Lecture – 13
Fundamentals of Optical Measurement and Instrumentation

Hello and welcome to the lecture series on optical spectroscopy and microscopy. So far what we have seen is that how to treat the interaction between the light and the matter and we were trying to obtain the expression for expansion coefficient ak to the different order and specifically we obtained an expression for ak to the first order correction.

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If you rehash, go back to our notes what we will see is that we have obtained the expression in the last lecture as ak of the first order the modulus square of that is equal to 4 by h cross square modulus square of ek Hamiltonian, the Hamiltonian this is a perturbation Hamiltonian eg and modulus square times sin square half omega kg + or - omega t by omega kg + or - omega. Now towards the end, what I claim is that this allows us to look at the process that we did not necessarily know about to start with or did not make any assumption about it to start with.

The process I claimed was that or the phenomena that I, it is not the process, the phenomena. The phenomena that I claimed was that the probability that the light will interact with the matter and take the system from a state eg to ek, is exactly equal to the light interacting with system already present in ek and then taking it to eg or in other words I said given the

expression of ek, the order in which the transition is going to happen is immaterial to its magnitude. So either going from g to k or k to g, it has equal magnitude.

How do we know that? The reason the way we know that is because it is actually goes as the modulus square right, so please note here we are using the modulus square and since it is a modular square, you are insensitive to the fact where are you starting from and as a result there are some interesting consequence and let us look at that in this class and try to see what we can actually learn or what we are going to measure when we take this system and put it in an absorption spectrometer, alright.

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So the first thing we realize is that, first thing I would like to state is in obtaining this expression, we made important observation that the 0th order correction for ak right, when we are looking at that ak dot turned out to be 0 and that implied ak to the 0th order can be written as a constant right, and I said this reflects essentially the initial conditions that is the condition in which you are starting your system. What we did here was that of all the possible ak's that of the various different values that the ak can take.

What we did was to say that okay, I am going to pick out one of them because I know that is where I am actually starting, that is where my system is starting, and I gave a rationale for the thermal equilibrium and so on and so forth., but the point here is I am going to pick a state in which the system is starting right and let us we call that state ak, the state in which I am starting as g, I said that equal to 1 that is the coefficient of that is equal to 1, which essentially means the entire superposition right, is dominated by this because for every other ak which is

not equal to g, I am setting that equal to 0, which is basically if you remember our psi is a linear combination right.

So that in the linear combination, we are saying that it is nothing but just eg and everything else is 0. So I could in principle have taken any state k, let us say for example here give a name not g but any state ak = 1 as 1 and all other states k not equal to 1 equal to 0. This would include that ag is also equal to 0. This is also a perfectly possible situation right, it is not contradicting anything. All that we need is that this were to reflect the physical reality of my system at time t = 0.

So, what would that be? That would mean that the label that I am giving ak = 1, the e1 the system is in the state e1 and I would not be able to find the system in any other state to start with. If that is so, now we can look back at our integral, look back at the expression for ak of t to the first order and then ask what the different terms in that expression mean? So let us look at this now. This is the expression right before the box that I am talking about, ak to the first order of as a function of t has many terms and let us look at.

Let us call this as term number 1 and the rest of it, the addition right, this as term number 2. Now if you notice carefully, they are different, where they are different is in the term omega kg - omega versus omega kg + omega that promptly gets reflected in here right. There is an omega kg + - Omega, so the minus term will correspond to the minus and the plus term will correspond to the plus and so forth. So now we are going to dissect out in scenarios so where omega kg is lesser than 0, let us call that as scenario number 1 and omega kg greater than 0 scenario number 2.

We can call omega kg greater than or equal to 0 as scenario number 2. All I am saying here is that omega kg is in one is negative and in the other is positive, alright and for both the cases, I am going to pick my light radiation such that the frequency corresponding to its energy omega is pretty close to omega kg, the frequency corresponding to the energy gap between them alright. So using these, we can look at, we can kind of try to reconstruct the physical equivalence of these 2 scenarios what would they would correspond to.

