INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

NPTEL

NPTEL ONLINE CERTIFICATION COURSE

Molecular Spectroscopy – A Physical Chemist's perspective

Lecture-12

Selection Rule

With

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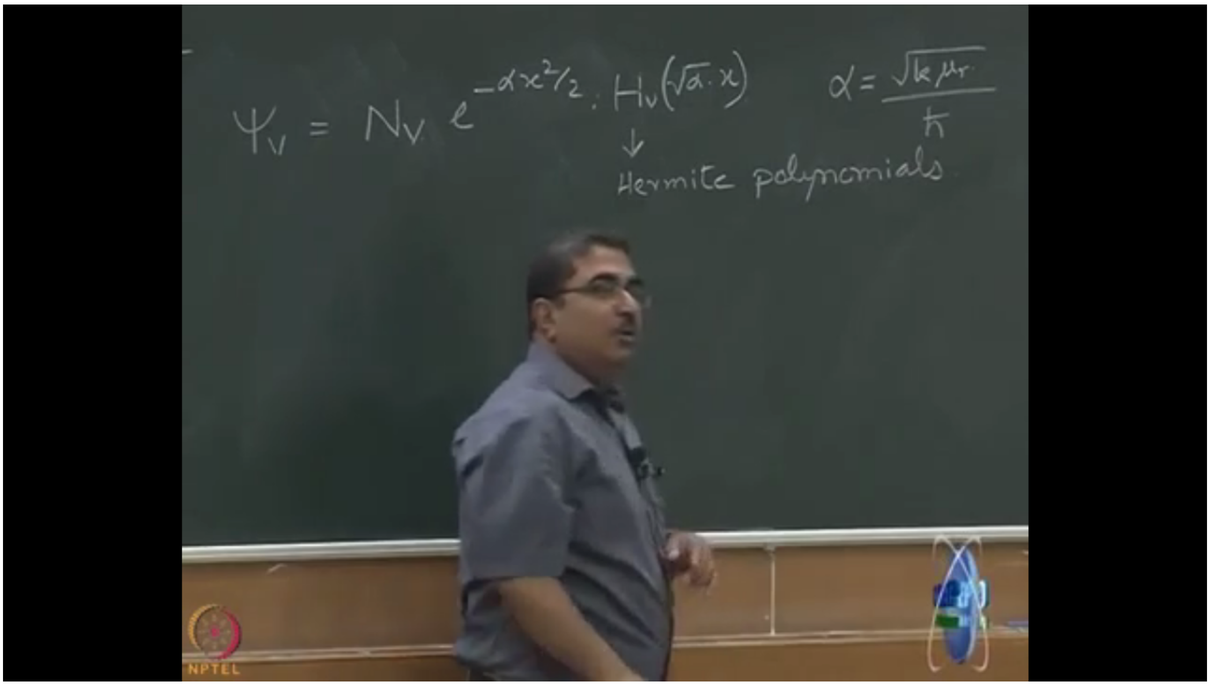
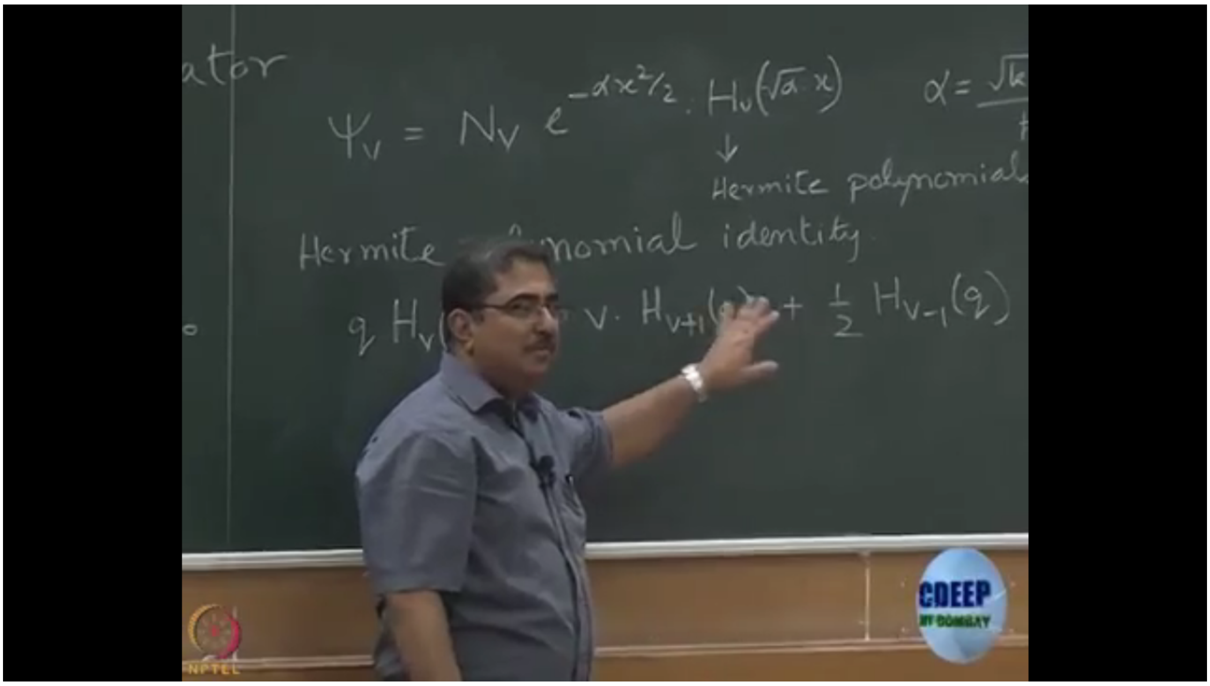


So far we have discussed simple harmonic oscillator as a model for diatomic molecules and we have learned what kind of energy levels we have in it. Now what we'll talk about the wave function and hence we are going to talk about the spectra. Again, you already know what the wave function is. So I'll just write the result. The wavefunction is something like this, Ψ_v is equal to, of course, it's multiplied by a normalization constant. You do not need to know the form of that normalization constant. As long as you write N, it is fine, multiplied by $e^{-\propto x^2/2}$ where x is what we have defined there. What is $\propto$? What is $\propto$? $(k\mu_r)^{1/2}/\hbar$. In most books, it is written root over everything and then in the denominator you have $\hbar^2$. Do you have to remember this? No.

