

Optical Spectroscopy and Microscopy
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Lecture – 17
Fundamentals of Optical Measurements and Instrumentation

Hello and welcome to the lecture series on the optical spectroscopy and microscopy course. So far what we have seen is that what happens when we take electromagnetic radiation and then quantize the electromagnetic radiation, the energy field itself if it is quantized, how do we approach that? In order to do that, I told that we need to look at a new kind of states called the Fock states and these are basically number states.

What do I mean by that? It means that just the way you are expressing energies in terms of eigenkets, here the eigenkets would correspond to number of entities in that state. In this context, we talked about 2 kinds of an operator, right, a creation and an annihilation operator, just to refresh your memories.

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$\hat{a}_k^\dagger + \hat{a}_k$

$\hat{a}_k^\dagger |n_k\rangle \rightarrow |n_k+1\rangle$

$\hat{a}_k |n_k\rangle \rightarrow |n_k-1\rangle$

$\hat{a}_k^\dagger |n_k\rangle = (n_k+1)^{1/2} |n_k+1\rangle$

$\hat{a}_k |n_k\rangle = n_k^{1/2} |n_k-1\rangle$

$\hat{a}_k^\dagger \hat{a}_k \rightarrow \text{number of entities } n_k$

$H = H_0 + H_I \text{ (semi-classical)}$

$H_I \propto \sum_k (\hbar\omega_k)^{1/2} (\hat{a}_k e^{-i\omega t} + \hat{a}_k^\dagger e^{i\omega t}) \cdot E_k^0 \cdot \langle e_k | r | e_g \rangle$

So we were talking about an operator called a dagger and a. The nature of these operators are such that when a particular operator a dagger operates on eigenket k, the property of the a dagger is such that when it operates on nk, now it is going to take the molecule or take the system from a state that is having nk entities to a state that it is going to have nk–1 okay. The ak dagger will take the system to a nk +1 and we call this kind of an operator a creation operator, while another kind of operator which is ak we call it as an annihilation operator.

The nature of that is, it is going to take the state from n_k entities to n_{k-1} . Well, that is good, and if you think in terms of e field, then what we have, we can start to talk about is that when there is a increase or decrease in the photon intensity or the light intensity you can think in terms of increase or decrease in the number of entities, the basic entities, the photons here we would like to think of the light as made up of photons and then there the basic entities number change from n_k to n_{k+1} or n_{k-1} .

When it gets operated by a creation operator, you are creating one more entity so it is n_{k+1} and when it is operated by annihilation operator, then you get n_{k-1} , you take away one of the photons, alright. So now interestingly there we use this a_k dagger and a_k to obtain the relationship, basically the normalization constants such that a_k dagger if you go back and we look at it, we know that a_k dagger operating on n_k is going to give n_{k+1} , under root n_{k+1} , the state n_{k+1} , while a_k would provide you n_k and the state n_{k-1} .

It is good to collect both the things together in one place, so the relationship the equation 1 here from the previous class and equation 2, both of them if we collected together and write it, we would have n_k giving you n_{k+1} under root and a_k operating on n_k , please note that in the creation operator, the normalization constant goes as n_{k+1} , just the square root of the number of photons that are represented by or number of entities that are represented by the state that it is landing on.

While the annihilation operator the normalization constant goes as the square root of the state it is starting from alright, so that is n_k , it is important, keep in mind. So now this is to say that okay let us say suppose we have e field and now how do we represent that in terms of entity space, number of entity space right, number of particle space and then an equivalent operator we talked about as called as a number operator which is nothing but a_k dagger a_k cap will give you the number of entities n_k itself okay and we had shown that in the previous class.

So this is kind of the summary of all we have done in this part of the course. Now what we would like to do is that we would like to see how we can actually take this to understand the light matter interaction. So in order to understand the light matter interaction, first thing we realize is that when we were talking about the perturbation right, we wrote down in the semi-

classical picture, the rate of a transition process right, so when we do that first thing we had to do was in order to get that was to write down a form for the perturbation Hamiltonian.

We represented as capital H and that actually for our convenience we wrote it as $H_{\text{dagger}} e^{-i\omega t} + H e^{i\omega t}$ and when we did that towards the end, so we had written the perturbation Hamiltonian of the form of H_{dagger} , this is actually the complex conjugate of each other. Actually, we have written it in 2 parts, one is a complex conjugate of the other and without actually proving or deriving how it is.

What I am going to do is that, I am going to say in here in this picture where we are treating the e field as consisting of number of photons, photons is a basic unit of light and if they are interacting with atoms or chromophores or molecules that can absorb or interact with the light. So then, the interaction Hamiltonian pretty similar to that of the perturbation Hamiltonian that we have written before for the semi-classical picture right, in the semi-classical picture this is exactly what we wrote, okay.

