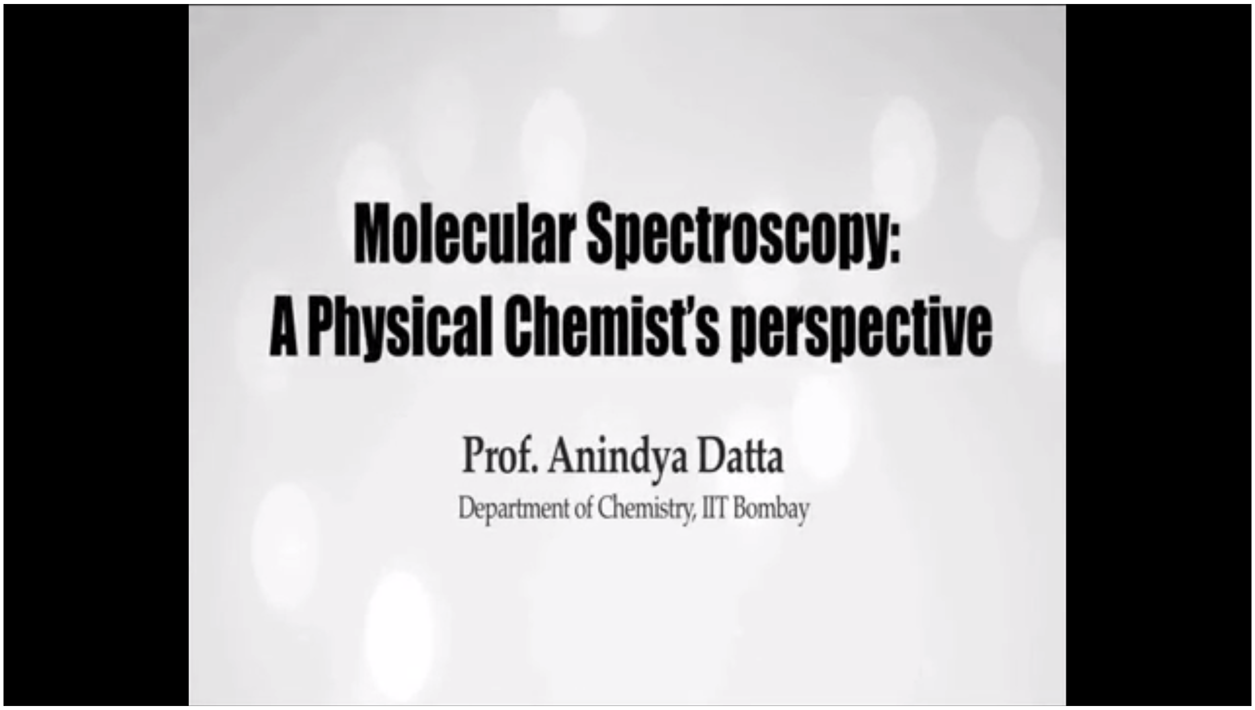

Molecular Spectroscopy: A Physical Chemist's perspective

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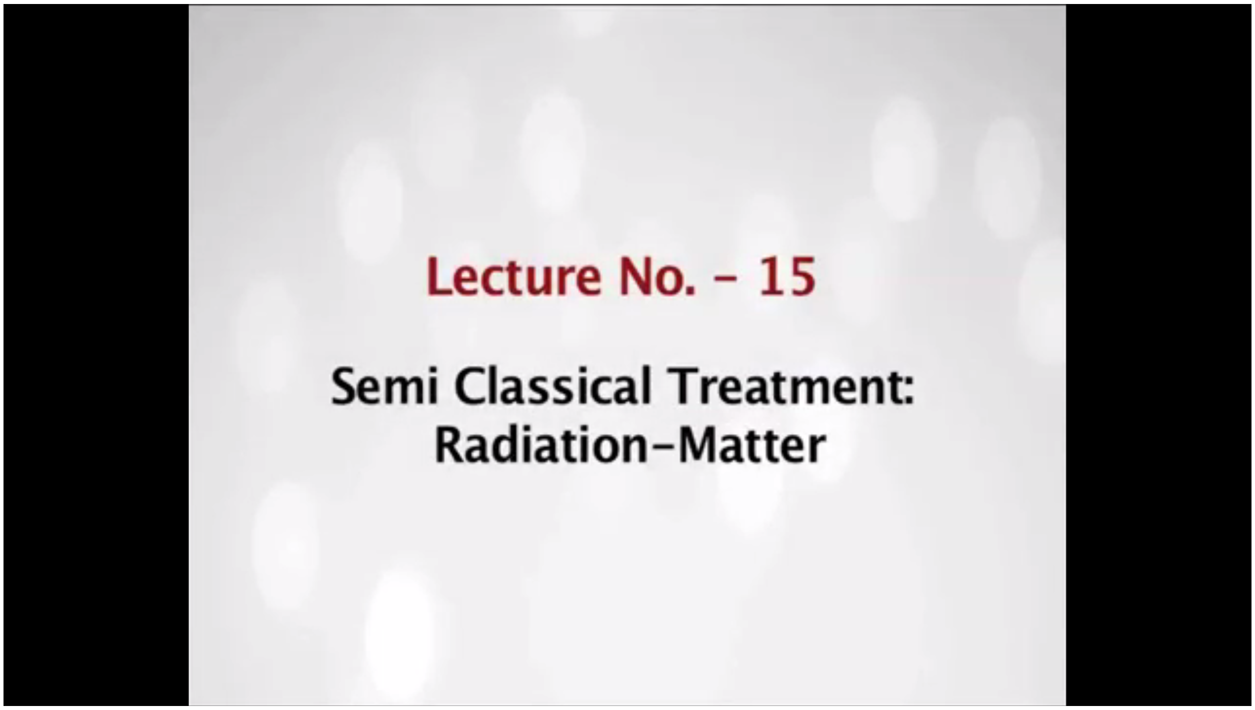

Lecture No. – 15

Semi Classical Treatment: Radiation–Matter

Prof. Anindya Datta: So in the last class, we had stopped with a question and the question was is it impossible to get an idea about rotational and vibrational levels of, say, hydrogen, dihydrogen, because what we've seen is that when you're talking about diatomic molecules, of course, we've not talked about anything beyond diatomic. So for diatomic molecules, we have understood that an essential condition for microwave activity is that there must be a permanent dipole moment, and for vibrational spectrum, for IR spectrum, essential condition is that vibration must bring about the change in dipole moment. But then it boils down to the molecule must have a permanent dipole moment for diatomic molecules, because if it is something like dihydrogen or iodine, then no amount of stretching can produce a dipole moment in, say, a homonuclear diatomic molecules, okay.

So we have said that it is possible to get an idea about these vibrational and rotational levels and we have said that it is possible to do it by using what is called Raman effect, by doing Raman spectroscopy, you can circumvent this problem, and that is what we initially thought we'll discuss now, but then, well, this morning I changed my mind, because there's a more fundamental question that remains to be answered. I think it is better to answer that question before going onto another kind of spectroscopy. So we have a little bit of change in plan. We take a raincheck on Raman spectroscopy for now, and today, we ask that question that has been haunting us for quite some time, and that question is, we're saying that all the selection rules are derived on the basis of transition moment integral or transition dipole moment being non settled. Where did that come from?

We have postponed that class. Usually that discussion comes first, but my experience is that if you do that first, very often we lose the class, because people think what is going on. So now that we have established that transition moment integral is a very important parameter that decides which transitions will take place and which transitions will not, let us now try to address this question over the next few classes, what is the origin of transition moment integral, okay. We do that by performing a semi classical treatment of interaction of radiation with matter and when I say semi classical what we essentially mean is that we're going to model radiation in the classical way.

What is the classical description of light? Electromagnetic wave. Light is an electromagnetic wave. What does that mean? Oscillating, so oscillating electric and magnetic field. Now you're saying that they're perpendicular to each other. But of course, I mean, and these two are perpendicular to the direction of the propagation of light, and that is the description of polarized light, right. In unpolarized light you have electric field oscillating in all possible plains, perpendicular to this direction of propagation of light and you have magnetic fields that are perpendicular to it. So that is the description of light that we're going to adapt here, okay. And for now, we're going to work only with the electric field, and we'll tell you why. So light is modeled as this oscillating electric field, classical description.

