Optical Spectroscopy and Microscopy

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Lecture – 19

Fundamentals of Optical Measurements and Instrumentation

Hello and welcome to the lecture series on an optical spectroscopy and microscopy. So far what we have seen is that how we can describe the light matter interaction using a quantum mechanical approach for both the light radiation as well as for the matter. What we did was that we introduced the notion of Fock states and these Fock states described a number of entities that we are actually talking about and in this space we talked about different operators, creation and annihilation operator.

Using these operators we said that we can actually rewrite not only the energy states of the light radiation itself but we can actually quantize the matter itself and I gave a parallel saying that now the question that we are asking here is that given energy state how many of the entities, how many of the atoms, or how many of the chromophores are present there and so that is how we transposed the problem and then we combined that into a interaction Hamiltonian and then said okay when we did that combination, then we got an interaction Hamiltonian with lot many different terms.

To simplify that, we took steps, first step being we said okay let us concentrate on 2-level atoms, atoms with only 2 levels and then simplifies quite a bit and gives you still 4 different terms and then for each of this term, we went ahead and wrote down Feynman diagrams representing what happens to the matter of particles as well as the light okay. So when we did that, we say that only 2 of the processes can be considered as a process which can physically possibly occur because energy need to be conserved and we need to take into account that energy conservation.

If you take into account the energy conservation, then on being consistent about which one of the 2 state is lower and the higher energy, then only 2 processors are possible as a natural of low to high energy transition we call it as absorption and high energy to the low energy transition and emitting of increasing the photon density by one we call it as emission and just to remind ourselves let us go back and look at the expression that we have gotten and then there are 4 different possibilities.

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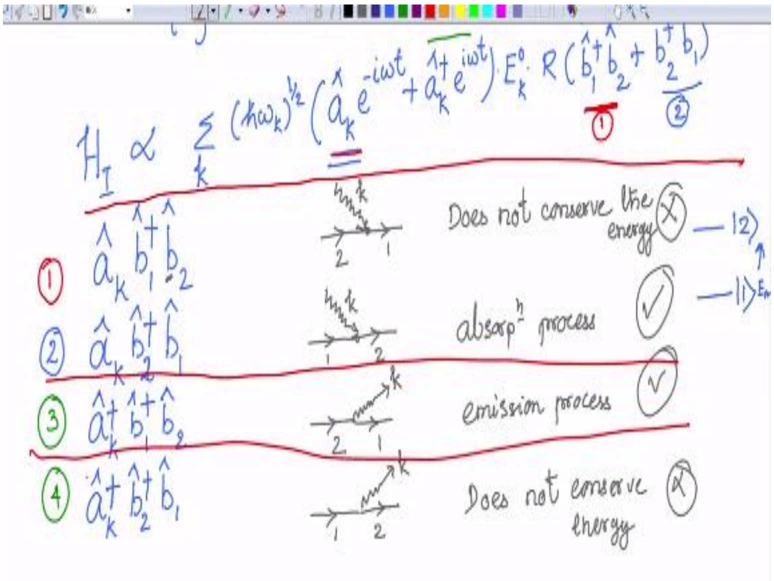

$$H_I \propto \sum_k (\hbar\omega_k)^{1/2}\left(\underset{=}{\hat{a}_k} e^{-i\omega t} + \overline{\hat{a}_k^\dagger e^{i\omega t}}\right) E_k^0\, R\left(\underset{①}{\hat{b}_1^\dagger \hat{b}_2} + \underset{②}{\hat{b}_2^\dagger \hat{b}_1}\right)$$

① $\hat{a}_k \hat{b}_1^\dagger \hat{b}_2$ Does not conserve the energy ✗

② $\hat{a}_k \hat{b}_2^\dagger \hat{b}_1$ absorp^n process ✓

③ $\hat{a}_k^\dagger \hat{b}_1^\dagger \hat{b}_2$ emission process ✓

④ $\hat{a}_k^\dagger \hat{b}_2^\dagger \hat{b}_1$ Does not conserve energy ✗

If you look at the screen, then you will see that the interaction Hamiltonian is written in the last class. We wrote the interaction Hamiltonian using this expression and then split that into 4 different possibilities and then said only these 2 possibilities exist, alright. So now what you are going to do is we are going to take the interaction Hamiltonian for these 2 processes which essentially means in the Hamiltonian because it is coming as additive operations, so we will take just this.