Now for the interaction Hamiltonian, we can actually write this as equal to or let us do some of this not so cumbersome coefficients and then we can write it as $H \times \omega_k$ whole to the power half times $a_k^{\text{dagger}} e^{-i\omega t} + a_k e^{i\omega t} E_k$ basically this is the electric field so that is the amplitude, so it is k times, we were talking about e_k r eg.

As I said I have not derived here and it is beyond the scope of this course, but my motivation here is to see that suppose if you could actually do this quantization in terms of the electric field or the modes of the electric field in terms of this number of states, in terms of the Fock states, then you can write down the interaction Hamiltonian and then there you will have terms corresponding to a_k^{dagger} and a_k . These are exactly same operators that we have seen before okay and the rest of the terms here we are familiar with already.

So, now the point is that how do we proceed in actually using this to estimate the rates of the transition following the quantization of the radiation. The trouble is you see that here we have them, the radiation field being expressed in terms of a_k^{dagger} and a_k , these are the creation and annihilation operators of the number states, but here we have in conjunction e_k and e_g which are essentially the energy eigenstates that are allowed for the molecule to be in.

So now one way to bring this whole process would be to write down even the matter, the matrix element that we have written in terms of $e_{k r}$ and e_g in terms of the creation and annihilation operators, now of states corresponding to the matter right. You can think of this as the number of entities of the matter, it could be number of chromophores that are present in the ground state, the number of chromophores that are present in excited state.

These two would correspond to two different modes, a ground state mode and an excited state mode and now we are operating between the Fock states of these entities. The entities can increase their number or decrease their number. So in this case, a ground state to an excited state population would correspond to an annihilation operator of ground state mode bringing down the number of entities at the ground state from some n_k to n_k-1 or n_g to n_g-1 while a creation operator operating on the excited state mode to increase the number of entities from n_k to $n_k +1$.

I am going to reserve n to the radiation mode and I am going to introduce b as I mean just some arbitrary thing b for representing the number of matter entities corresponding to the matter, the number of entities in that matter to a mod k , so the mode could be the ground state or the excited as I was telling you because these different energy states would now correspond to different modes.

So in essence if somehow we could write this matrix element $e_{k r} e_g$ in terms of this creation and annihilation operators, then we would be able to nicely use this expression that describes the interaction Hamiltonian in conjunction with the new description of the matter and the radiation field in terms of number states to see how the rates of these different processes have evolve and emerge, alright. So the goal is now then how do we actually write a given matrix element or more importantly a given operator in terms of different basis sets, right.

Essentially what we have is that we have a Hamiltonian whose natural basis set is energy eigenket, so we have been writing the energy eigenkets corresponding to the Hamiltonian as $e_g e_{k e_n}$ in general. Now if I were to describe this Hamiltonian in terms of number states number of the matter, so what it amounts to is that how does one write the operator in a new basis? So this is very handy and so let us look at this trick in a little bit more generalized fashion okay.

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$$\begin{aligned}
 |i\rangle, \quad \langle j|i\rangle &= \begin{cases} 1, & i=j \\ 0, & i \neq j \end{cases} \\
 |\psi\rangle &= \sum_i c_i |i\rangle, \quad c_i = ? \dots \textcircled{2} \\
 \langle j|\psi\rangle &= \sum_i c_i \langle j|i\rangle = c_j \\
 c_i &= \langle i|\psi\rangle \dots \textcircled{3} \\
 |\psi\rangle &= \sum_i |i\rangle \langle i|\psi\rangle \\
 &= \sum_i |i\rangle \langle i| \cdot |\psi\rangle \\
 &\xrightarrow{\text{projec}^n \text{ operator}} \sum_i |i\rangle \langle i| = \mathbf{1}
 \end{aligned}$$

So now let us take a set of eigenkets our set of ket vector represented by i . If they were to form a complete basis, then you could a complete orthonormal eigenbasis then, we could write a few terms. Number one we know that since they are forming a orthonormal basis, we could take this ket vector and operate it on and then take the scalar product of that vector with any other bra vector right the j corresponding to state j , then the product of this would be equal to 1 only if $I = j$ or 0 otherwise right.

We know this. We have not explicitly stated it, but we have seen such kind of operators, the kind of an operator that we are going to talk about, it is called projection operator. We have used this initially when you are trying to follow the polarization state of the photon following our polarizer experiment okay. Now what are these projection vectors? Now let us say we have an arbitrary ket ψ , now you could since the kets i form a complete basis, we could expand ψ in terms of a new basis i .

So how would you do that? Very simple, we have done this again during the time while describing the time dependent perturbation theory, exactly the same. We would write it as summation over i , okay I am going to use here different, let us call it as $C_i i$, right, C_i of the coefficients of the basis vector i and I am going to run through the entire basis right. I can do that and all for me to write down completely what I need is, I need to know what my C_i 's are right, that is all the game is.