What about matter? For matter, we have to use wave function, that's why it's called semi classical. You can do a complete quantum mechanical description of this problem as well, okay. So now, and in doing this, see in chemistry, more often than not, we stick to this time independent Schrodinger equation, hydrogen atom problem and all that, we have -- it has been sufficient to work with time independent Schrodinger equation, not in this case. Here, we will have to use time dependent Schrodinger equation and what we're going to use essentially use eventually is time dependent perturbation theory.

You're familiar with time independent perturbation theory, you've dene that already. Time dependent perturbation theory is actually easier, I think, than time independent perturbation theory. So it will take that as it comes, so it will come today itself. But before plunge into that, let us remind ourselves of some basics of this time dependent Schrodinger equation, okay.

Now I've written ψ in a little funny matter, a little different from what I usually write, right. This is given my poor artistic abilities, this is capital ψ and when I write capital ψ what I essentially mean is that this capital ψ is a function not only of the special coordinates but also of time, all right. You have dealt with wave functions like this earlier I hope. Whenever you have done that, what is the first step that you have taken? Yeah. You try to do a separation of variables, right, separate the special variable from temporal variable. For that, what is the first condition, you have to write this wave function, which is a function of special as well as temporal variable. We have to write it as a product of space dependent part and a time dependent part, and the convention we're going to follow is this is a product of ψ, which is a function of (x, y, z).

Now this is capital Ψ, this is small ψ, but how many times will I say small ψ, I'll just say ψ. If I mean capital Ψ, I'll say capital Ψ, multiplied by time dependent part φ, and once again, how many times will we write, x, y, z, t and all that, we'll simply write it as $\psi . \varphi$. So please don't get confused. Remember small ψ means time independent special part of the wave function; φ is the time dependent space independent part of the wave function. Are we clear so far?

And with this, we have to remind ourselves what is a Schrodinger equation, time dependent Schrodinger equation, okay. What is time dependent Schrodinger equation? Before that let me write the Hamiltonian for that, and I'll write it as $H^{(0)}$, because we're going to use perturbation theory. We're going to bring in a correction term later on. So $H^{(0)}$ as you know is $-\hbar^2/2m\ \Delta^2$. I will not repeat Δ^2, everybody knows, right, plus a potential, this potential is dependent on (x,y,z), time independent special coordinate dependent potential, okay.

Now what is the time dependent Schrodinger equation? When this $H^{(0)}$ operates on capital Ψ, it gives you minus $\hbar/i\ \partial/\partial t$ of Ψ, okay. Of course, we're going to write this as a product of space and time parts. We write it like this, $H^{(0)}$ operates on $[\psi\ \varphi]$, this is also $\partial/\partial t$ of $(\psi\ \varphi)$, and this $H^{(0)}$ is time independent, isn't it, right. So φ is a constant as far as this is concerned, so we might as well bring φ out and write like this, $\varphi H^{(0)} \psi$ and here, this ψ is time independent, so that comes out, so I can write it like this, ψ [$-\hbar/i\ \partial/\partial t$ of (φ)], but then it doesn't make sense write ∂ anymore, isn't it, because whatever it is operating on, the derivative is a function of time and nothing else. So I might as well write this as [$-\hbar/i\ d\varphi/dt$], and the next step is also simple.

Divide both sides by the product of ψ and φ, what do you get on the left hand side. You get $H^{(0)} \psi/\psi$, on the right hand side you get this whole thing divided by φ. Now left hand side is a function of special coordinates only no time, right hand side is a function of temporal coordinate time only no special part. So both sides have to be equal to some constant, and as we know already, what the left hand side is, we write this simply as E energy and that is how you get, first of all, the time independent Schrodinger equation, $H^{(0)} \psi = E \psi$ and time dependent part separates out like this, you can write $-\hbar/i\ d\varphi/dt = E \varphi$ or $d\varphi/dt = -iE\varphi/\hbar$, is that right. Hence, what is the expression for φ that you get? Yeah. $E^{-iEt/\hbar}$. You can write it in two, three different way, this is what we'll write for now. So far so good.

So this ψ then -- I don't need this anymore. This becomes the space dependent ψ. $e^{-iEt/\hbar}$, okay, right. So this is our separation of variables into special and temporal ones. We separate the equation into a time independent part and a time dependent part and we get this expression of the wave function, which is dependent on -- which is a product of a special part and a temporal part. This is the form of the wave function that we're going to use in our subsequent discussion. I think this is something that you know already. So I hope this was as recap for everyone. Any questions so far, any doubt, great.

