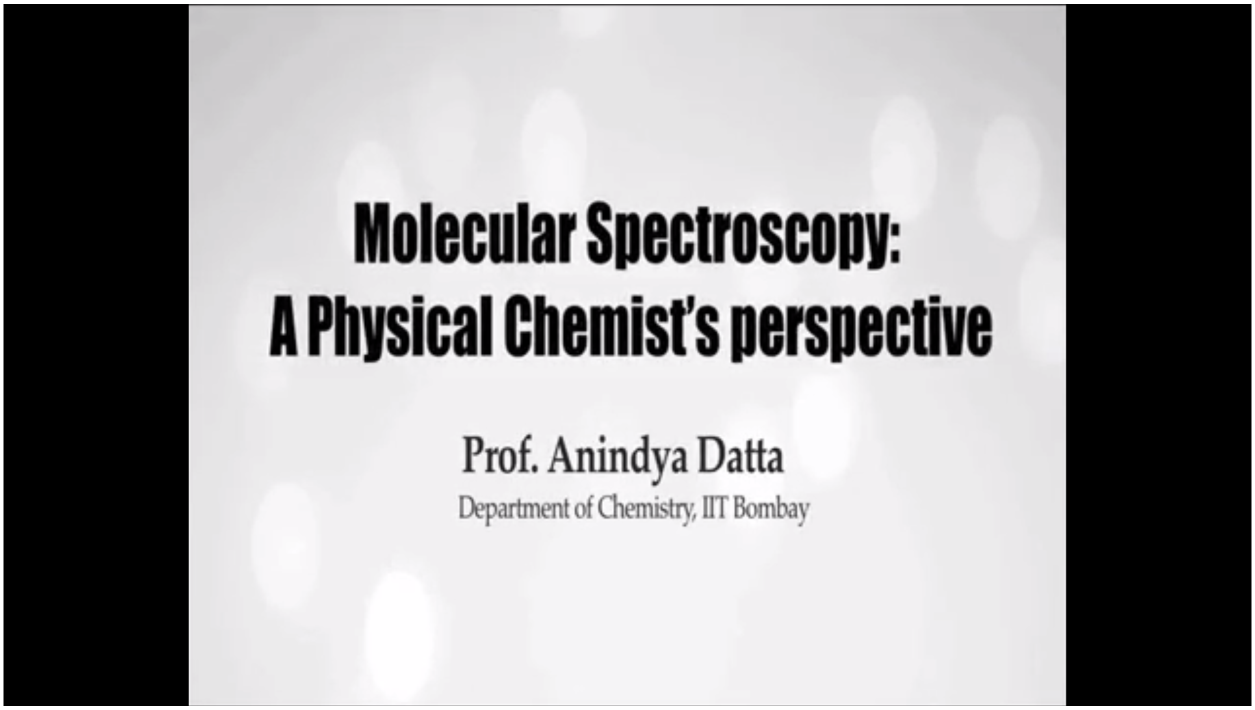

Molecular Spectroscopy: A Physical Chemist's perspective

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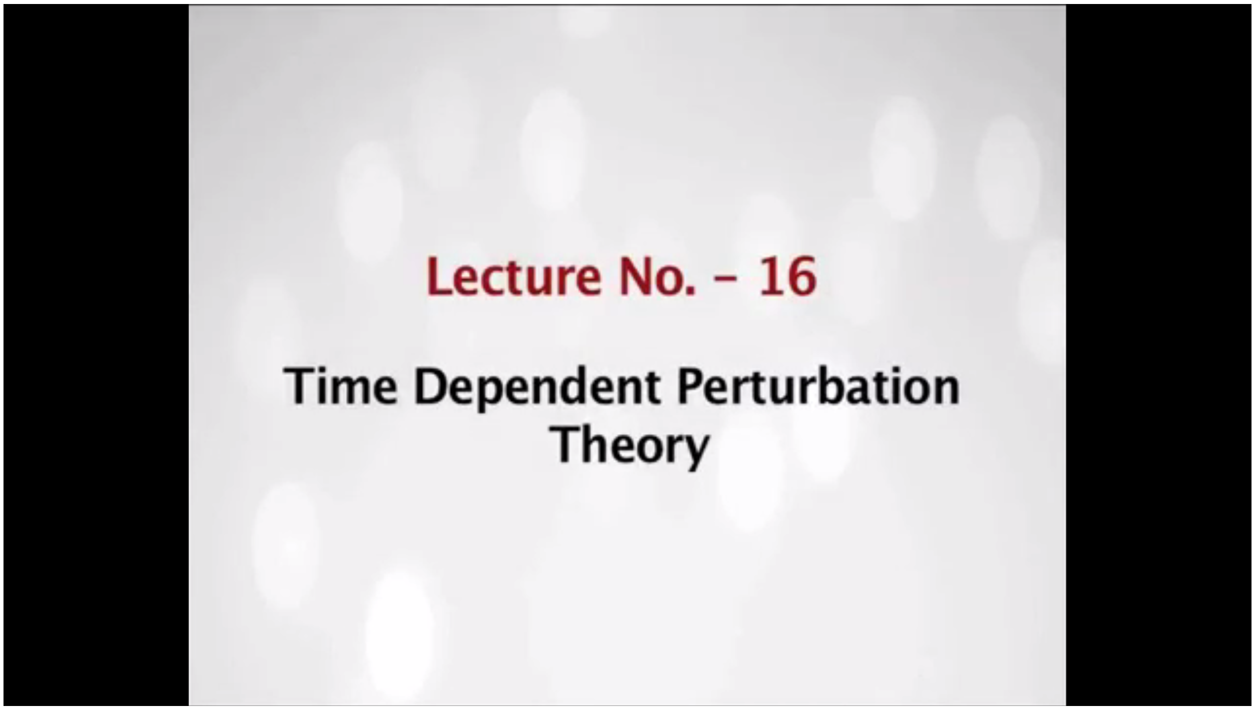