I am sure I will forget this in a couple of days. You do not have to remember $\propto=(k\mu_r)^{1/2}/\hbar$. If you require it we'll give it. But you should remember the general form of the wavefunction. Multiplied by, now we are getting familiar with the plot, multiplied by a polynomial. This polynomial is H_v and it's a polynomial in $(\propto^{1/2}.x)$. Okay, $\propto$ is defined already.

What are these polynomials called? Hermite polynomials. Excellent.

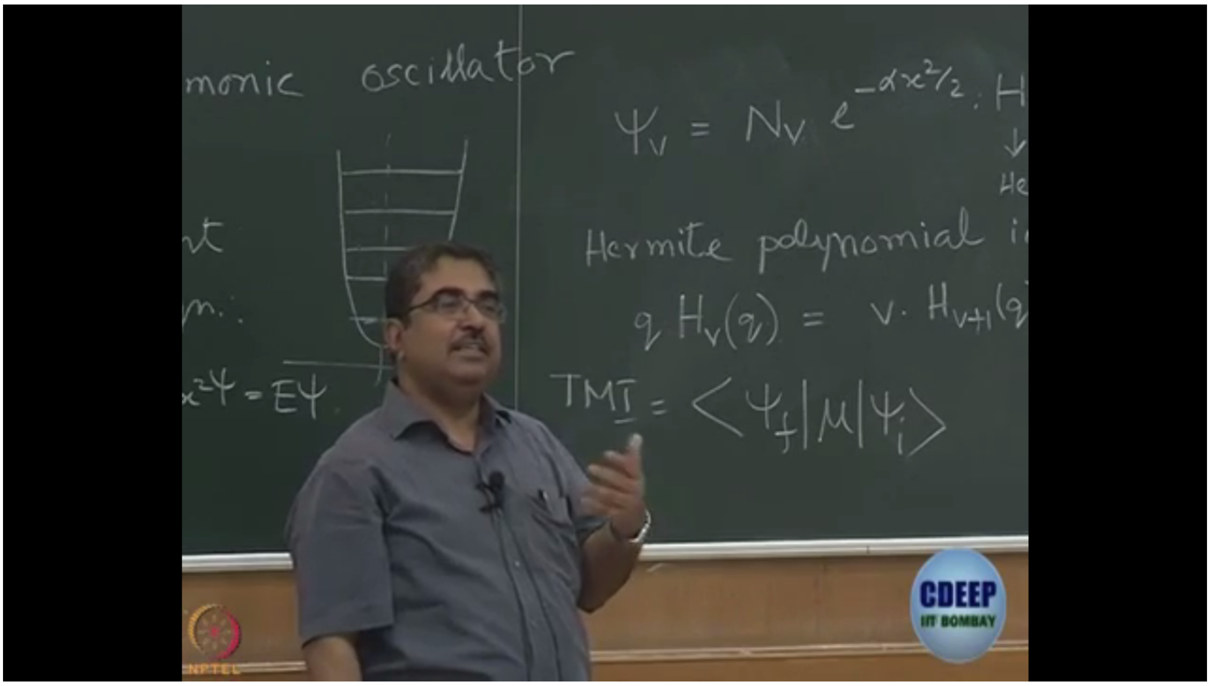
Do you know the form of some Hermite polynomials? What is say H_0. Yes, okay, I'd say it's a constant but 1 is a constant. What is say H_1? H_0 is 1, H_1 is 1. This is kind of taking things a bit too far. It is the same as the variable. What about H_2? So it's a second order polynomial. Just remember the order. 0^{th} order polynomial, first order polynomial, second order polynomial and so on and so forth. V determines the order of the Hermite polynomial. This is what you need to know. Nothing else. As you'll see this becomes rather important later on when we discuss vibration of polyatomic molecules. But that is the still one-and-a-half months away.



Okay, Hermite polynomials, and should I write it now, should I write it later? I'll write it now. Like our old friend, associated legendary polynomials, these Hermite polynomials are also not unrelated to each other. They are also related to each other by a very, very similar kind of relationship. In this case it is called Hermite polynomial identity and this is how it's generally written.

Let us say you write it in terms of some variable q. If you multiply a Hermite polynomial in q by the variable itself, then you get, now you are getting used to this. You get $v.H_{v+1}(q)$. I think it's $_{+1}(q)$ not that it matters, plus $1/2H_{v-1}(q)$. $v.H_{v+1}(q)+ 1/2H_{v-1}(q)$. So you are allowed to forget v and ½, no problem. As long as you can remember a_1 and a_2, it's fine. So like legendary polynomials these Hermite polynomials are also, even though the name is Hermite, they are not hermits. They don't live in isolation, they are related to each other. Every Hermite polynomial when multiplied by the variable can be expressed as a linear sum of the polynomial before it and the polynomial after it. The polynomial higher than it and the polynomial lower than it in the series, very similar to your legendary polynomials and this would kind of give you a hint of what is going to follow.