Now what we'll do is -- where are we going to use it? We're going to use it in spectroscopy. Spectroscopy means transition from one state to the other, right. And in the systems that we've studied so far, rigid rotor and harmonic oscillator, anharmonic oscillator, there are of course many states, right. But then we always talk about one transition at a time, don't we, right? There is something called one photon rule. Do you know one photon rule? What is it? One photon can bring about only one transition, right. So your photon is not like Rajinikanth's bullet. Rajinikanth can kill multiple villains using the same bullet and knifer and everybody knows that clichéd story, but your photon is not like that kind of a bullet. One photon can only bring about a transition from one state to another state, it cannot get separate and bring about many, many transitions, okay.

So what we'll do is we will at least to start with, keep it very simple and we'll try to understand a two-state system, a two-level system. Yes sir. Physical significance is something that we've studied long ago, that it travels as packets, right. So what it says is that you cannot split a photon. So you can actually add two. So there is something, if we get time, we're going to discuss. There's something called nonlinear spectroscopy. Nonlinear spectroscopy means, well, you know this ball resonance condition, right, you have an energy gap ΔE. If the frequency of the photon is such that $H\nu = \Delta E$, then it will be absorbed. Sometimes what happens is energy gap is $2.H\nu$. Even then if you use an intense field of light, say laser light, then you can bring about a transition. What's happening essentially is that, you can think in the classical way, two photos are adding up to bring about this transition. So what we do is we invoke, what are called stationary states. We'll encounter them when we talk about Raman spectroscopy, but then one photon cannot get split into two. Photon is a fundamental unit of light, you can think, okay, that's where it comes from 14:41 Law, that's where one photon rule comes from, okay.

So we're going to talk about now a two-level system. Let us say, this is characterized by Energy E_l, l for lower, but this one is m, not u for upper but m the next letter in the alphabet. This of course is also characterized by Ψ_l and this is wave function for this Ψ_m, all right. Let us start with a situation where this level is populated and this level is not, very much like your harmonic oscillator or anharmonic oscillator. So population of this is 0, population is this is some finite population, there's some probability of this state being populated, okay.

In that case, what will be the wave function of the system if only the lower level is populated? It will be ψ_l, right. You don't worry about whether there is any ψ_m, ψ_q, ψ_r, nothing is there, right, but what happens when you bring in light and cause a transition. In spectroscopy what we call a transition is in the language of quantum mechanics, super position or mixing of states. What we are trying to say is, the slide comes in and perturb the system, so that this probability of the upper state being occupied also increases, okay.

Now after some time, sometime after you switch on the perturbation, let us say, then what happen, what should be the wave function hat properly describes the system? Yes, what you're saying is right. What you're saying is $\Psi l + \lambda. \Psi_m$, okay. To keep it more symmetric, as you'll see, symmetry is very important in chemistry actually, not just spectroscopy, we'll write a more symmetric expression, and that expression is this Ψ is equal to let us say, some $C_l. \Psi_l + C_m. \Psi_m$, fair enough. Instead of one end λ as coefficient, I am trying to use C_l and C_m as coefficients, all right.

Let us go back one step and think, at time $t = 0$, what is the value of C_l, what is the value of C_m. $C_l = 1$ and what is C_m, 0. So I'll just write that down, so that I don't forget. At time $t = 0$, $C_l = 1$ and $C_m = 0$. What happens for initial time, small time, let us say, a very small time has elapsed, after I've switched on the perturbation, C_l will still be close to 1, C_m will still be close to

0, right. So let me write like this when time t tends to 0, I can write to a good approximation, C_l is approximately equal to and C_m is approximately equal to 0. We are going to use this approximation a little later. Are we okay with this, understood?

I am not saying -- okay, let's come back to that discussion later. What happens sometime after I've switched on the perturbation? Let it be initial time. Now C_l will decrease a little bit from 1, C_m will increase a little from 0. Now you need to write the linear sum as a wave function, okay. And if you work at long times after switching on the perturbation, then of course, C_l and C_m can even become comparable depending on what kind of system you're working with, what kind of electric field you've used.