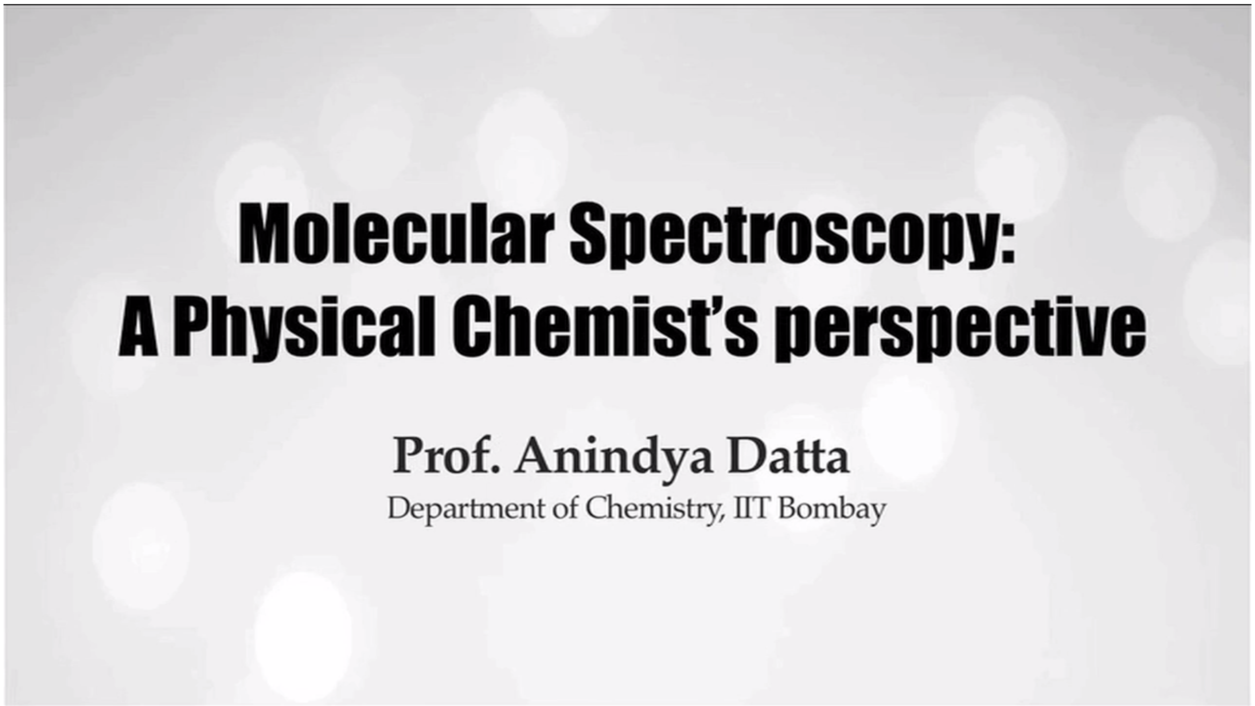

Molecular Spectroscopy: A Physical Chemist's perspective

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Lecture No. – 17

Transition Moment Integral

Prof. Anindya Datta: Okay, now in the previous section, we have performed a discussion of time dependent perturbation theoretical treatment of a two-state system characterized by wave functions ψ_l and ψ_m. We are more or less working with the understanding that ψ_l has lower energy, ψ_m has higher energy, but it can be the other way around, it does not matter. In doing that, if you remember, we have written the wave function of the perturb system as a linear sum of two-wave functions, where C_m is the coefficient of the state that is not populated at 0 time, okay. So if you're talking about absorption spectroscopy, the higher state. And we have derived this expression that $dc_m/dt = -i/\hbar$ an integral over space multiplied by an exponential term, an exponential factor in time.

Now the next step is to use the expression for the first order correction to the Hamiltonian, which is this, well, actually multiple by µx, okay. Put it in there and see how the expression evolves, okay. That is what we are going to do now. Yes. How do we get Hamiltonian as -µx? E_x. So the question is how do I know that this first order term -- does that answer your question? Okay, one was missing. How do I know that the correction terms is -µx. E_x, because if you remember, how this fab mechanical treatment of quantum mechanics is carried out, we always start from classical mechanics, don't we, right.

When you worked with the harmonic oscillator, for example, how did you write the Hamiltonian. You wrote the Hamiltonian -- well, the kinetic energy part is the same anyway, but for the potential you wrote ½ Kx^2. Where did we get that from? We got that from our understanding from classical mechanics that for a simple harmonic oscillator, ½ Kx^2 is the potential energy. Here also, we're trying to think how we can model our system. So building model is a very important step in any theoretical treatment. What is the mode that you want to use? Of course, then the question that comes is that, is the model correct or does the model apply, and if it does, how far does it apply?