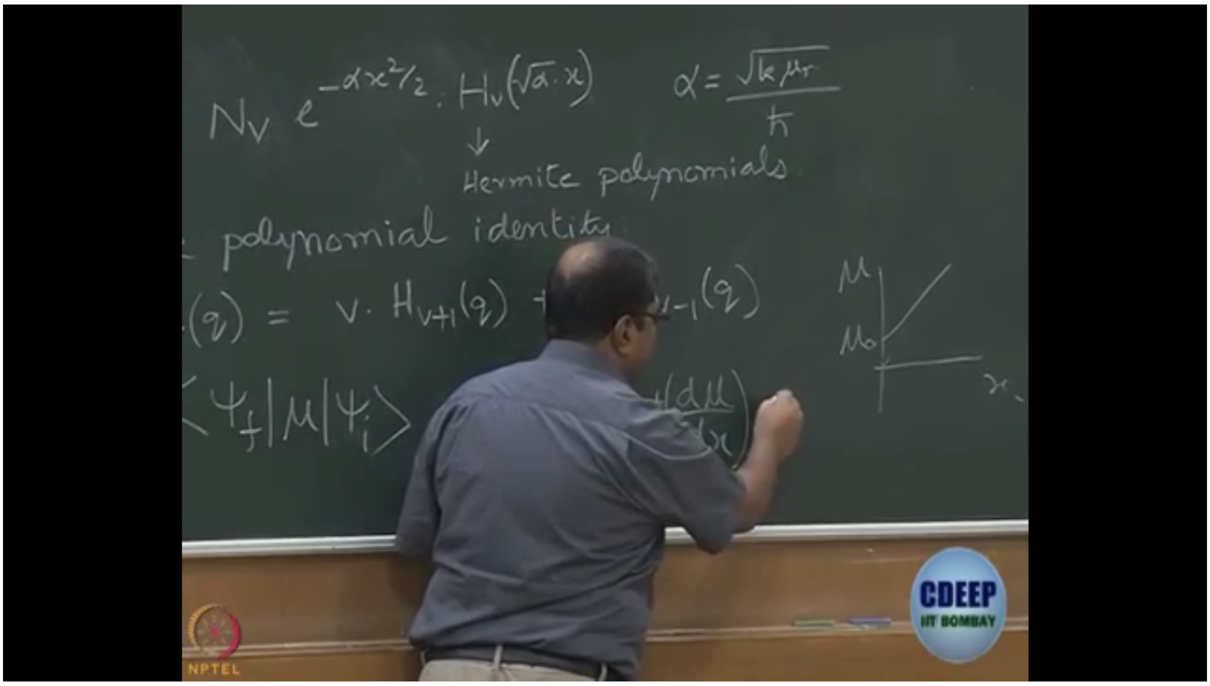
What is going to follow is a selection rule. Since we discussed rigid rotor already I think you can guess what the selection rule will be if you don't know already. But before that, we still have to deal with this dipole moment. So let's write first.



How do I know which transitions are allowed, which transitions are not allowed. This is a recurrent question in this course and the answer is also recurrent, I have to look at the transition moment integral. Transition moment integral as you know by now is, yesterday I have written integral. Today can I write brackets? Okay, thank you. Something like this $\langle \Psi_f|\mu|\Psi_i \rangle$. Ψ_i is the wavefunction of the level of origin, Ψ_i is the wavefunction of the level that is destination.

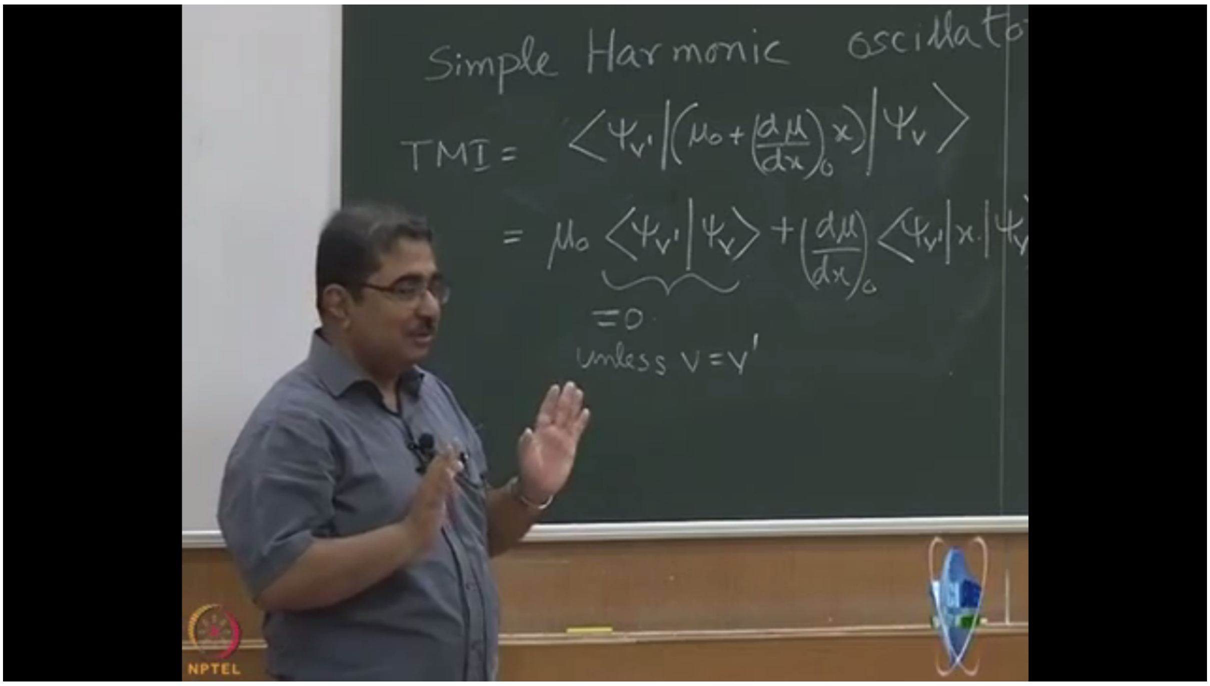
Okay, now so before we proceed we already know what Ψ_i and Ψ_f are. Let me see what μ is? How do I write μ? So when we have a molecule and the bond length changes, should the dipole change or should the dipole remain the same provided there is a permanent dipole to start with if you are talking about a diatomic molecule. In case of polyatomic molecules there can be situations where there is no dipole moment to start with but dipole moment is created during the course of vibration. Think of carbon monoxide. What does carbon monoxide look like? It's a linear molecule.

