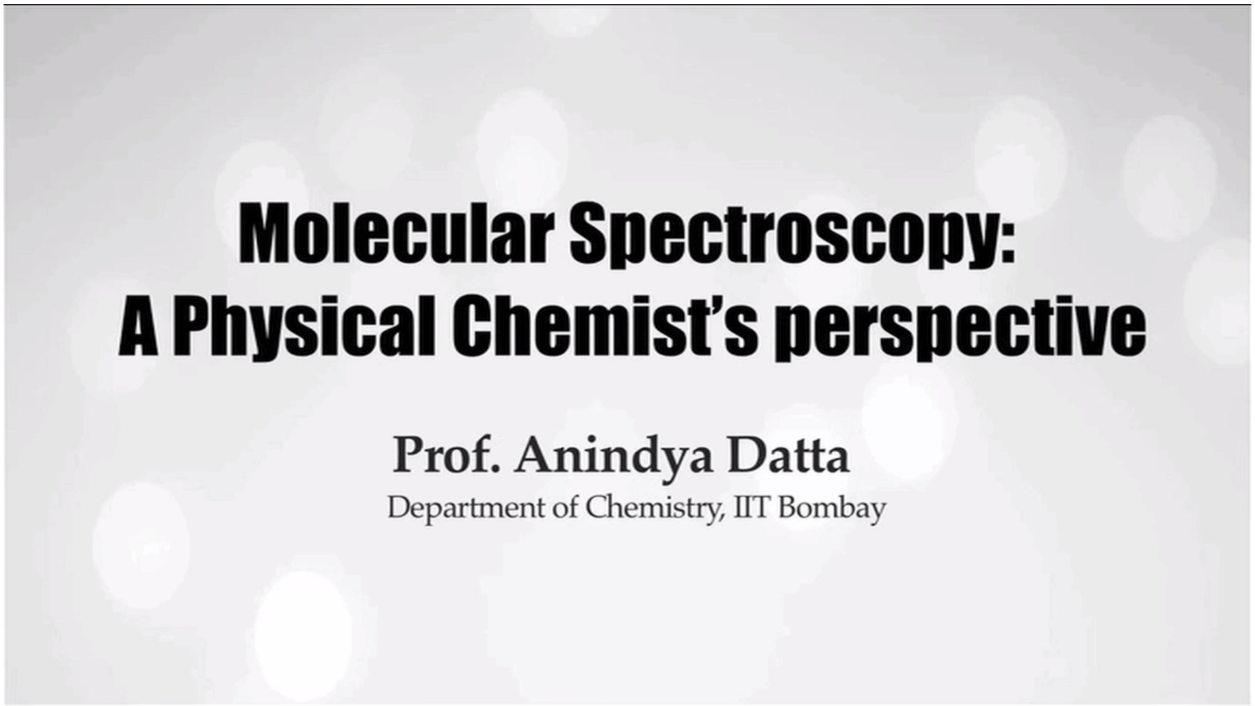
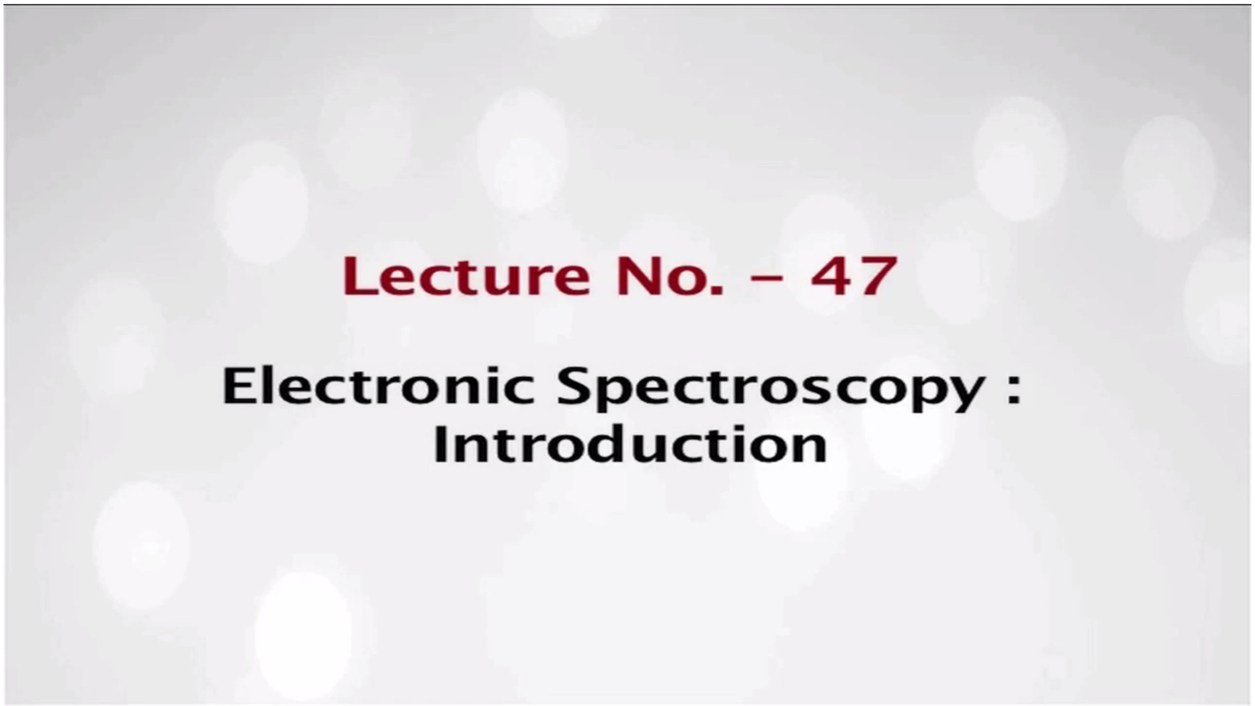