Lecture No. – 16

Time Dependent Perturbation Theory

Prof. Anindya Datta: We are going to start with a revision of what we had done in the last class, and then we'll go on and we'll try and derive an expression for the probability of the higher level getting populated as a result of excitation by light, okay. Shall we begin? Great.

So let us remind ourselves a little bit about what we have discussed already about your time dependent perturbation theory. TDPT is time dependent perturbation theory. As you remember, we’re now working with time dependent wave function Ψ, and it looks like I have gotten a little better at writing Ψ with a little bit of practice. So this is equal to time independent space dependent wave function, ψ, multiplied by -- yeah, but I’ll write the expression of φ anyway, since we have done it once, into the power $iEt/\hbar$. Is that right, or is there a minus sign? Os that is what I was saying, do not assume that whatever I write is correct, okay. You have to correct me wherever I go wrong, $e^{-iEt/\hbar}$, and the problem that we’re dealing with involves two levels. One is l and other is m. I can just write like this, all right.

So what have we said? We have said that when there’s no light, the Hamiltonian of the system is the unperturbed Hamiltonian and the wave function of the system is Ψ_l, okay. Then we said, what happens when I turn on the light. In presence of light, and one of you asked the question, how is the light on or has it gone off, so the answer is light is on. We’re taking it as an oscillating electric field, as we’ll discuss shortly. So of course there’s an oscillation and all, but the light is on. What we do is at some 0 time, before the light is turned on, the system is described by wave function Ψ_l, then we turn the light on and keep it on, okay. We have not turned the light off yet. When we turn the light off, it becomes a different ballgame altogether. So in presence of light, the system is described by a wave function $\Psi = C_l. \Psi_l + C_m. \Psi_m$ and we’re working with initial time t tending to 0. So this C_l tends to 1 and C_m tends to 0. This is an approximation that we’re going to use shortly. So far so good.

And then the other thing, and this is where I had made a mistake. In presence of light, what is the Hamiltonian? Hamiltonian is $H^{(0)}$ plus some perturbation term $H^{(1)}$, yeah, right. We are working within ambit of first order perturbation only, small perturbation, first order is good enough. And today, we’re going to write an expression for this perturbation, and that is, we’ll write it as, $-\mu_x E_{x.}$

To start with, we’re going to confine our discussion to one axis, X axis only. So talking about plain polarized light, right, and that’s where it is. So μ_x is the x component of the dipole moment of the molecule. So we’re considering the perturbation to be an electrostatic interaction between the electric dipole of the molecule and the oscillating electric field associated with light. Does that mean that there is no interaction between the magnetic field and the magnetic dipole? It doesn’t meant that. Does that mean that there is no interaction between the electric field and magnetic dipole? No. All it means is that, we’re starting with the interaction that is largest. Electric field, electric dipole, this interaction is the largest.

So if you have learned this solute solvent interaction, you might remember that the most important interaction is iron dipole considering a dipolar solvent, followed by a dipole, dipole interaction, followed by induced dipole induced dipole interaction and so on and so forth. So different interactions are there. Some are large, some are small, we're focusing right now on the largest interaction. In the later stage of the course, there will be occasion to talk about weaker interactions, right, but this is only the starting point.

How do I write E_x? Is this part of the board visible from the back? Can you read this? Ex is written as $2E_x0 \cos 2\pi \nu t$ when ν is the frequency of light, okay. We're going to use this expression today and we'll see how this gets modified, but before that, let us redo what we had done in the last class and get an expression for time derivative of this coefficient DCM, okay. We'll do it quickly.