So the model we are using here is that, we're modeling this molecule as an electric dipole, okay, and we're only working in the X direction so µx. We are modeling light as an oscillating electric field; we're neglecting every else. Why? Because this electric dipole, electric field interaction is going to be the strongest among all the interaction that are possible within this model. You can start with x, y, z, it doesn't matter, okay. What we'll do is this, we'll get some expression for X direction only.

Now do you think for an isotropic radiation, isotropic radiation means, in all direction you have oscillation, for isotropic radiation, you'll get the same expression, right, for E_x, E_y and E_z, right, then it's very easy to combine them. That is what we'll actually in the next class, okay. A factor of three comes in, that is all. Any other questions? Okay, good.

So let us tidy up this a little bit before we go ahead and put it there. What is the first order correction terms for the Hamiltonian? It is -µx. Ex of course, we'll now write the expression of E_x. 2 E_x^0 (cos 2π νt), all right. Now see, this is what is going to go in here, all right. And what should we try to do? We should try to separate the factors. The one in special coordinates and one in temporal coordinate, time. So I think you can see from this expression and that expression that it appears that the problem should become simpler if we convert this cosine term, cosine factor, to exponential term, some of exponential terms, because they already have something that is an exponential term in time, right.

If I write this cosine in the exponential form, then it should become easier to handle this problem. So see please understand the line of thinking. This part of sometimes intimidating for us, chemists, because we see a lot of algebra and what we tend to do is we tend to remember, all of it, all right. That being said, and now we have to be careful because this is the point where my derivation and Ramy's derivation become different, okay. So what do I write, -µx. E_x^0, what is cos Kt, E^{-iKt}, plus or minus, E^{-iKt}, sure, plus, and is there an i multiplied somewhere, no, that is for sine. So it's something like this -- and is there a ½, right. Yes.

So I can just do it step by step, $2E_x^0$ ½ [exp (2πi νt) + exp (-2πi νt)], is that right? Whole by 2, I've written already. You cannot read it only because my handwriting is bad, $2E_x^0$. ½, okay. Of course this 2 and that 2, thankfully cancel off. So I have one -- it sounds very strange if I say, I have one 2 less to think of, anyway. Is this expression correct? I'll modify this a little bit and I'll modify that a little bit also. What I'll do is here instead of ħ, let me write it complete as h here and 2π here. What am I trying to do? I am trying to make these two expression completely compatible.

Here I already have 2π, right, so why don't I divide by h and multiply it by h. Why did I do this? I did it so that he two expressions look similar, so it become a simpler for us in the next step. Also, here now I have hν, here I have hν. Hν and E are of the same dimensions, right, okay. So I am just demonstrating that these are actually dimensionally consistent, there is no problem.

Let me now write -- okay, there is one -1 here and one -1 here, multiple -1 by -1, it becomes 1, right. Right or wrong? According to Graybiel, it does not. So this is where the difference begins. Okay, i/ħ, what else do I have here, I have E_x^0, E_x^0 is a constant, right, E_x^0 is a constant so I keep it here. I'll µx inside the integral, because as you have seen, when we derive the selection rules for your vibration and rotation, µx can actually take a different term for different problems, so I cannot µx outside the integral, I have to take it inside. So when I do that, this is what I get. I am taking µx inside, so I write$<\psi_m|\mu x|\psi_l>$ integrated over all space. Does that look familiar? What is it? Yes, that is our transition moment integral. That's we have been seeking so far. we wanted to know where transition moment integral came from. Now you know the answer; transition moment integral came from this time dependent perturbation theoretical treatment of transition between two states, okay.

Even before I write the remaining factor, tell me this. What happens when transition moment integral becomes 0? $C_m = 0$, step by step, don’t jump steps, right. Dc_m/dt is 0, right. You start with $C_m = 0$. So this is what we’re saying, C_m versus t, initially it is 0, to (0,0) point, right, and initial time, it is something like this. So if dc_m/dt is also, then after time you don’t reach anywhere, your C_m remains 0, okay. So that is why we have been talking about transition moment integral in our previous discussion. If transition moment integral is equal to 0, then the system remains in the lower energy state or rather the initial state characterized by l, quantum number l. There is no questions of it mixing with the state characterized by quantum number m, okay, $dc_m/dt = 0$ and we’ll come back to it and put it in a little different way, actually it is the same thing, a little later.