Molecular Spectroscopy: A Physical Chemist's perspective

Prof. Anindya Datta

Department of Chemistry, IIT Bombay



Lecture No. – 47

Electronic Spectroscopy : Introduction

Prof. Anindya Datta: For the last few classes, we've been discussing vibration of polyatomic molecules, and we have discussed it using the concept of symmetry that we have developed. In fact, we'll need to come back to symmetry once again for discussion of electronic spectroscopy, but today, let us take a break from symmetry and let us discuss, well, spectroscopy,

spectroscopy at least one day, then next day onwards, we’ll get back to symmetry once again.

One thing I want to ask you. Are you familiar with this LS coupling, are you familiar with term symbols, have you learned that in organic chemistry? No, I know you haven’t. What about the -- how many of us know term symbols? Okay. LS coupling, JJ coupling? Okay. So we’ll see what we do about that. The problem is once again if I get too much into LS coupling and all, that will take time, but anyway, it’s not as if we don’t have time. of course, the syllabus that we discussed at the beginning was too ambitious. We’ll not be able to discuss things like field detail, so let’s take it easy, we’ll see what would happen. One module today, and I am starting now.

Today, what we’ll do is we’re going to do a brief introduction to electronic spectroscopy. So what we do in electronic spectroscopy of course, we’ve talked about rotational levels, we’ve talked about vibrational levels, now we start talking about electronic levels, and to start with again, today’s discussion will be largely on the atomic molecules, but it can be seamlessly integrated with the discussion of electronic spectroscopy of polyatomic molecules, but when we really want to discuss the polyatomic molecules, you’ll require what is called the symmetry of stats, right. So that is something we’ll take up next day onwards.

But before I go there, let me start with one question. What Is an electronic state? What is it that defines an electronic state? Yeah, electronic states are specific energies, of course. We are talking about stationary states. But is there anything else, some molecular property, that defines the state? Of course, stationary states have, but -- okay, anybody else. Quantum number, okay. Anything else, something easy as usual? Sorry, chemical bonding. Well, the answer I was looking for is electron configuration.

See electrons are -- electrons reside in different molecular orbital as you people have said correctly, right. Now how many electrons are there in 03:51 molecular orbitals and what are their speeds? Whenever you talk about more than one electron system, spins become important, as you have studied in the discussion of things like multielectron atoms. So an electronic state is defined by electron configuration and the spin of the electron, all right. But then when you look at electronic states, you cannot really neglect the vibration and rotations either. This is important to either.