So I presence of light, your Schrodinger equation should be something like this. The Hamiltonian as we have said already is the uncorrected Hamiltonian first plus the first order perturbation term. That Hamiltonian operates on the wave function. What is the wave function, tell me? What is the wave function when light is on, $C_l. \Psi_l + C_m. \Psi_m$, we have to consider both the states, $[C_l \Psi_l + C_m \Psi_m]$. I am trying to write the time dependent Schrodinger equation. So can you tell me what the right hand side will be? $-\hbar/i\ \partial/\partial t$ of this whole thing, $-\hbar/i\ \partial/\partial t\ [C_l \Psi_l + C_m \Psi_m]$, and before proceeding further, we need to remember one thing that the C_l and C_m, these coefficients are functions of time, okay. These coefficients are not independent of time. At time t = 0 Cl is exactly equal to 1, Cm is exactly equal to 0. As the time proceeds, the value of C_l decreases from 1, value of C_m grows from 0, all right, but we are working under the approximation that our discussion is confined to initial time where C_l deviates not too much from the value of 1. C_m deviates not too much from the value of 0.

Please remember this. This is usually a source of confusion, because what we often think when we read this part is that we are saying $C_l = 1$, we are saying $C_m = 0$, then how do we even talk about DC and DT. Please remember we are not saying $C_l = 1$, we are not saying $C_m = 0$, all we're saying is that, the deviations of C_l and C_m from the initial values of 1 and 0 respectively are not too much, but deviation is there; otherwise, what are we talking about, okay, right.

So when we expand what happens? On the left hand side, what are the first two terms, $H^{(0)} C_l$ -- maybe I'll do it. $C_l H^{(0)} \Psi_l + C_m H^{(0)} \Psi + C_l H^{(1)} \Psi_l + Cm H^{(1)} \Psi_m$, and the right hand side is $Cl\ \partial \Psi l/\partial t + Cm$ -- oh who is going to write this $-\hbar/i$, I always forget that, I'll write it once, save chalk. $-\hbar/i[C_l\ \partial \Psi_l/\partial + C_m\ \partial \Psi_m/\partial + \Psi_l. Dc_l/dt + \Psi_m\ dc_m/dt]$. Okay, so far so good, all right. Am I allowed to write dc_m/dt or do I have to write $\partial c_m/\partial t$? Was that a yes or was that a no? For both? Then, we can write Dc_m/Dt, very good, okay.

Now what happens, look at this term and look at this term. They’re actually equal to each other. That is your time dependent Schrodinger equation for Ψ_l. Look at this term and look at this term. Time dependent Schrodinger equation for Ψm just multiplied by C_m, so they cancel off, okay. We are left with. Do not forget that ħ/i. This is what we are left with, right. Is it right? Then what did we do? We said, there’s no point trying to talk about Dc_l/Dt and Dc_m/dt both at the same time, because it’s not as if they’re uncorrelated. Dc_l/dt and Dc_m/dt are correlated. Dc_l/dt is the rate of disappearance of Ψ_l, the state associated with Ψ_l. Dc_m/dt is the rate of production of the state associated with Ψ_l. It is enough if you work two, and if you work with two, it’s complicated anyway. So you want to eliminate one of the terms.

We just decide that we’re going to work with Dc_m/dt. I want to eliminate this. What is the best way of eliminating the first term? Left multiple by the complex conjugate of Ψ_m and integrate over all space, right. Then what will happen? This is going to vanish, because Ψl and Ψm are orthogonal to each other, okay. Let us do that. When I do that, this is what I get. On the left hand side, I get $C_l <\Psi_m H^{(1)}|\Psi_l>$ over space or time or both, space, only space not time, that is what bracket means, right, space, + $C_m <\Psi_m|H^{(1)} \Psi_m>$ is equal to -- I can just write it there -- = -ħ/I dc_m/dt.

We have already discussed why on the right hand side we have only one term, because the other term vanishes. Is it okay now? There is a minus sign, because of ineffective erasing of what was in it earlier, I think, or maybe not, whatever, but this is correct. Now we are okay, okay. So far so good, all right. What is the next thing that we have to do? Now we use our approximation. In fact, so far, have we used any approximation? No, right. So far, it has been an absolutely exact treatment. Now we use that approximation of ours that the C_l is more or less = 1, C_m is more or less = 0, all right.

So what we do is we put this to 0 and we erase. So finally, you are left with Dc_m/dt = what do I put this to be, we put this to be 1, = -i/ħ. Now I can simplify this a little bit, can I not, because integral is over space. So I can keep the space dependent part of the wave function inside the integral and I can bring the time dependent part out, right. So I can write it like this $<\psi_m| H^{(1)}|\psi_l>$. Please note ψm and ψl written here are different from what are written here. This is ψ, these are Ψ. So these are product of space dependent as well as time dependent part; these are only the space dependent part, okay, and the time dependent part comes out. What does the time dependent part turn out to be? Exponential, what will it be $[i(E_m - E_l)t/\hbar]$. Is that right? Yeah. Okay.

Well, in the textbook it is written as $-i/(E_l - E_m)$, so it’s the same thing, it doesn’t matter. So far so good. So this is where we had reached. Now we are going to use this and we are going to proceed with the next part of the discussion. Is there any question up to this? Up to this, we are all good. Now you have to be careful because now is where our opinions seem to differ.