Hamiltonian en e to the power minus iEnt over h cross + ek Hamiltonian en e to the power minus iEnt over h cross = summation of n ih cross e to the power minus iEnt by h cross this same term an dot of t minus an iEnt over h cross ek over en and since this the eigen kets has the property illustrated in this equation, equation number 4, this whole thing can be rearranged into as a simple form. Simple form wherein we can say ak dot alright, where is ak coming from, let us look at the previous equation, ak is coming from the fact that you are on the right hand side.

On the right hand side what we see is that this term let us underline here, this term will ensure only things of ak of the form where ek n = k survives, rest everything goes to 0 because the n is going from 0 to whatever the number it is, so which means when we go one term after the other only for the term where the n becomes equal to k you have this product working out to be ek given by en = k right. It is only for this will become equal to 1 and everything else it will be a 0, right.

Wherever n is not equal to be it will be 0 which means this whole term from this entire summation infinite number of terms only one term survives and that term will have the n = k, which means all of these ns we can safely replace it by k, maybe we should write that right hand side first. If you do that, so we are going to replace that which is ih cross e to the power minus iEkt by h cross right, that will be the first term.

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$$\sum_n a_n \langle e_k|\mathcal{H}|e_n\rangle e^{-iE_nt/\hbar} = e^{-iE_kt/\hbar}\left[\dot{a}_k(t) - \cancel{\frac{a_k i E_k t}{\hbar}}\right]$$

(✓)

$$\dot{a}_k(t) = \sum_n a_n \langle e_k|\mathcal{H}|e_n\rangle \cdot e^{-\frac{iE_nt}{\hbar}} \cdot e^{iE_kt/\hbar}$$

$$= \sum_n a_n \langle e_k|\mathcal{H}|e_n\rangle \cdot e^{-i\Delta E_n t/\hbar}$$

$$\Delta E_n = E_n - E_k$$

$$\boxed{\dot{a}_k(t) = \sum_n a_n \langle e_k|\mathcal{H}|e_n\rangle \cdot e^{-i\Delta E_n t/\hbar}} \quad \ldots\ldots (5)$$

So let us write down e to the power minus iEkt by h cross within bracket an dot becomes ak of dot of course it is dependent on time minus what we have here, this an becomes ak again and iEkt by h cross. You will have akiEkt over h cross, good. So what it means is that this whole term got simplified now ek en becomes equal to 1 which means this whole term now gets simplified into one and only one term. Similarly we can also think about the left hand side now.

So since the same logic operates here, so what is going to happen is that the Hamiltonian operator is operating on the energy eigen ket of this guy, so it is going to spit out its energy eigenvalues and if you write down those energy eigenvalues what do we have is, what we can actually do is that we can make use of the fact that this H0 represents the unperturbed Hamiltonian operator and it is operating on its own eigen kets which is going to give you the energy eigenvalues.

So you put that in, so then you will see that a similar term ek en will come out resulting in terms corresponding to n = k surviving, let us circle it with the green, in this part of the term alright. In this part of the term, what you will see is you will have a similar term because Hamiltonian is the operator which whose eigen kets are en blah blah. So what you have is that you will end up having this kind of vector see ek en products, which means this whole series of term will collapse into things corresponding to n = k.

On the other hand here, this Hamiltonian that the perturbation Hamiltonian here, it is not necessarily having ens as its eigen kets, so we cannot do much about this side of the term.

However what is going to happen is that we can actually nicely write that as summation over n we have an times ek H en e to the power minus iEnt over h cross this term right, this whole left hand side comes from this part of the equation alright, this part of the equation we are just carrying it forward right because there is nothing that you can do about this.

So this whole series comes out as a term here, so just to keep it color consistent, I will have rewrite it, however, what happens to this one, the first term right, the one that we have written in the green. So now we will see that that first term in turn can be when you write it out will correspond to this okay. Please work it out at home as an assignment, I am pretty sure you would be able to see that. When it comes out as this right ak i Ekt over h cross all that we are doing is that this is going to have, this whole thing is going to boil down to ek en with n = k similar thing something like this.

So then you can use that and when you use that you will see that the left hand side cancels, the green color right that is that term will be equivalent, so it will cancel out, this whole thing will cancel out with the extra term that we have, not specifically written but I asked you to evaluate. The end result is that you are able to write down an expression for not ak per se but instead derivative of ak as a function of t, we can write it down as the following an en Hamiltonian, sorry this should be ek, en times e to the power minus iEnt over h cross.

Now this exponential right, the exponential that is hanging around here right, so now that exponential is going to come. If you notice, this does not have any ns right and when we move it to the right hand side you can actually take it in and then what you can write it down as e to the power iEkt over h cross or in other words we can abbreviate this as n an ek Hamiltonian en times e to the power minus i delta En t over h cross where delta En is given by En – Ek.

So here we are specifically writing minus of delta n which will be Ek – En, so Ek is positive and En is negative, so that is why we are able to write it as like this. So now what we have is specifically an expression for ak the first derivative of the coefficients in terms of the expansion coefficients an times ek Hamiltonian en times e delta Ent over h cross. Now, let us call this as our expression number 5.

In the next class, what we will see is that how we actually go ahead and evaluate ek dot from this expression, but then I would request you to remember or write down this expression in a bold form so that we will go back and refer to this many times in the course, but as again for people who really could not keep track of what we are doing mathematically please bear with me, do not get bogged down by the mathematical steps that we are taking and writing down things, I am going to illustrate just the way I am talking to you about here.

I am going to illustrate as and when we reach a critical point or the critical step what is that that you need to take away from this derivation okay. Right now, what we have done is that we have made some assumptions about the nature of the perturbation and we have made use of the frameworks, the Dirac's formalism of the ket vectors to describe an atomic system or a molecular system at that microscopic level and said that how we can use the framework to obtain the coefficients of expansion.

The hope is that we would be able to write this in more measurable terms in the coming class, from there we would be able to relate this to an experiment that we can and normally do in our lab on a day to day basis. Thank you. I will see you in the next class.