Why? Because if you think of an electron potential energy surface -- this is the same diagram that we drew for our anharmonic oscillator, isn’t it? It’s just that when you talk about electronic states, you talk about not one more scur but similar more scurs, the lowest one are the ground states, the higher ones are the electronic excited states. Each of the states is associated with vibrational levels and each of these vibrational levels is associated with rotational levels. So when I say that a molecule is in the ground state, the ground electronic state, I also have to specify where is it. It will be int B = 0, that we know, but it can be in different J levels.

Again, when we talk about the transition, transitions would originate here, I understand, but they can go here, they can take the system here. The moment transitions take place, you have to state what the destination is, not only the electronic state, but also the vibrational level, but if you have that much of accuracy, the rotational level as well, all right. So that is why we have to discuss electron -- we have to discuss vibration and rotation before we can talk electronic spectroscopy.

Now our starting point here is going to be Born-Oppenheimer approximation. I think we have talked about this in this course earlier. Have we or have we not? What does Born-Oppenheimer approximation say? So suppose I want to write Born-Oppenheimer in terms of wave functions, how do I write it? If ψ is the wave function of the system, how do I express it? Ψ, I'll write es, just to remind ourselves that spin is also important, e for electronic, s for spin, multiplied by, I'll just write ψv, v for vibration, multiplied by ψr, r for rotation, okay. And what about the energy? Total energy will be energy of, this time I'll just write electronic, or I can write Es + Ev - Er, v for vibration, r for rotation, oaky. This is just a sum.

Now of course, let us not forget what is the magnitude of energies we are talking about, what is the typical energy associated with rotation, how many centimeters inverse, 10. 8 to 10 is making a little too stringent, I would say, 2 to 10 or something, 10^0 to 10^1, okay. What is the typical energy associated with vibrational levels? Number, I am just looking for numbers. You can either be right or you can be wrong. Nothing to worry. Rotation is 10^0 to 10^1 centimeter inverse. What do you think vibrational energy would be in centimeter inverse? Yes, not 4, I would say, 10^2 o 10^3, right. So you think of the numbers that you see on our vibrational spectrum, 1000 cm inverse to 3000 cm inverse, 10^2, 10^3.

What about electronic levels? What is a typical energy? Yeah, 5, even 4. You can do a quick calculation. Electronic means what, UV based, right? So 400 nanometer is a typical -- 300 nanometer, then it might be easier. No, why would it be easier? 400 nanometer. 400 nanometer, how many centimeter inverse is that? 400 nanometer is what kind of light, red or blue or green or yellow? Okay, violet. There is a 09:05 anyway. So what is the centimeter wave number of that? It is 25000. I said wave number, so when do we express wave number in nanometer. 400 nanometer is the wave length. What is wave number? Yeah. It's 25000 right. Why complicate thing? If 25000, say 25000, that's what we understand. Now tell me 10 to the power, how much is that, 2.5 into 10^4 or something like that, 10^4, 10^5.

So when you're talking about something number like 25000 or 18000, 10000, even 10000, 10000 is actually no even in visible range, your instrument has to be really, really good if you also want to detect something like 2 cm inverse. So generally, it is enough if we consider this. For most of the discussion, we don't even talk about donation. So we write the wave function like this, we write the energy as sum of electronic energies and vibration energy, okay. Of course, you can see if your instrument is good enough, that shows up as rotational fine structure in your spectrum. Once we're done with our discussion of electronic spectroscopy, we'll quickly go back to rotation, and we're going to use this form of the wave function to talk about an aspect of rotational spectroscopy that we have neglected so far, okay.

In fact, because of this kind of wave function, nuclear spins also affect the nature of rotational spectrum, we'll come back and talk about that as well, but in a couple of weeks maybe. For now, what we do is for most of our work, we restrict to electronic and vibrational energies, sometimes if we have an instrument that is good enough, then we talk about rotational fine structure, maybe we'll discuss that tomorrow, not tomorrow, next Monday.

Now before proceeding further with this, let us remind ourselves, a little bit about spin, okay, and this is how I like to do it. I don't know if I've done it in class already. Let us say, I have a molecule, this is Homo, this is Lumo. For most of the organic molecules what you have is, you have two electronic in Homo, right. So I am going back to the question that I asked at the beginning of the discussion today, what is a state, okay, how do we define a state in an easy manner?