I am going to replace these product by ak, b2, b1 and I am going to call that as an absorption Hamiltonian and then with other things and then I am going to replace by ak dagger b1 dagger and b2 two. I am going to call that as an emission Hamiltonian. Again, the absorption Hamiltonian is going to have ak, b2 dagger, and b1 while the emission will have ak dagger, b1 dagger, and b2 okay.

So now before we jump into that, we need to pay a little attention into how we can go about calculating the matrix element, right, that is the transition rate that we are after. So the way we do that from time dependent perturbation theory is that the transition rates are estimated.

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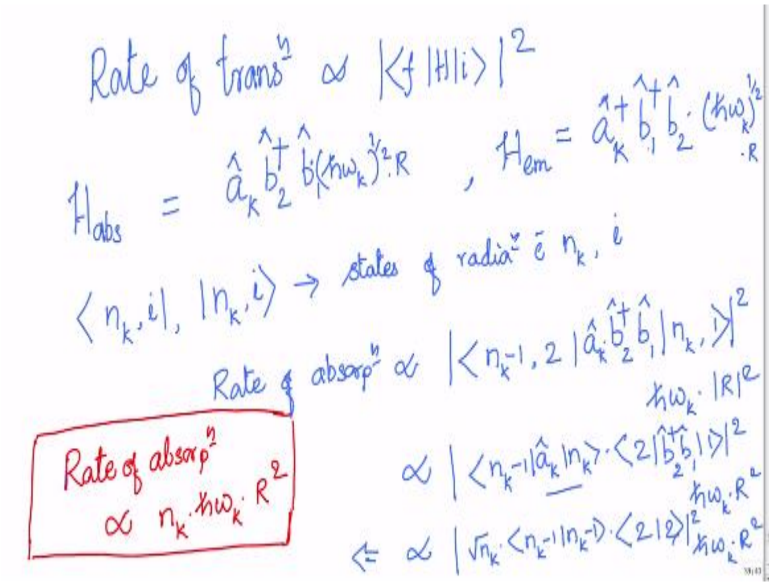

Rate of trans^{n} $\propto |\langle f|H|i\rangle|^2$

$H_{abs} = \hat{a}_k \hat{b}_2^{\dagger} \hat{b}_1 (\hbar\omega_k)^{1/2} \cdot R$, $H_{em} = \hat{a}_k^{\dagger} \hat{b}_1^{\dagger} \hat{b}_2 \cdot (\hbar\omega_k)^{1/2} \cdot R$

$\langle n_k, i|, |n_k, i\rangle \rightarrow$ states of radia^{n} $\bar{c}$ n_k, i

Rate of absorp^{n} $\propto |\langle n_k-1, 2|\hat{a}_k \hat{b}_2^{\dagger} \hat{b}_1|n_k, 1\rangle|^2 \hbar\omega_k \cdot |R|^2$

$\propto |\langle n_k-1|\underline{\hat{a}_k|n_k}\rangle \cdot \langle 2|\hat{b}_2^{\dagger}\hat{b}_1|1\rangle|^2 \hbar\omega_k \cdot R^2$

$\Leftarrow \propto |\sqrt{n_k} \cdot \langle n_k-1|n_k-1\rangle \cdot \langle 2|2\rangle|^2 \hbar\omega_k \cdot R^2$

$$\boxed{\text{Rate of absorp}^{n} \propto n_k \cdot \hbar\omega_k \cdot R^2}$$

We know that the rate of a process is, I am going to change the color to blue, rate of transition is directly proportional to modulus square of this matrix element okay, the final state and the initial state okay. So now the final and initial, here we are talking about 2 different entities right, 2 different kinds of entities here, one is the matter itself, other is the light radiation okay. So now we need to be able to write the final state for both of them and what we are going to do is that the Hamiltonian of the absorption process let us write it as H absorption is equal to our 2 which is ak b2 dagger b1 which is ak b2 dagger b1.