So if I need to know the C_i , then the trick that we do is that we actually do this scalar product and when you do that you will see that in in this summation actually only thing that survives would be C_j , right, everybody else would go to 0 right and C_j that is the only term that survives. So we could in general just j is an index right. In general we could write C_i as nothing but i psi, using this in the above expression, so let us call this as equation number 1, actually equation number 2.

Let the equation number 1 be the description of the interaction Hamiltonian and so now we could use the expression of C_i into, so you can actually write psi as summation over i since this is a number, we have to write like that or in other words just to distinguish so, we could write it as $C_j i$, this whole operator operating on psi. Now this operator is called as a projection operator, why is that?

Now if you carefully watch it, what we have done is we have expressed this some arbitrary ket vector χ in i space right and then when we did that the number C_i is representing the coefficient of our component i or in other words it tells you the contribution of that particular basis towards making this psi. So now when we finally went and then solved for C_i what we see is that is C_i is nothing but the scalar product of that particular vector with the psi itself.

So basically it is telling you the component of the psi along the i if you were to remember what the scalar product would give you, so then what we did was, we put this number because this is a number we have to be careful in keeping the order in which we write this because the end result here is a vector C . So if you keep that in mind, then actually this i of psi, this is our C_i . So I am writing that in instead of C_i . So then all that you are doing is that we have written this expression of psi being equal to C_j of i dot of psi.

This is a projection operator and as summing the projections over this entire i space should equate to 1, alright. For this to be true, what it would imply is that this would equal to 1. This is extremely convenient. So what it tells you is that if you actually want to expand an operator or move an operator, you write an operator in a different space, then this can come in really handy, okay. Now how?

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$$\begin{aligned}
\hat{H}_m &= \sum_i \sum_j |i\rangle \langle j| H_m |i\rangle \langle j| && (\sum_i |i\rangle \langle i| = 1) \\
&= \sum_i |i\rangle \langle i| \cdot \hbar \omega_i \\
&\quad \leftarrow \quad \rightarrow \\
&\quad \text{III} \\
&\quad \hat{a}_i^\dagger \hat{a}_i \\
\hat{H}_m &= \sum_i \hbar \omega_i \hat{a}_i^\dagger \hat{a}_i
\end{aligned}$$

Let us take the example of our Hamiltonian itself, so what we are looking for is, how do we write this Hamiltonian in terms of a different basis right? So just to distinguish I am going to write this Hamiltonian as corresponding to that of the matter right m so H_m I am writing it. So can be written in terms of, since remember in the previous sheet we have proved you could do this right. So that is i or j, so let us be consistent, so let us take we are summing over i, i being the eigenkets corresponding to the space alright, any space so.

We know that, equal to 1. Now you see these eigenket that the j right, j is nothing but 1 of the eigenkets defined in the space of ii eigenket. So these could kind of corresponding to any operator, so the operator corresponding to these eigenket could be anybody, we do not know, we have not said anything about them right, all we said is they form a complete eigenbasis, that is all we said, right. We have not talked anything about that operator.

So now if I have to be able to write another operator alright, an operator such as our Hamiltonian operator in terms of these states j and i, I mean i basis, then it presents a possibility of us writing an operator or expanding an operator in a new space. So where I am going here is that I have this matrix element of Rkg right, that we have written the rate process or even in the interaction Hamiltonian in terms of Rkg where the Hamiltonian, the matrix element is described in terms of the energy eigenbasis right.

So we want to write this in terms of number basis or the Fock state basis. So if I know how to transform this operator or how to write this operator in a different basis, then I can easily take that and then write it down that is where I am going. So let us look at that quickly, how do we

write the Hamiltonian of the matter? So this we can write it as summation over i , so I am going to write matter Hamiltonian and I am going to expand it in both the sides.

So since the summation over i , summation over j , this completely allowed because we know this is equal to 1, summation of j , i is equal to 1, i and j are just indices arbitrary name, so I could have called j as i and i as j right. so, does not matter which means okay, which means I am allowed to do this or in other words, I could write it as summation over i ij okay the eigenvalue of H_m or you can write it as $\hbar \omega_m$, I am sorry hold on, I am going to correct this, this does not, this can be written also.

I can write this as $\hbar \omega$, sorry this whole thing can be rewritten as I am sorry, so of i j $\hbar \omega_i$ okay and we know that this projection operator right, this whole thing can be written as a_i^\dagger because it is in the i basis i , so a_i^\dagger . So you could write this H_m in terms of the creation and annihilation operators something is like a_i^\dagger and a_i itself that is or in other words, we could write for the matter corresponding to this as $\hbar \omega_i a_i^\dagger$ and a_i okay.

So now what we are going to do in the next class is that we are going to use this okay except I am going to use this in conjunction with the interaction Hamiltonian that I have just written down before and see how we can actually parse out an expression for rate of a transition, alright. Thank you, I will see you in the next class.