Now, the omega kg is lesser than 0 scenario number 1 what it means is that remember omega kg is omega k - omega g. The situation here is that we are going to say that omega k is lesser

than omega g okay and in the scenario 2 what you are saying is that omega k is greater than omega g. Now remember that k and g are arbitrary terms that we have introduced. All it means is that this is the state that we started with right, g is the state that we start with you can think of, this is the assumption that we made.

This is the statement that we made and the assumption that we made and then obtain the expression that we discussed in the previous lecture or the expression for the ak itself., which means you can see that all it tells you is that the starting energy state is of a higher energy than the ending state okay. Now this I am going to claim corresponds to the situation where my ek in this case just to distinguish between ek you can think of the label being 1 and eg okay, this would mean that we are starting.

So we are still looking at the transition between k and g, however, the omega kg will be negative only in the situation where if we have started from the higher energy state. That is to say that for some reason I am choosing my initial state such that ak for equal to k is 1, but for all other cases including ag equal to 0. So it could be just ak or ak prime or whatever. This is an arbitrary label that we have chosen right. So this corresponds to the fact that we are starting from the excited state and going down that is what omega kg being negative would imply.

However, for omega kg greater than or equal to 0, all it means is that omega k is greater than omega g, this allows us to order the eigenkets terms of energy okay, that is all it is. We saying ek which is equal to 1 or just ek and this is eg. Here the initial state is here the eg okay and then we go to ek, so this would reflect absorption alright. So the key point here we need to remember is the g is an arbitrary label that we have introduced in our derivation. So at that point there is no necessity for us to order them in energy okay.

So you would order them in energy only if you are trying to relate it to a system that is taken physically and then at that point, then you have these different possibilities okay. In such a case what we are looking at is that 2 different processes, a process starting from the ground state going to the excited state, where ground state has the lower energy and you could as well start from a state corresponding to a higher energy that is from ek in this case, I could have set my ek of 1 or ak of the excited state to be 1 and all other coefficients to be 0 that would be the scenario number 1.

So for each of these scenarios, you will see one of the terms will dominate, why? Because of this denominator, omega kg - omega right. So, we are going to take the omega that is pretty close to omega kg, so if it is pretty close to omega kg this is going to go pretty close to 0 and you are actually looking at the limiting value of this expression. On the other hand still it would be this term, term number 1 when omega kg is positive and since it is going to close to 0, this term will be much greater than the second term where it is omega kg + omega and all it boils down to is 2 omega kg and that is not going to contribute much at all.

On the other hand when omega kg is negative, the situation reverses wherein you have the second term dominating over the first. So, you could think of this corresponding to the second term, corresponding to transition from the higher energy state to the lower state you may think of that as emission process and this as absorption process. Remember for this to happen, you need to have the light, you need to have the perturbation right.

If not for the perturbation, we will not have even come this far and hence the emission that is resulting from here we never intended to have any emission, we just took the system and shine the light on the system, but yet here we are where we arrive at an expression that predicts that the system can undergo a transition from a higher energy state to the lower energy state in the presence of the light.

Light can induce that transition with equal probability, why I am saying equal probability? Now when I said that one term dominates over the other, practically what you are saying is that ak of t is either this or the other and they are exactly equal except for the signs and if you take scenario 1 or scenario 2, you will see that both of them if you calculate the ak of t keeping in mind omega k is greater than omega g and omega k is lesser than omega g in scenario 1 and otherwise in the scenario 2.

You will see they are absolutely equal, they are exactly equal, ditto equal okay. Now that is why we say that the emission, the stimulated emission probability is exactly equivalent to that of the absorption okay, Now that is about the probability, but in reality if that being the case, then why do we even see an absorption, right? We visited this little while ago when we are talking about setting the initial condition right.

There is a thermal equilibrium, so in that situation what happens is rarely, almost never, you see a situation where the ground electronic state is sparsely populated than the excited electronic state when a thermal equilibrium is reached that is at a normal condition okay, and unless you have a special way of doing that, in fact we will see it later on in the course when you are talking about lasers and so forth, you actually want to create that and we have to take some extra measures to be able to really create that.