So what is the electron configuration then, Homo 2, Lumo 0, right. This defines a state, all right, and it is lowest energy state, ground state. What is that state called? I think we know this. That state has a name, right. It's the singlet ground state, right. We called it the S_0 state. This is how we generally denote it. And the easy convention that we use is we draw a picture like this and we say that this spin is ½ , this spine -½, so total spin, S, is ½ - ½ is 0, so 2S + 1, spin multiplicity, is 2 (0 +1), which is 1. So it's singlet state.

Now when you do a Homo to Lumo excitation, then what happens? You have one electron in Homo, one electron in Lumo, Homo 1, Lumo 1, that kind of an electron configuration. And in the easy convention, what we say is, we say, there are two possibilities, the spins can be paired or the spins can be parallel. So in this situation, what is S? When the spins are paired, S is 1, ½, -½ is 0, last time I checked, right. So what you're saying is spin multiplicity is 1. 2S + 1 is 1, so this is also a similar state, but will its energy be more than or less than 0, definitely more. So it is a higher energy excited similar state, and since it is a first state that you get upon excitation, you call it the S1 state, all right.

Now what about this, what is S for this 1, ½ + ½ is 1, that is S, 2S + 1 is 3, so it is a triple state. That is what we are used to thinking. And then is the energy same? See in both the situations, we have one electron in Homo, one electron in Lumo, right. Are the energies same? Spin reversal is occurring in S_1. Spin reversal is taking place in T_1. So? That will require extra energy, so triplet has more energy, T_1 has more energy than S_1. So Manthan says, T_1 has more energy than S_1, but that depends also -- both possibilities are there. That is a safe answer. Now he decided to fence it. Sit on the fence and say, this is possible, that is also possible. Do you have somebody who can decide either this side or that side of the fence?

I am saying always energy of S_1 and T_1 are different. So now fence sitting on this at least. T_1 will have greater energy. Does anybody want to say that T_1 will have lower energy? Why, why will T_1 have lower energy? Highest multiplicity, so? According to Hund's rule, right. So we'll accept this answer but the actual answer is a little more complicated, but at least for now, it is fine if we say that according to Hund's rule, what does Hund's rule say, everything else being the same, the state with the higher multiplicity has a lower energy. That is the way in which we have learned Hund's rule bypassing all the mathematics, okay.

So if you stick to that simplistic kind of thinking, T_1 does have lower energy, all right, so that is why generally you draw the energy when you fold like this, I'll just move it a little bit away, S_0, S_1, T_1, something like this. But let us not forget, something all of us know already. Let us not forget that this picture is only approximate. The singlet and triplet really comes from a discussion of the spin wave function of the two-spin system, right. We have two spins, two electrons, each can have either alpha spin or beta spin. So one situation is that, both have alpha spin, $\alpha(1)$, $\alpha(2)$, 1 and 2 are identifiers of electrons, names of electrons, and alpha, beta, these are the spin wave functions. Alpha means the magnetic spin angular momentum is ½, beta means it is -½, up spin down spin as we generally call them. So both can have alpha spin, no problem.

Can both have beta spin? Yeah, no problem, but as you have learned when you studied multielectron atoms or molecules, the moment we go to the situation that one has alpha spine and one has beta spin, you cannot say that the wave function is $\alpha(1)\,\beta(2)$ or $\alpha(2)\,\beta(1)$, because electrons don't wear jerseys, right. This 1 and 2 are not written on electrons; they are indistinguishable. So all you can say is that one of the electrons has alpha spin, the other has beta spine, but you cannot say for us that 1 has alpha and 2 has beta or the way around. So the situation is al linear combination of this and this, $\alpha(1)\,\beta(2) \pm \beta(1)\,\alpha(2)$, all right. And then as you know, if I write $\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)$, this is one possibility, and $\alpha(1)\,\beta(2) - \beta(2)\,\alpha(2)$, this is another possibility.

So as you can see, this α α -- very commonly what we do is we draw, we don't even say 1 and 2, we say, alpha, alpha, the implicit meaning is first one is 1, second one is 2. A(1) α(2), α α, β β, α β + β α, all these symmetric with the spectrum exchange, okay. You can even say, symmetric with the spectrum merge. A β - β α is antisymmetric, right. If you interchange 1 and 2, then your wave function will change sign. So if you remember, poly principle, it taught us that the overall wave functions must be anti-dimension. In fact, when we talk about that rotational spectrum, this is what we'll use later on, but for now, this is what it really means. We have three wave functions, that are symmetric, they together make up the triplet many fold. A β - β α is a unique wave function, which is antisymmetric, that is the single wave function. So when we single triplet, the implicit meaning is that singlet is actually one wave function, triplet is a combination of three wave functions. That is where it comes from.