Now does it have any dipole moment? No, because the bond moments are opposed to each other. But then suppose it vibrates like this, this is called bending vibration. Then what happens? In this case, the vector sum of this and this would be something like this. So dipole is created. When it's here, the vector sum is like this. So essentially, for carbon dioxide, the dipole moment oscillates like this. We are going to discuss this in much more detail when we talk about polyatomic molecules, but for diatomic molecules actually if you think of hydrogen, H_2, no matter how much the bond stretches, are you going to have a dipole moment? No. So for diatomic molecules actually you need a permanent dipole moment but we'll see what the treatment tells us.



So let's write like this. Let us say the permanent dipole moment is μ_0. Of course, if there is no dipole moment, permanent dipole moment will be, well, μ_0 will be equal to 0 anyway. So we work under the approximation that since you are talking about simple harmonic oscillator, what is the meaning of simple harmonic oscillation. Maximum amplitude is small. If the amplitude is too much, it is no longer simple harmonic. Remember, the pendulum, we started in physics, what was the maximum angular displacement allowed for it to be simple harmonic? Yes, exactly four degrees. So if it is 15 degrees, it is no longer simple harmonic.

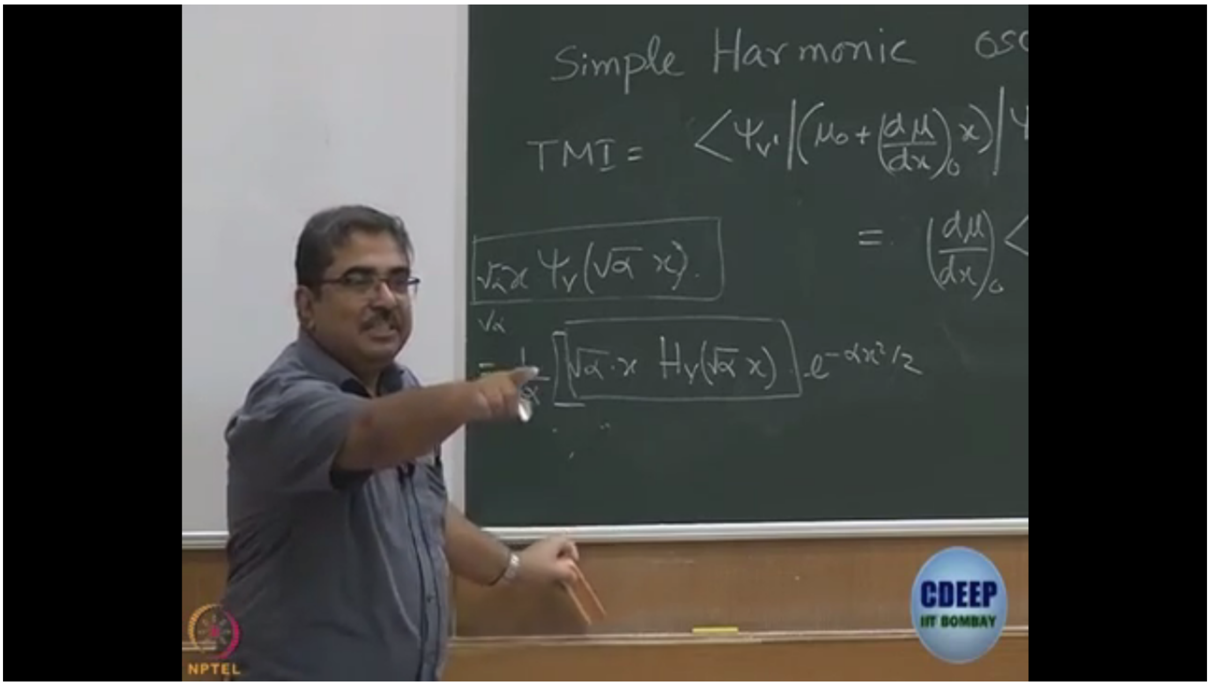
So within that small displacement you can assume – that's a wrong way to do it. It to be something like this. μ_0 when x=0 and then within that small range of x you can consider it to be straight line. If that is a straight line, what will my equation be? μ will be $\mu_0+(d\mu/dx)_0x$. Okay, are we clear with this? Slope multiplied by displacement, displacement starts from 0.



Okay, now, we know this, we know this Hermite polynomial identity and I hope we can erase this now. What is the transition moment integral then? It will be something like, I'll just write it like this $\Psi_{v'}$, instead of dipole moment, I am going to write, $< \Psi_{v'}|(\mu_0+(d\mu/dx)_0.x)| \Psi_v>$. So what kind of transition are we talking about? v-v', v is the origin, v' is destination. Okay, so right away I can write it as sum of two integrals, can't I? So the first one will be, μ_0 is a constant or not? μ_0 is a constant so it comes out. So I get it like this, $\mu_0< \Psi_{v'}| \Psi_v>+(d\mu/dx)_0$. Can I take $(d\mu/dx)_0$ outside the integral? When can I take it outside the integral? When it is independent of x.