Emission I am going to write it ak cap dagger and b1 dagger b2 okay and then we have other terms okay. These Hamiltonians are resultant of this, then we have our usual h cross omega k to the power half the R itself okay. So we have along with this h cross omega k whole to the power half R and we will leave the unit vectors e cap and all that stuff. So if we leave that alone, then things that we have is just this and same way here times okay h cross omega k whole to the power half R okay, R here corresponds to the final state, I mean R12, it does not matter in our case R12 = R21 which is equal to R for a 2-level atom.

So we are just going to write it as just R, okay. So now, how do you write the final state or any given state when you have mix of components right. So clearly, the b operators represents the matter, so they will operate only on the matter states while the ak operators represent the photon state and they will operate only on the photons. So notations we could write like this such as nk, i there is a bra vector and the corresponding ket vector would be nk i would represent states of radiation with n photons of kth mode and molecule being in the ith state or actually let us I mean i here correspond to the state.

So let us say the i correspond to the number of molecules in the ith state okay. So if you take an atom, then it corresponds to saying whether the atom is existing in the ith state or not because the atom can be in one of the states at any given time. So we can think of if the atom is present in ith state, state then the number equals 1 and if it were to make a transition to some other state, then it will if you probe for how many number of atoms are there in ith state, it will be 0. So that is how you would like to think about this.

So in that case if you write like this, then you could represent this matrix element for absorption and the emission process and then calculate the rate of transition. So let us do that first for a absorption process. So in an absorption process, the rate of transition we can talk in terms of rate of absorption is directly proportional to modulus square of the final state. Now what is the final state here? Since it is an absorption, the number of photons okay let us say we are talking about kth mode photon, so the number of photons in the kth mode would have gotten reduced by one number, so we can call it as nk-1.

So nk-1 state and then the molecule goes to the, I mean the absorption process if you go back, the molecule goes to the state level 2 right, I mean energy level 2 two, so we would write that as 2, this being a bra vector representing the final state okay and the Hamiltonian itself is given by, I am going to write only the operators and collect all the other terms outside, so the operators here are ak cap b2 dagger and b1 one cap operating on the initial state. Initially, we had nk number of photons and the molecule was in state 1 okay.

This modulus square times the h cross omega k to the power half and R we can safely take it out, it is modulus square. So, it will be h cross omega k times the R square okay. So now what we can do is we can go ahead and be consistent with what we said, which is the ak's operate on the nk's and the b's operate on the matter states. So if you do that, then you will see what we have is that there will be the modulus of 2 things, which is a product of 2 things which is nk-1 ak of nk and we have state 1 okay and the whole modulus square.

We carry forward the h cross omega k and R square okay. So now if you remember so this ak is an annihilation operator which basically when operates on nk is going to give you, we have worked out this right, this product which is going to have under root nk times this right nk-1 nk-1 which is equal to 1, alright. Similarly if you look at this, the b1 is an annihilation operator okay and b2 is a creation operator. So it annihilates state 1 and creates b2.

So this remember we can represent as a projection operator basically it takes the component along the b1 and then projects it and generates another vector along the state 2 right. So this would then correspond to something like that times the number, number here is just the 1, so we will just, that will come out as just 1. So this modulus square h cross omega k times R square, I mean modulus I am just leaving it off. So, the end result would imply that the rate, okay I am going to write it a little albo so that we can also change the color so that it is an important result.

So the rate of absorption is proportional to modulus square right, this is one and that is one, so what we have is under root k modulus square which is actually nk h cross omega k R square. So what we have gotten is an expression for the rate that tells you that the rate of absorption is directly proportional to nk h cross omega k R square, so there is this usual suspects which is rate we expect it to go as that of the intensity of the light.

Intensity here you remember now we have moved from representing the light as electromagnetic wave into number of photons, so the intensity here really is about the number of photons and that is exactly what we have here nk and not any photons, but photons of mode k, energy k, and then goes as R square, the molecular property right that we have written down. This depends totally on the electronic configuration of the molecule and the electronic energy states okay 1 and 2.