And also, you can think that, okay, this means the spins are parallel, fine, β(1) β(2) is also, that means spins are parallel, but α(1) β(2) - β(1) α(2) means the spins are actually paired. So you can also think that the triplet state really is only 67% spin parallel state, right. So these arrows that we drew, they give us only an approximate picture, this is the real accurate picture, okay. Please don't forget this. I am sure I've said this earlier, but this is something that I have seen we forget. This is so convenient and it's used all the time in photochemistry courses and it works for all practical purposes. So more often than not, we tend to forget this, but we will need it.

In fact, somebody asked me once in class, is it possible to see the three triplet wave functions. What do you think? Do you think it's possible to see some signature of the three wave functions? We are saying that there are three wave functions, which had degenerated, okay. Is it possible to see, do you know? It is possible to see. We apply a magnetic field. What happens is they interact differently. The moment you attract magnetic field, things which have different orientations or angular momentum, they separate out in it. So there are experiments in which you apply a weak magnetic field and you can split. Not weak actually, you have to apply something like I think one tesla magnetic field. And then not only can you see a signature of the three different wave functions, you can actually cause the system to shuttle between singlet and triplet states by application of magnetic field. So they are actually there, it is not something we are making up from some weird unrealistic mathematics. Fine, that is a point I wanted to make.

Next. What did I wanted to say next? This is we have defined what states are. Now let us go a little bit into spectroscopy of the states. We will need the signatures later on. Let's just leave it here. So as a first approximation, this is what we will deal with, and we talk about what kind of spectrum we can expect when you go from singlet S_0 to S_1 or can you go from S_0 to T_1 and so on and so forth, okay. These are the wave functions that we'll use. Of course, in order to say whether we can have transition between two states, we need to talk about some kind of selection group.

Before we go there, we'll need something more and that something more is Franck-Condon principle. Frank-Condon principle is something that I think everybody knows already. It is already depicted in this diagram. See when I drew the arrow, I drew vertical arrows, didn't I? I did not draw an arrow like this. Franck-Condon principle essentially says that you cannot draw a bent arrow. What does that mean? When you draw a vertical arrow, what is X axis? If it's a diatomic molecule, it's very easy to understand. X axis is inter nuclear distance. So if you draw a vertical arrow, what do you mean? That means energy is going up but inter nuclear distance does not change. That is essentially what Franck-Conon principle states that since nuclear are much heavier particle than electrons, during the motion of electron, you don't need to consider the motion of this big fat nuclear. That's too sluggish. In fact, that is something that comes from your Born-Oppenheimer approximation as well. So that is why we always draw vertical arrow.

Now with that understanding, let us see, what kind of selection rules we are going to have. The other wave functions, and you have your dipole moment, so you have to write the transition moment integral, all right. This discussion we had so far I think is there in any standard textbook, even Atkins physical chemistry or Banwell's spectroscopy, everywhere. What we are going to discuss now is there in Harris and Bertolucci's book. We have not really used that book too much so far, now we will, Harris and Bertolucci. So this discussion now is from Harris and Bertolucci's book. What will the transition moment integral be?

One thing we should not forget is that we have two kinds of coordinates now. You have nucleus and you have electron, right. When you talk about vibration, vibration is associated with movement of what, nucleus or electron? Nuclei with respect to each other, right. So what we'll do is we'll write the -- and when you have vector dipole moment, of course, you can write it in terms of nuclear as well as electronic coordinates, you need both, one is not enough, isn't it, specimen of nuclei and specimen of electron both are required.

So we'll μ as $\mu_n + \mu_e$, nuclear and electronic component, and transition moment integral will become, suppose I say that this first state is 1, second state is 2, this kind of transition is what I am talking about, it will be how do I write it. Ψ1es -- why am I write 1es -- $\langle\psi_{es}^{(2)}\ \psi_v^{(2)}|(\ \mu_n + \mu_e)|\psi_{es}^{(1)}\ \psi_v^{(1)}\rangle$. Are we okay with this form of transition moment integral? This is the wave function of the origin; this is the wave function of the destination. Instead of writing l and m once again, I am just writing 1 for the level from which the transition begins, 2 for the level at which the transition terminate, okay. And I have neglected ψ_r for now, we'll just consider vibrational levels.