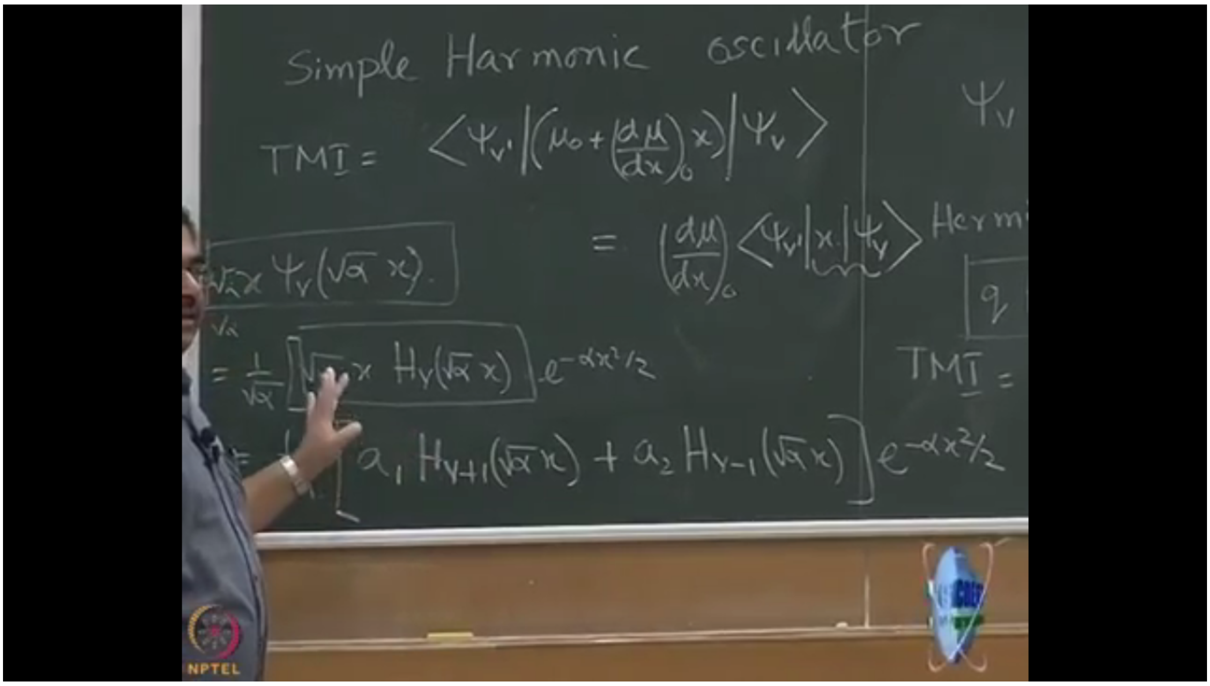
So if you work under this kind of approximation then $(d\mu/dx)_0$ is independent of x and we are saying $(d\mu/dx)_0$ anyway which means it is very close to the equilibrium position. That comes outside the integral and inside you have $< \Psi_{v'}| x|\Psi_v>$.

All right, now see. Can you say anything about this integral? That is 0 unless v=v' because Ψ_v and $\Psi_{v'}$ are members of an orthonormal set. So this integral has to be 0 unless v=v' and if v=v', then there is no question of transition. What are we talking about? So for the purpose of spectroscopy, for the purpose of transitions, first integral vanishes and when it vanishes it takes μ_0 along with itself. So you see μ_0 is no longer important. It doesn't matter whether your molecule is highly dipolar or less dipolar or well, even $\mu_0=0$, you want to put it that way. As long as $(d\mu/dx)_0$ is non-zero, you are going to have IR activity.



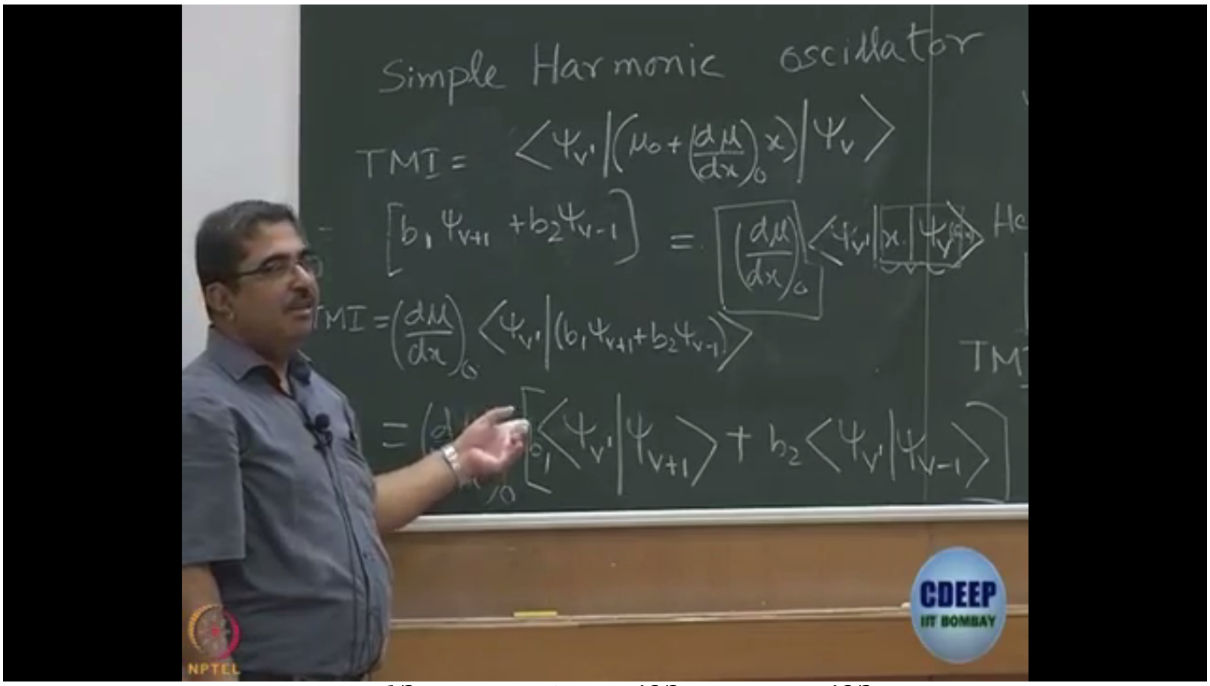
Okay, so far so good. So I can erase this. You are left with this. $(d\mu/dx)_0$, so this and this gives you the first condition that this cannot be equal to 0. You cannot have a vibration in which the dipole moment does not change. Once again, it becomes more important when we talk about polyatomic molecules later on.