In such a case, what we are left with is even though the probability is equal you have to start with a bias towards some more number of molecules present in the ground state. As a result what you see is a dominant absorption process and the rate of such process we can actually go ahead and start to write down because that is exactly what you are going to measure when you are taking the system of a chromophore and then put it inside your absorption spectrometer and shine some light and then and then see how much of the light that you are shining is getting absorbed.

So if this were to be true, the whole framework and whole expression that you have obtained for measuring this transition, the probability of this transition is true, we should be able to predict what we would see in an absorption spectrometer. Now, we can actually do that and we are going to do that now. How are we going to do this? First we need to understand there are a few important things that is away, I mean that is different from what we have done here in an absorption spectrometer than here.

Number one it is going to be a broadband spectrum that is what we are going to use to excite the molecules. So what we need to do is that we need to estimate not the probable, it is not just sufficient to know the probability of transition caused by a light of angel of frequency omega. We actually need to know the probability of or we actually need to know the number of transitions per unit time in some sense that is exactly what we are going to measure in a spectrometer over a broad range of omega okay.

These are broadband excitation as we call it. So we would like to know if I were to give a light that is having a bandwidth okay, you can alter this bandwidth, you can actually make it very sharp but still there is a finite bandwidth of that light, if you are going to give that how is the system going to interact? There is also another way of looking at this whole thing. Even in a situation where we have, I mean in a hypothetical situation of where we have very

defined light with the supremely sharp bandwidth okay very very very very small bandwidth, very precise wavelength.

The energy states themselves alright, can fluctuate in its energy, why is that? There are several reasons starting from collision broadening to in the sense that when you have a system either in a solution phase what you are actually doing is that the chromophore molecules are in constant collision with that of the solvent molecules. When they are engaged in these collisions, what you end up having is a situation where the energy states are not necessarily sharply defined but rather it is spread about the ek's that we have actually proposed, I mean as eigenkets of that.

The eks are the unperturbed eigenkets, but then the collision by themselves can act as a perturbation right, the result of that is that you can you will see that the eks are not exactly defined as the ek, but there is a probability of you finding an eigenket which is slightly different because of you can think of this as a the spread of the ek about a mean okay. In such a case, you can think, you can talk about what is called as a density of the states okay.

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So if I were to diagrammatically represent this, we would like to draw or we would like to imagine the eigenkets to be sharp lines on the energy axis okay. So you have the energy axis here, increasing energy, so you would like to represent the eigenkets as sharp lines. What I am trying to claim here is that a more general case, a more useful case would be to think of this not as a straight line but really as you can think of the energy states as not as broad but these are my true energy states of energy eigenkets okay.

Now if I had a more general case what I was trying to argue for is really a situation where it is spread like that okay. The width and then if you were to remark the probability that you will have an energy state in a given energy, if you are to plot that, then you can think of them being existing as, this is the probability of you finding energy state and all I am claiming is that is dependent on omega k and hence the omega kg itself.

This probability that we are actually plotting this, so if the probability that you will see a state with an energy gap of omega kg is somewhat distributed like this where the central line is basically omega kg and here I am actually plotting the energy of an omega axis like energy axis where E goes in like this. So if there is a spread okay, this spread it is more practical and more useful to take this approach. If that is the case, then we can actually go ahead and calculate what will be the probability ak of t that is the probability of the transition, does it get modified or if it gets modified, how does it get modified right?

So you can think of this as is pretty much the same okay. So pretty much the same as what? As our this equation, equation 10, I am going to write down for let us copy this. It will be pretty much the same as equation 10 except now what I am going to do is, I am going to do 2 things. One is going to say that there are many such transitions possible around the kg. There are many states, so there are many such transitions possible, so I am going to multiply that by the density of the states.