Of course, you break it -- okay, what is beta, when you write like this sometimes you forget what ∂ is, volume element. Volume element will also comprise of a nuclear term and electronic term, right. Right or wrong? What was the volume element in, say, Cartesian coordinates? Dv = or $\partial_o = d_x\ d_y\ d_z$. What was it in terms of spherical polar coordinates? R2 D_r = sine theta, d theta, define. So that's what I am trying to say, when you have two coordinates, 1 and 2, ∂ is essentially $\partial_o^{(1)}\ \partial_o^{(2)}$. So let's not forget that I am not writing it explicitly, but is there. So in fact, if you read Harris and Bertolucci's book, they have not used this bracket notation, but Harris and Bertolucci is a printed book, so if you see that, they have actually used explicitly, $\partial_o^{(n)}$ and $\partial_o^{(es)}$. Don't forget ∂_o is a product of $\partial_o^{(n)}$ and $\partial_o^{(es)}$.

So let me write like this, $<\psi_{es}^{(2)}\ \psi_v^{(2)}|\ \mu_n|\psi_{es}^{(1)}\ \psi_v^{(1)}>$ over all space + $<\psi_{es}^{(2)}\ \psi_v^{(2)}|\ \mu_e|\psi_{es}^{(1)}\ \psi_v^{(1)}>$, all right. Now if you look at the first integral, I can write it as a product of two integrals, one in nuclear coordinates, one in this electronic coordinates. What will be the factors in the integral in the electronic coordinates, $\psi_{es}^{(2)}\ \psi_{es}^{(1)}$, integrated over all $\partial_o^{(es)}$, and that will be multiplied by $\psi_v^{(2)}|\ \mu_n|\psi_v^{(1)}$. Are we clear? Maybe I don't need this anymore. Right here, TMI = first term is $<\psi_{es}^{(2)}\ \psi_{es}^{(2)}>$ integrated over all space, when I space, I mean electronic space and multiplied by $<\psi_v^{(2)}|\ \mu_n|\psi_v^{(1)}>$ integrated over all space in nuclear coordinates. First term is taken care of. Are we clear about the first term? Any questions?

Second term, plus. What will the second term be? This time, this -- so this what will it be? It will be $\psi_{es}^{(2)}$ multiplied by μ_e multiplied by $\psi_{es}^{(2)}$, integrated over all space in electronic coordinate, that will be one integral, that will be multiplied by integral $\psi_v^{(2)}\ \psi_v^{(1)}$, over all space, okay. So I'll write that, $<\psi_v^{(2)}|\ \psi_v^{(1)}><\psi_{es}^{(2)}|\ \mu_e|\psi_{es}^{(1)}>$, okay, these are the two terms we have.

Now look at the first term. Integral of a product of two electronic wave functions, two different electronic wave functions of the same molecule. What will that be? That will be 0, because they form -- they are a member -- yeah. Yes, they form an orthonormal set and that is why it is 0. So good thing is this first term becomes 0, okay. We agree that this is equal to 0. Why? Because these two are members of an orthonormal set, two different members of orthonormal set, all right. So in the TMI, you are left only with the second term.

Now tell me, similarly, if this integral is also equal to 0, then TMI is always equal to 0 and we can go home. We can have an early lunch today and there will be no electronic spectroscopy in the world. So obviously, this is not 0. Can you tell me why integral is not 0, $<\psi_v^{(2)}|\psi_v^{(1)}>$, why is that not 0? Different states, okay, but they are of different electronic states, right, so they belong to different vibrational manifolds. Don't forget that this$\psi_v^{(1)}$ is here $\psi_v^{(2)}$ is here, right. So this is one orthonormal set; that is another orthonormal set. A wave function from here and a wave function from here are not orthogonal to each other, right. My 1S orbital and your 1S orbital are not orthogonal to each other, okay. That's what it is.

So the second term, thank God, it survives, otherwise, there would be no electronic spectroscopy. So transitional moment integral then would be equal to, I'll write this, $<\psi_v^{(2)}|\psi_v^{(1)}>$ and I'll expand this a little bit. Before that, let me tell you what this called. Does anybody know what this is called? What is this called? It is called the Franck-Condon factor. It is called the Franck-Condon factor.