Okay, now we can expand this thing a little bit. Let me just work with this part. What is $x(\Psi_v.\propto^{1/2}.x)$. Well I can write it as $(\propto^{1/2}x)/\propto^{1/2}$. No problem with that and you already what is $(\propto^{1/2}x).\Psi_v$ of $\propto^{1/2}$, what is that? It is I'll just write a_1, a_2. Let me do one more step. This is equal to $1/\propto^{1/2}[\propto^{1/2}.x.H_v(\propto^{1/2}.x)]e^{-\propto x^{\wedge}2/2}$. Is that write? I've just expanded the wavefunction.

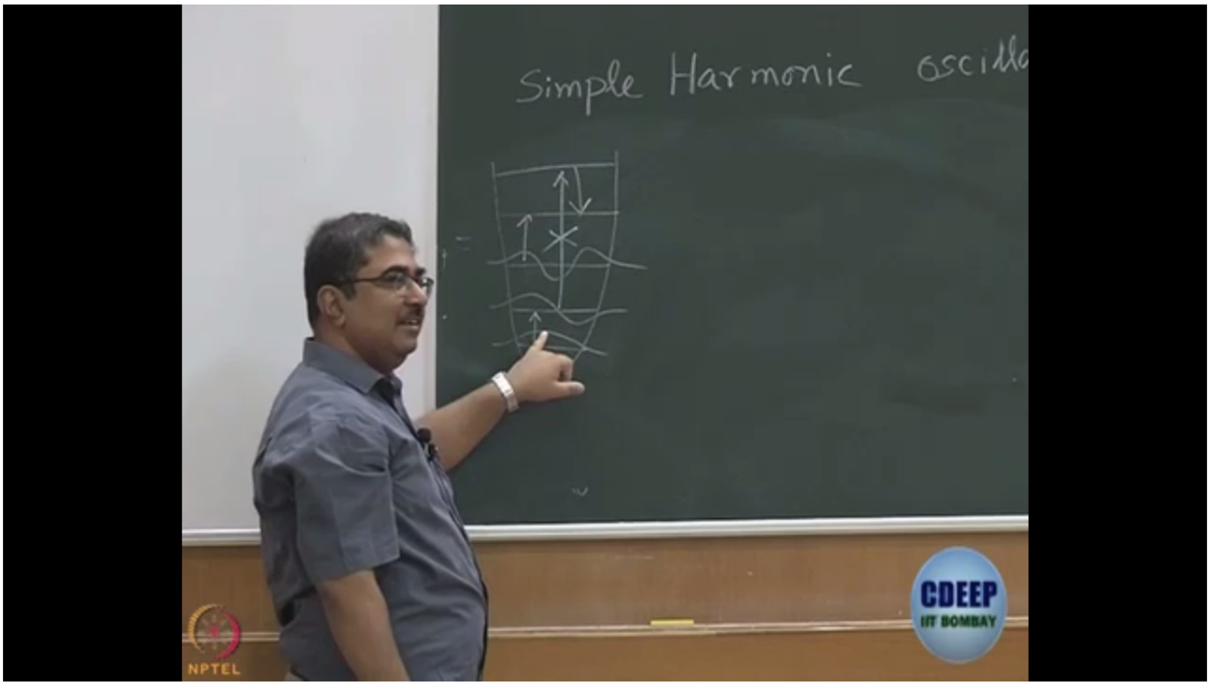


Now I know what this is. I can use the Hermite polynomial identity, can't I? Question? Sure? Have you understood all the way? All right, now I can use this Hermite polynomial identity and I can write, this is equal to – last bench, can you read if I write here? $1/\propto^{1/2}$ $[a_1H_{v+1}(\propto^{1/2}.x)+a_2H_{v-1}(\propto^{1/2}.x)]$ $e^{-\propto x^2/2}$. Are you okay? Can I extend what? Oh, see what do you have here. I am ignoring the Bra-vector, I am only working in the Ket-vector. In the Ket-vector you have x. Ψ_v and Ψ_v is in $\propto^{1/2}.x$. So I am just writing that, $x.\Psi_v.\propto^{1/2}.x=\propto^{1/2}.x.\Psi_v.\propto^{1/2}/\propto^{1/2}$. $\propto^{1/2}/\propto^{1/2}$ is just 1. The reason I want it is if I just this $1/\propto^{1/2}$ out I have $\propto^{1/2}.x$ multiplied by a Hermite polynomial in $\propto^{1/2}.x$ which I know how to expand using the Hermite polynomial identity. Are we clear or do you have a question? Are we clear what I am trying to do?