So this is your transition moment integral, fine, multiplied by, now I have two exponential terms, right. First one is [exp {2πi/h(E_m - E_l), then what do I do, +hν)t}. Have I written it correctly? I also get confused when there are two many brackets. Have ai closed the brackets in the right place, okay? Then I can write the second term + exp {2πi/h (E_m - E_l =- hν)t}]. Is this correct? Can we go ahead? Have you understood all of this? Any questions Vikas? No questions, very good.

Okay, now we need to understand what these functions would look like, but before that, maybe let us do the integration. So this is the first integration that we promised to do today, and this is where I get an answer that is different from this waybill, so I want you to do it. So, so far you agree with me, right, whatever I have done. Now what I want is I want to know what is C_m. How do I get a value of C_m? Your derivative is known, okay, so C_m would be what, C_m 0 plus this multiplied by whatever changes. So basically we integrate the right hand side with respect to time, and when you integrate with respect to time, what are the limits, 0 to 2 exactly. Can you do the integration and tell me what term turns out to be? What? You’re saying that because you know BOLD resonance condition, okay. Right now, let us say, it may or may not be equal to 1, okay, let us say, this is a constant, for get what it is, some constant K, all right. What that, let us do the integration.

So what Manthan is saying is actually correct. What he is saying is the second term, in the second term we have (E_m - E_l - hν). Isn’t that equal to 1? It is equal to 1 when E_m - E_l = hν. But then, even here, this is also equal to 1 when E_l - E_m = hν, right. So we’ll talk about that. That is actually what brings us to do second important aspect of this discussion, that is BOLD resonance condition, but before that, please do the integration and tell me what you get. Meanwhile, I’ll just go ahead and write this.

Show me now what’s the answer. You’re getting of this, right, I also have got negative of this, but I don’t know why in Graybiel, this is the expression that is given. It doesn’t matter, I can always write a minus sign outside. And what happened to this ħ, that got cancelled during integration, right. So for now, what we'll do is we'll go by Graybiel's expression, because it doesn't really matter. My expression really has that minus sign outside, and it looks like, you're also getting that. What about you Manthan? Just tell me do you get this or do you get a negative. You get a negative. Okay, let's just go with this expression now, let's not bother about the minus sign outside, because as you'll see, eventually, we take mod square, so you don't have to worry about minus.

What is the second term? + 1-exp whatever, it's coming as -1, right, mine is also -1, but then Graybiel has written the book not I, not you. So we'll follow it, but it does not matter, that's the point I am trying to make. You can write a minus sign outside, it does not matte, because eventually, what is important is your mod square. Of course physically, what it means that dc_m/dt can never be negative, isn't it. Dcm/dt has to be positive. So that is the only place where I have a little bit of a hitch. Anyway, we'll just continue from here, $2\pi i/h(E_m - E_l - h\nu)t$ / $2\pi i/h$ (E_m -- I don't have the $2\pi i/h$ -- $E_m - E_l - h\nu$. Yes, because we've cancelled the ħ. So this is okay, except for the minus sign, let's proceed with this.

Now look at these two terms. Will you agree with me if I say that most of the time, both the terms are actually very, very close to 0? Will you agree with me if I say that? We're dividing by h right, here. Dividing by h here means what, h is a very small number. What is the value of h? So if I may digress a little bit, a very favorite question in B.Sc. that was there when I was a student, I don't know if it's still favorite is that what would happen if $h = 1$. So if $h = 1$, then what is the product of uncertainties. There is $h/2\pi$, right. So the problem is that uncertainty would enter the real world, microscopic world, not real world, yeah, microscopic world. So everything you, I, chalk, board, everything would be uncertain, right. So thankfully, h is not equal 1, h is a very small number.

So because of that what happens is that the follow off of both the exponential terms is rather sharp, okay. We can safely say that both the terms are actually equal to 0 unless the denominator is equal to 0, oaky. If the denominator is equal to 0, then what will happen, the term will blow up, right, okay. So first thing is both the terms cannot survive together, because the condition for blowing up is $E_m - E_l = h\nu$ or $E_l - E_m = h\nu$. Of course, both cannot be satisfied at the same time. Hν, is that positive or negative? Hν, frequency is always positive, h is a universal constant that is also positive. So right hand side is always positive. So that means left hand side has to be positive. So what does the first one mean? E_m - E is positive that means E_l is smaller than E_m, okay? What is the step -- what is the level that is populated at 0 time l or m? What are you saying, l, okay, l, m, anyway, l, right, l for lower. This is the situation in that case.