So let us take an example. Let us say, the situation is like this and I think many of you might be actually familiar with what I am drawing now. The two energy minima can be connected by the same vertical line. What does that mean? Equilibrium bond lengths are same in ground and excited state. In that case what will happen? Of course, all upward transition will be gin at V = 0. So this is your wave function, this is your $\psi_v^{(1)}$. In this case, think of $\psi_v^{(1)}$ and think of $\psi_v^{(2)}$. What does this integral mean? This integral means I should take this $\psi_v^{(1)}$, if I try to plot $\psi_v^{(2)}$ on top of this, I hope you'll agree with me that there will be a more or less complete overlap, right. This integral means you multiplied this by this and find out the area, right. Agreed or not? Okay.

This is something like what we have learned in bonding. In bonding, we talked about overlap integral. What was overlap integral? You have one 1S orbital of atom A, you have another 1S orbital of atom B, they overlap. Overlap integral is integral φ_a φ_b over all space, right. Why is it called overlap integral? Because this integral has an onset of value only in areas where the two wave functions have overlapped, because it's a product. This is the same thing, but with vibration wave functions, right.

So what it means is that, if there is a good overlap, then this Franck-Condon factor will be large. Now think if there is a little bit of displacement. This is your 0th vibrational wave function of the lower electronic level. Let us say, the equilibrium bond length is a little more. What will happen? Now the overlap is this, less than what it was earlier. So if the equilibrium bond lengths are not same in ground and excited state, then what happens is that the Franck-Condon factor for the 00' transition or 0'0" transition, whatever you want to call it, that becomes smaller and smaller, okay.

What effect would that have on it? This is what is multiplied by the second integral, right. So a larger Franck-Condon factor would mean a larger transition moment integral, and right now, you know very well, what is the meaning of a larger transition moment integral. How is transition moment integral related to probability of transition? Square, right. So larger transition moment integral means a larger probability of transition. How is a larger probability of transition manifested in the spectrum? Greater intensity of the spectrum light. So the intensity is determined by the Franck-Condon factor.

Next, please read the discussion in Banwell’s book about what spectra look like, which line is most intense when the equilibrium bond length goes from being the same in ground and excited state to being the equilibrium bond length being longer in the excited state to equilibrium bond length being shorter than the excited state, okay. Those pictures are drawn very nicely in your Banwell’s book. You can read them from there, absolutely descriptive. Just don’t forget that the reason there is the change in Franck-Condon factor. Let me write, the second part, second factor now, and while doing it, let me do a little bit of expansion. Yes. Sorry.

So if the equilibrium bond length is different, what will happen? Let us say this is V = 0 wave function, right, and this is a V= 0 wave function of the excited state. If equilibrium bond length is same in both the cases, then you have an exact overlap, right, like your total eclipse that kind of thing. So you can understand Franck-Condon overlap will be maximum. Now if the equilibrium bond length is a little more, what will happen? The overlap will be like this. So the area will be much smaller and in that situation, what is likely to happen is that now think of V = 1. Initially, what happened, this is V = 0, V = 1 is something that I cannot do with my hand, because I don’t have enough joints. It’s a complete sine wave, right. So what was happening then was that the sine wave had a minimum in the middle, okay, and then this is sort of minus, so overlap would be 0 actually. Now if that moves a little bit, then it might move sufficiently so that the half of the sine wave comes exactly here, then the transition between 0 and 1’, 0 vibrational level of ground electronic state and V = 1 of the excited electronic state, that might have the greatest Franck-Condon factor. That is what I am trying to say. Are we clear? Yeah.

Oh. So for that, what you need to do is you have to write the form of the wave function explicitly. You know the form of the wave function anyway, right, so the only difference is that you write the vibrational wave function in terms of X. What will X be here? This and that will be related by, if I call this X1 and X2, they will be related by the difference in equilibrium bond length. That is how it will show up mathematically, okay.