Now we do that same thing for, so as I said there is no surprise it is a straightforward simple and it comes out quite naturally that the rate of absorption is directly proportional to the incident light intensity okay. Now, how about the emission?

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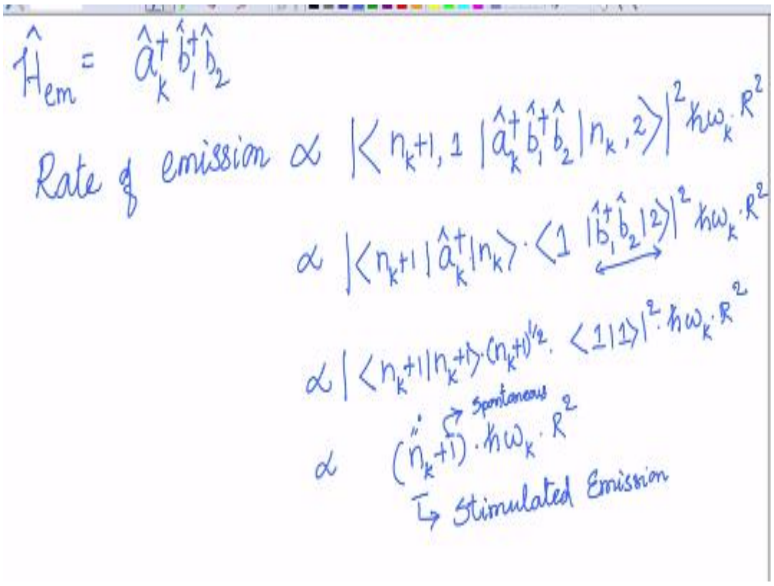

$$\hat{H}_{em} = \hat{a}_k^\dagger \hat{b}_1^\dagger \hat{b}_2$$

Rate of emission $\propto \left|\langle n_k+1, 1 | \hat{a}_k^\dagger \hat{b}_1^\dagger \hat{b}_2 | n_k, 2\rangle\right|^2 \hbar\omega_k \cdot R^2$

$$\propto \left|\langle n_k+1 | \hat{a}_k^\dagger | n_k\rangle \cdot \langle 1 | \underleftrightarrow{\hat{b}_1^\dagger \hat{b}_2 | 2\rangle}\right|^2 \hbar\omega_k \cdot R^2$$

$$\propto \left|\langle n_k+1 | n_k+1\rangle \cdot (n_k+1)^{1/2} \cdot \langle 1|1\rangle\right|^2 \cdot \hbar\omega_k \cdot R^2$$

$$\propto (\underset{\text{Stimulated Emission}}{n_k} + \overset{\text{Spontaneous}}{1}) \cdot \hbar\omega_k \cdot R^2$$

Now for the emission, let us do the same thing. What we are going to do is we are going to take this Hamiltonian Hem okay. So the emission Hamiltonian is given by ak dagger b1 dagger b2 alright. So, I am rewriting that Hem is given by ak dagger b1 dagger b2, good. So similar to what we have done in the absorptions case, we can calculate the rate of transition for the emission. Rate of emission will be directly proportional to the matrix element, again the same thing.

We have to write the final state except now here the final state that we are going to see that the number of photons, it is an emission process, so the number of photons in whatever the mode nk that it could be 0, it could be 1, whatever it is and we are going to have one extra photon of that and then we also going to have the state to be the 1 state in our description right. The one state is the lower state, so that would be there instead of 2 and then the operator is this ak dagger b1 dagger b2.

That is a final state for the emission and then the initial state for the emission would be we start with nk number of photons but start in state 2 alright modulus square h cross omega k times R square, now we can work out this. So this will mean that we can write nk+1 and being operated by ak, sorry +1 is not a subscript, it is a being operated by ak dagger times b1 dagger b2, sorry we are just segregating the photons from the matter state. So nk1 and then we have the nk alright times the final state 1 here b1 and we have h cross omega k R square.