So where I represent the density of the states around kg right, so that I represent it as rho, you can also think of that as the density of the incident light around omega. Essentially what we are trying to look at is that how different is our energy gap with respect to the incident light energy okay. So the spread could be coming from the inherent system or from the light radiation or in general could be from both. So if you take that as the power density distribution incident light radiation, then what we need to do is that we need to be able to integrate these probabilities over this entire omega, alright.

So given omega that is our probability, but there is also a possibility of system going to a state that is close to omega but not quite omega because the incident light radiation itself could be having the light whose frequency is slightly lesser than omega, slightly higher than omega. So, taking that into consideration, how do we do that is that we are going to integrate

this expression, to be general we will write it as minus infinity to plus infinity d omega. Now at this point we can take a closer look at this whole expression.

Of course now let us say for simplicity sake we are going to concentrate on the semi-classical representation of the electromagnetic wave and then we can say that the perturbation H that we have been talking about can be approximated to an electric dipole right. This is called as a dipolar approximation, basically this is telling you how does the potential gets perturbed at any given place r at a given displacement R because of the electromagnetic radiation with an amplitude E r epsilon as I have written it here.

So we can actually write this whole expression as 4 by h cross square modulus epsilon square minus infinity to plus infinity ek, epsilon has been taken out, so we can actually do that as r eg modular square sin square half omega kg + - omega t whole divided by + - omega square rho omega and d omega. At this point, what we can actually think of is looking at this right ek r eg the modulus square. So now clearly what is going to happen is that this ek is, this term is very specific, the term I am underlining in this line, this term is very specific for the transition between two defined states eg and ek okay.

Now since that you can think of as independent of the incoming omega that you are coming up with, what you can actually do is that you can write this term as independent as a result outside of this integral minus infinity to plus infinity.

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Now when we do that, we end up having 4 by h cross square modulus ek r eg - infinity to + infinity your sin square this term times t divided by this d omega. Now it is a sin square omega kn + omega divided by omega kg + omega divided by omega kg + omega here. So this integral you can estimate that to be 4 by h cross square modulus ek r eg square and it will turn out to be 2 pi into t okay. Now since we would be quiet often encountering this term, so it is very cumbersome to keep writing like this.

So what we can actually do is that we can equate, we can introduce a term called capital R represents that is the operator that we are using and this whole matrix element as can be written, I am going to write it as Rkg. So we could write the expression for ak modulus square which is the probability that the transition will happen given that you are shining a broadband light is given by 4 by h cross square times Rkg 2 pi t. Rate of transition is given by d by dT of this probability or in other words how this probability ak of t, actually the modular square of ak of t changes with respect to time.

If you do that, you will see that corresponds to 8 pi by h cross square Rkg modulus square the t is d by dt of t which is equal to 1, so it will boil down to this 8 pi by h cross times RKg square or in other words is directly proportional to modulo Rkg square okay. This we missed this term rho of omega, rho of omega kg around the kg, so it has to be kg so that is also, so this term carries over here. So this expression of the rate of transition being directly proportional to modulus Rkg square is also called as the Fermi's golden rule.

Fermi's Golden Rule abbreviated as FGR, it tells you that rate of transition between any two states k and g in presence of a perturbation, in this case electromagnetic radiation, goes as the modulus square of the matrix element and that is the bottom line of this entire derivation that we have seen. As long as you get that or you remember that, that is what you will be expected out of from this whole derivation.

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Fermi's Golden Rule: (FGR)

$$\text{Rate of trans}^n \propto |R_{kg}|^2 \cdot f(\omega_{kg})$$

So, I am going to just rewrite this which is Fermi's, this is such an important result, so I am going to write it as Fermi's golden rule. What you say is that rate of transition is proportional to the modulus square of the matrix element Rkg and the density of the states. This we will come back to time and again in this entire course when we go from studying one kind of interaction to the other interaction.

In the next lecture, what we will see is that using this how we can actually predict or how we can obtain the relationship between the intensity that we observe in a spectrophotometer and the atomic system alright. I will see you in the next lecture.