Now how can I expand this? I have written ψ_{es}, which mean that that is the wave function for the electronic state, which includes the spatial part, the orbital part and the spin part. As a first approximation, they should separable, so I should be able to write something like $\psi_{es} = \psi_e \psi_{es}$, okay. When this happens, we say, there is no spin orbit coupling, okay. So this then becomes $<\psi_e^{(2)}| \mu_e|\psi_e^{(1)}>$ integrated over all space -- now I need this part -- multiplied by $<\psi_s^{(2)}|\psi_s^{(1)}>$. Are we clear? No spin orbit coupling. So I should be able to write this integral as a product of two integrals, one is electronic coordinates, one is spin coordinates, okay. When I do that, this is what I get.

So now see, when will transition moment integral be non-0? Of course, your Franck-Condon factor will always be not 0. Whether it is large or whether it is small, determine whether the transition is strong or not. What about this? Will it always be non-0? No. How do we know whether it is non-0 or not? From symmetry. That is why we will have to go back to our discussion of symmetry. What about this? This is a spin coordinate. A spin coordinate is a funny customer as we know, right. When is this 0, when is this non-0? When spins are same, then it is non-0; when spins are different, then 0.

So one example -- of course, when I spins are same, spins are different, what do I mean? If you take $\alpha(1)\ \alpha(2)$ and $\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)$, please work I out. This particular problem I think is worked out in Harris and Bertolucci’s book. So I encourage you to work out that integral using all possible combinations. What are the possible combinations? One is singlet, singlet, that will be non-0, you will see. Second is you can do singlet with each of the triplets, they will always be 0, all right.

Next, you can of course do, each with itself is trivial now, you can see that, if the initial spin function is $\alpha(1)\ \alpha(2)$,final spin function is $\alpha(1)\ \alpha(2)$, it will be non-0. I encourage you to try out, and you can see it again, you don’t even have to do it. What happens if there is a transition between $\alpha(1)\ \alpha(2)$ to $\beta(1)\ \beta(2)$? Is that possible? $A(1)\ \alpha(2)$ to $\beta(1)\ \beta(2)$, what will the integral be? Integral will be $<\alpha(1)\ \alpha(2)\ \beta(1)\ \beta(2)>$ over all space. Now this is in terms of coordinates of 1 and coordinates of 2. So it will be product of $<\alpha(1)\ \beta(1)>$ over all space and $<\alpha(2)\ \beta(2)>$ over all space. That is 0.

So what we know already is deltas must be equal to 0, what we also need to remember is deltaM_s also has to be equal to 0. I am not doing it here, because in any case when you talk about NMR spectroscopy, we are going to deal with the spin wave functions, but please go through Harris and Bertolucci’s book and satisfy yourself and work it out yourself, it’s very simple algebra, satisfy yourself that this is the condition.

So if this part of the transition moment integral is 0, then the transition is spin forbidden, if this part is 0, then is orbitally forbidden, okay. And generally, what happens is there are ways by which you can beat these forbiddeness. As we’ll see, using arguments of symmetry, an orbitally forbidden transition can be vibronically allowed. Vibronically allowed means you don’t have to always go from 0 to 0, right, $V = 0$ to $V = 0$, no necessarily. You can go from $V = 0$ to $V = 1$. The moment you do that, symmetry of $V = 1$ will come into play and something that was not allowed will become allowed. We’ll study it next week, okay. So orbitally forbidden transitions sometimes are rendered allowedness vibronically, but is not so easy to render some allowedness to spin forbidden transition. What is the mechanism by which spin forbidden transitions can become allowed to some extent? I think you know this, most of you. It is called spin orbit coupling. Your spin orbit coupling, the nature of the spin can get modified, we'll discuss that briefly also.

So this is the expression for transition moment integral. If this is 0, then it is orbitally forbidden. It can become vibronically allowed. So typical epsilon values for orbitally forbidden but vibronically allowed transitions would be something like 10^1 to 10^3. If it's spin forbidden, typically, values would be 10^{-3} to maybe 10^{-1}. And if this is non-0, this is also non-o, then you have really high epsilon. That is the case in this dye molecules that you use, right, brightly colored stuff. For them, the epsilon values are 10^3 to 10^5, in some cases it can be even 10^6, okay. So that is the definition of a fully allowed transition. Fully allowed transition means both these integrals are non-0. Orbitally forbidden transition means this is 0; spin forbidden transition means this is 0, okay.

That is a terminology we haven't used that. We are going to make use of this next day and let us see how far we can do. Before talking about symmetry of states, we'll try to provide a brief discussion of LS coupling. So that is what we are going to do next week.