For first one, $E_m - E_l = h\nu$, this is E_m, this is E_l. For the second one, the upper one is E_l, the lower one is E_m, okay, and I'll just draw the arrow to indicate the nature of transition. So the first one, $E_m - E_l = h\nu$ -- well, it's a little strange because this is actually the second term, right, $E_m - E_l = h\nu$ that is satisfied by the second term not the first one, $E_m - E_l - h\nu = 0$. So when $E_m - E_l - h\nu = 0$, what we're essentially saying is that we're dealing with an absorption, the transition is absorption, going from lower to higher level. When E_l is higher and E_m is lower, we're saying that we're dealing with emission, that's all, okay.

So this term is going to blow up when we discuss absorption; this term is going to blow up when we have emission, right, but the point to note is that for absorption as well as emission, the terms are exactly similar, right. Is it right? $1 - E^{Kt}/K$, you can right both in the same way, it's that K is different depending whether you're talking absorption or emission, same kind. So please remember this, please remember. So what I am trying to say that is the expression for C_m, for absorption and emission should actually be same, isn't it, because E^{Kt}/K, that's all that is there. Understand what I am saying? Well, $1 - E^{Kt}/K$ that is the general form that is there for absorption as well as emission. So the Cm or later on when we talk about C_m*, they should have the same kind of expression for both the process.

The only thing that we have to remember is that when we talk about absorption, I mean induced absorption, of course. What is the meaning of induced here? Induced means something is brought about by external light. Second part is perhaps a little more difficult to understand. When I talk about emission here, I am talking about induced emission or stimulated emission, emission that is brought about by presence of light, not spontaneous emission. As you know, if you excite something, many time it just gives out light by itself, it has to come down. We're not talking about that kind of emission here. We're talking about induced or stimulated emissions. Please don't forget this. This is a very important point at this juncture, okay.

So well, I have promised two integrals today, but looks like we have to be satisfied with one, because our time is almost up. Let me just write the final expression. So what do we deal with -- which one do we deal with to start with, absorption or emission? We'll deal with absorption; absorption happens first, emission happens subsequently.

So for absorption, the expression for C_m turns out to be then 1- -- well, I should writ the whole thing -- E_x^0 multiplied by your transition moment integral, multiplied by $1 - \exp\{2\pi i/h\,(E_m - E_l - h\nu)t\} / E_m - E_l - h\nu$. This is the closing expression for today and opening expression for the next class. What we'll do now is that we're going to take this C_m. C_m give you amplitude, okay. Amplitude of what? Ψ_m. Now if I take mod square of that amplitude, do you know that this mod square of amplitude gives me the contribution or probability, yeah. So we want an expression for mod square of Cm. That is what we'll work out the next day, a little more algebra, that is all. And then we're going to reach another important observation.

What have we learned today? Let us summarize. We've learned two things. We have understood where transition moment integral comes from and we've understood that Cm is 0 if transition moment integral is equal to 0. Cm = 0 means there is no mixing of states brought about by light, or in other words, there is no transition brought about by light. There is a first important thing that we've learnt. The second important thing that we've learnt is BOLD resonance condition. We have seen that unless BOLD resonance condition is fulfilled, you cannot have an induced transition, may it be absorption, may it be emission, okay.

We have been taking BOLD resonance condition for granted so long, and it makes sense also, right. Even without doing any math, it makes sense if we say delta = hν, we can understand it from our commonsense, but what we see is that we can arrive at using uncommon sense as well, okay. So these are the two take-home message from today's discussion. Next day, we're going to talk about mod C_m^2, and then we'll get access to one more thing.

See so far, whatever information has come is from the space part, right. The time part has given us one information that is your resonance condition, but there is something more that will come out from here. From here, we'll learnt that -- what kind of system are we talking about so far, how many levels? Two levels. What are the energies? E_l and E_m. So kind of spectrum do I expect? One line, right, one line, no widths. When we do the rest of the math here, we'll see that even for this system where you E_l and E_m, two energies, you can never have a 0 line width, some finite line width will always be there. That will come form the time part, right, and that is what is going to be related to your uncertainty principle. So that line width that you get is called natural line width, okay. This is what we'll discuss the next day and then we'll go on to what is called your Fermi's Golden Rule, and we'll also talk about the Einstein's discussion, and we'll see what is the relationship between the different absorption coefficients, okay. This is what it is for today.