Now what we will have is that let us look at this which is it is the creation operator, so it is going to increase. When it operates on nk, it is going to increase the nk, we know the expression for this right. We have seen this before and we have solved it in the class before, so what is that, ak dagger operating on nk is going to give us nk+1. It is going to generate this nk+1 state and the normalization constant there if you remember it is unlike annihilation operator, it would be nk+1 to the power half.

In the annihilation operator, we had just nk to the power half, this is nk+1 to the power half times this here again the same thing is going to the b2 when it is operating on 2 it is going to take this whole process right, this whole thing is going to generate our vector i proportional to the number here right b2. It is basically spitting out that number that is 1, so we will just leave it like, I mean we can state it or just leave it like that and say square h cross omega k R square okay.

Now, you can see if you expand it out and simplify, this will correspond to nk+1 whole square times h cross omega k R square. This is very interesting, why? First thing we see is that the rate of emission is directly proportional to nk+1, so first thing we see is that the emission is directly proportional to the number of photons that we started with nk, so which is the incident intensity right. So now this then clearly corresponds to stimulated emission right, but the interesting thing is you could start with nk being equal to 0, nothing stops you from that right.

So you could start with atom in a state 2 and then no photons in the nk mode at all. This predicts you would still have the emission process because if you set nk = 0 in this expression, even if this goes to 0, you have this the whole expression not going to 0, it is nonzero because there is a 1 here. Now that is your spontaneous emission process right, even in the absence of the any radiation, you would have this predicts that there will be an emission process.

Now this comes quite naturally in the second quantization or the quantum mechanical description of the light and the matter put together and unlike the previous version where Einstein had to argue out him taking the system and equilibrating with the blackbody and then saying okay the rates need to be equal but we know the rate constants are equal, then what is happening that the number need to be different and yet the number is different.

So if the number need to be different, then there has to be additional process that is independent of the light so that there can be a leak, thereby making the number being unequal, number of atoms in the ground state and the excited state being unequal. Now here, we do not have to do any of that. If you were to describe the light radiation in terms of photonic states of different modes, the 4 states here represents different number of photons like the Fock states and then similarly you do that for the atom 2.

The atoms existing in ground state, atoms existing in the excited state, then you put together these two description and ask what is the rate of a transition, either absorption or emission, maybe you are not doing that and if you say that for a 2-level system, then it comes out very naturally. You just take the emission process, I mean the emission Hamiltonian and look at it you see that the emission Hamiltonian naturally predicts that there will be emission even without an incident light being present.

Interestingly for the rest of the course that is of pretty important is that we also see that the rate of emission is directly proportional to nk the number of photons at the kth mode, thus stimulated emission. Now, this gives rise to the whole regime of generating light of its own kind okay. So, the transition is directly proportional to the number of photons of that particular kind, that particular mode nk, see the photon that is coming out is going to be of that kind, nk kind.

So, this tells us that if we ensure by some means that only, I mean there is a preferential selection for one kind of a photon of various possible modes okay, the preferred mode being k, then the generated photon as a result and if somehow if you do a cascading process, you can keep generating the same kinds of photon again and again and that is the principle of operation of the lasers. We will get into that in our course and before going there, let us look at the other part which is the spontaneous emission part.

The spontaneous emission part tells you that even I take the molecule to the excited state and leave it there and once I leave it there, it will with a finite probability come down, thanks to the nature of the light and the matter. Now, this process of spontaneously coming down, I have talked about this before and this spontaneous coming down we call it as fluorescence and it has some wonderful properties and we are going to study a little bit about one of the property.

Then I will tell you how useful that is to study many of the biophysical processes and the property here that I am going to talk about is that, there are many properties, but I am right now going to focus on one of its property, the property here is about isotropicity okay. So, now we have an atom, we know now we can excite the atom or a chromophore or a molecule and when it goes to the higher energy state and you leave it there, it has a finite probability of coming back.

When it comes back, it can emit a light photon and I am going to ask some final questions about the nature of the light photon that is coming out naturally, like this in the spontaneous manner okay.