So then we use the Hermite polynomial identity and I expanded this and what I get is a sum of two terms; one in the Hermite polynomial of order v+1 and the other Hermite polynomial of order v-1. Each is multiplied by $e^{-\propto x^2}$. So can I now write something like this? Can I erase this part.



So that would be equal to $1/\propto^{1/2}$ $[a_1.H_{v+1}.x^{1/2}.\ e^{-\propto x^2/2}]$. $H_{v+1}.\ e^{-\propto x^2/2}$, what is that? This Ψ_v, well Ψ_v/N_v, that's all. But I am not writing the normalization constants. So it's something like a_1 multiplied by -- well you can write b_1 instead of a_1 because there is another constant anyway. $b_1.\Psi_{v+1}$. I'll just write Ψ_{v+1} and what is $H_{v-1}.e^{-\propto x^2/2}$ that is Ψ_{v-1}. I'll write $b_2.\ \Psi_{v-1}$. In fact, I'll even take this inside the constant. I am not writing what the constants are. So everything goes in b_1 and b_2. So now this is what this part is. So what is TMI. The Transition Moment Integral boils down to $(d\mu/dx)_0\langle\Psi_{v'}|(b_1\Psi_{v+1}+b_2\Psi_{v-1})\rangle$. Instead of x. Ψ_v, we have found out we can write $(b_1\Psi_{v+1}+b_2\Psi_{v-1})$. Are we clear? What does that boil down to? $(d\mu/dx)_0[b_1\langle\Psi_{v'}|\Psi_{v+1}\rangle+b_2\langle\Psi_{v'}|\Psi_{v-1}\rangle\}$. When will the first integral survive? When $v'=v+1$. When will the second integral survive? When $v'=v-1$. So what are the only two possibilities that come out from here? $v'=v\pm1$ or you can say $\Delta v=\pm1$. This then is my selection rule for a simple harmonic oscillator and additionally, I get the condition that the vibration must bring about a change in dipole moment. Otherwise, it will not be IR active.



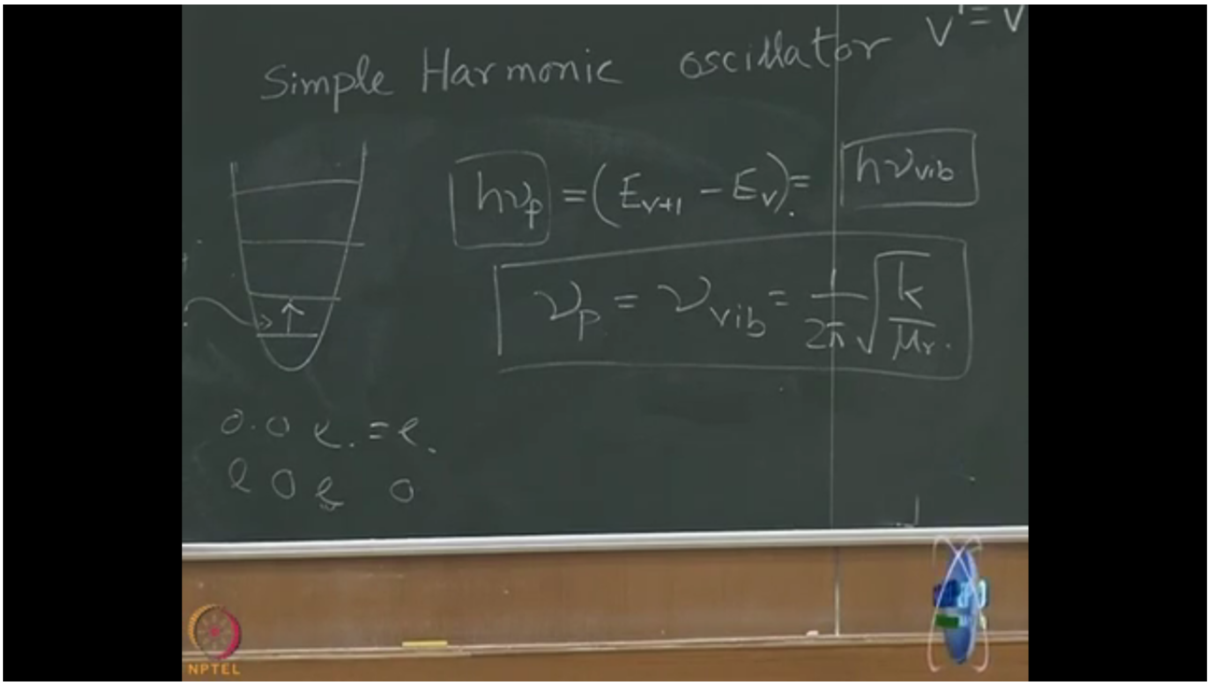
If that is the case what is the physical significance of selection rule is it tells you which transitions take place, which transition don't. For example, I'll redraw this potential energy surface, please accept that is a parabola. Selection rule $\Delta v=\pm 1$ tells me that this transition is allowed. This transition is allowed. This transition is also allowed, downward transition. However, this transition is not allowed. Are you answered? Yes. Mathematics is the language of science. So it tells us how the spectrum will look if that's what you are asking. Physically without doing mathematics there is no way of -- well, actually there is. If you look at the wavefunction and if you work with parity, then you can also say that odd-even transitions is like this. What does this wavefunction look like? It's like this, right? What does this one look like? Something like this. What does this look like?

Okay, are you familiar with odd and even functions? Is this an even function or an odd function? Even or odd? What about this? Odd. What about this? Even. So alternatively you are odd and even functions. Now if you take this and this, now what will happen. This is an even function, this is an odd function, what about dipole moment? Even or odd? Definitely odd; if we change x, μ becomes $-\mu$. So now if I take a product of one wavefunction, another wavefunction and dipole moment. If these two wavefunctions, one is odd and one is even then what will I have? Odd multiplied by odd multiplied by even. So odd into odd into even, what is that? Is it odd or is it even? It is even.