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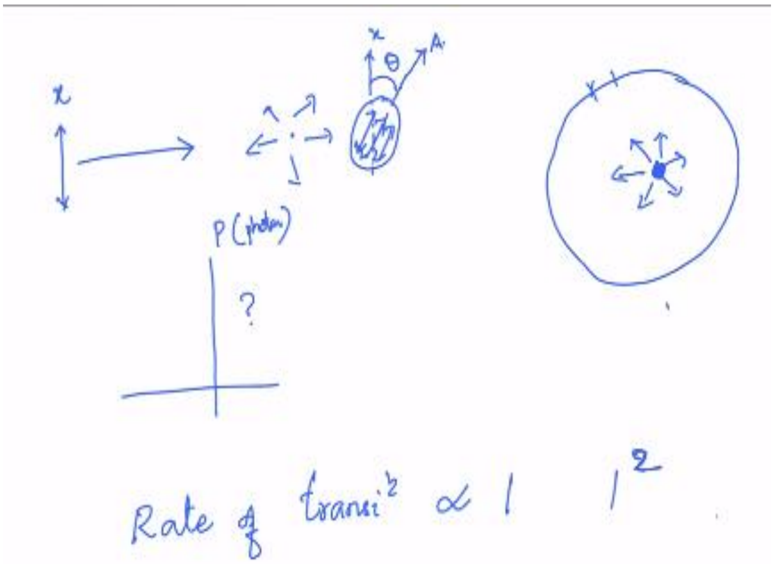

So first thing one would realize is that if you say that the chromophore represented by this circle here is present at this point as and we can say that if you approximate that to as a point object, then we can ask what is the probability that the photon will be emitted in any one of this direction. The direction here is a 4 pi solid angle right. So now, I am going to take a small chunk of it and then ask what is the probability of me locating a fluorescent photon?

It turns out that probability is isotropic, meaning if you draw a sphere around this and then ask how many numbers of photons in any given time would come out in a given area as long as you take the area elements to be same, then that is equal all throughout this sphere. So that is an isotropic probability of emission direction. However, there is something more interesting that happens when you introduce the polarization of the light, remember the polarization we have talked about and you can also talk in terms of the polarization of the photons, individual photons right from our beginning classes.

Now if you say that if you are exciting the molecule in a polarized manner, I mean using a polarized light and ask what is the probability of me finding a fluorescent photon whose polarization is similar, I mean same to that of my original photon, then you see that there is a distribution right until this probability. That is you not only get the fluorescence photon whose polarization is similar to that of your emitted photon.

But you also get photons whose polarization is slightly different from your initial starting state now or in other words, there is a distribution of source and photons whose polarization varies about the incident photon's polarization. So now can we estimate it that is the key here right, can we estimate it? If we can estimate it and what is the procedure that we are going to adapt to actually estimate it? The answer is of course we can estimate it, otherwise I would not be talking to you in the class. Now, how are we going to estimate it?

For that what we are going to see is that we are going to move away from individual molecules and then take an ensemble of molecules and think of this ensembles, and when you think of this ensembles, then you can bring in few properties. There in the resemble state, I mean in a solution state let us say, does not have to be a liquid but it could be gaseous or liquid, but let us say if you take a solution and the solution of fluorophore it is a solvent or then what we are going to do is we are going to come up with a light photon of a polarization along a preferred direction.

Let us call that as polarization along x and z being the propagation direction, y is orthogonal to this plane okay. So now I am going to incident this light onto my fluorophore and going to ask when I know that the intensity of the light that is coming out in any of this direction is equal, but what I can actually do is that I can actually put in a polarizer and ask and plot what is the probability, this is the probability of me finding the photon okay as a function of.

Okay, I am going to generalize this polarizer a little bit so as a function of the polarizer's crystal axis with respect to the incident polar images which we said is along the x direction. So what we are actually asking is, so that is our polarizer's crystal axis, so let us call it as some A and if I increase the theta, right, so what kind of a distribution do I get okay? In order to do that, we are going to go back to writing the expression for the rate of transition and then as the square root of the matrix element.

We will introduce the notion of how do we interpret the amplitude in the wave description in terms of the photonic distribution and then take that amplitude and put in here and see how it evolves okay. We will do that in the next class.