Okay, so if I think of these two, the transition moment integral, the integrant is an even function. If you say an even function then if you just change the sign, integral will not vanish. However, if you take this and this, this is what even? Your dipole moment is odd and this is also even. So even odd even, what is that product? Odd.

Now see, if you are talking about v=0 and v=2 then your integrant is odd. That means if you just interchange x and -x, then what happens? Then it changes sign, integral changes sign. But then that cannot happen. If you just change x and -x, if integral changes sign, that can happen only when the integral itself is 0. That is why you cannot have this transition but you can have this transition. Does this make sense? But see, even this is mathematical. When I talk about odd even integral not vanishing, even that's mathematics. It's just that we are putting it in words that's why it seems less mathematical and more physical to us, actually it's all the same.

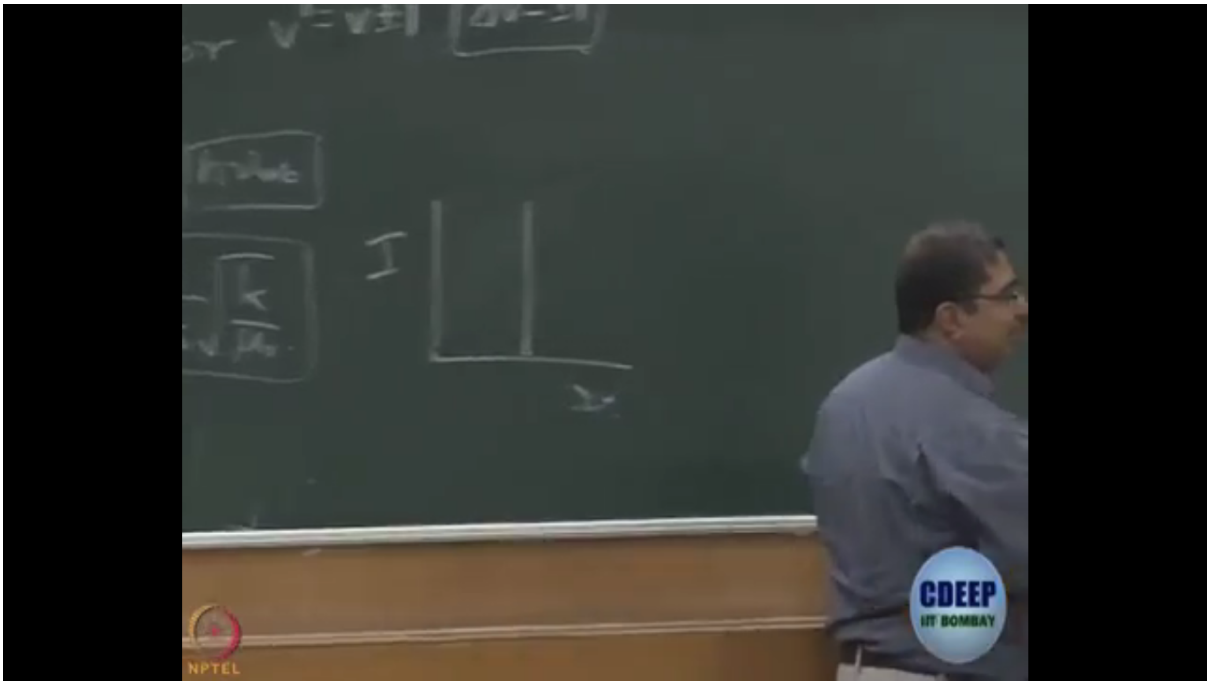
This is more rigorous mathematics, this is less rigorous. Why I am saying this is less rigorous is this by this argument, can you say that from here to here the transition is not allowed. You cannot? Because this is even odd even, this is also odd. So how do you know that 0 to 3 is not allowed? You cannot because you've performed a more qualitative less quantitative argument. We can only say transition between odd and even will take place but what we have done is a more rigorous mathematical treatment which tells us that this is allowed but this is not allowed.



Wait for me maybe two minutes, perhaps you will be answered in a little better way. Now see, $\Delta v = \pm 1$. If you remember what we had said, what is E_{v+1}-E_v? hν_{vib} where ν_{vib} is the frequency of vibration. $(k/\mu_r)^{1/2}$. Now if this transition is allowed, then I made it very complicated.

This transition is allowed we are saying. So that means if I put in light let us say frequency of light is hν_p, p for photon. Can we live with that, hν_p,? hν_p, what is ν_p? Frequency of the photon or frequency of light. That is equal to the energy gap. Which condition is that? Bohr resonance condition. So what you see is Bohr resonance condition leads to hν_p being equal to hν_{vib}. And of course, it's simple mathematics to eliminate h from both the sides and you come up with this. I find this to be very amusing. Frequency of the photon must be equal actual frequency of vibration which is equal to $1/2\pi(k/\mu_r)^{1/2}$ so that the photon is absorbed.

Frequency of light has to be equal to frequency of oscillation. Then and then only it is going to be absorbed.



What kind of spectrum do we expect in that case? How many lines in the spectrum? One. Do you get one spectrum? Do you get one line? If we have a bad spectrometer, then yes, you get one line. If you have a good enough spectrometer, a spectrometer with high enough resolution then you get a spectrum that looks like this.

So next day we are going to continue from here and we'll discuss why if you have a good spectrometer with enough resolution this one line shows up actually this two-wing kind of structure and then we'll talk about your un-harmonic oscillator.