INDIAN INSTITUTE OF TECHNOLOGY BOMBAY
NPTEL
NPTEL ONLINE CERTIFICATION COURSE

Molecular Spectroscopy – A Physical Chemist's perspective

Lecture-11

Simple Harmonic Oscillator

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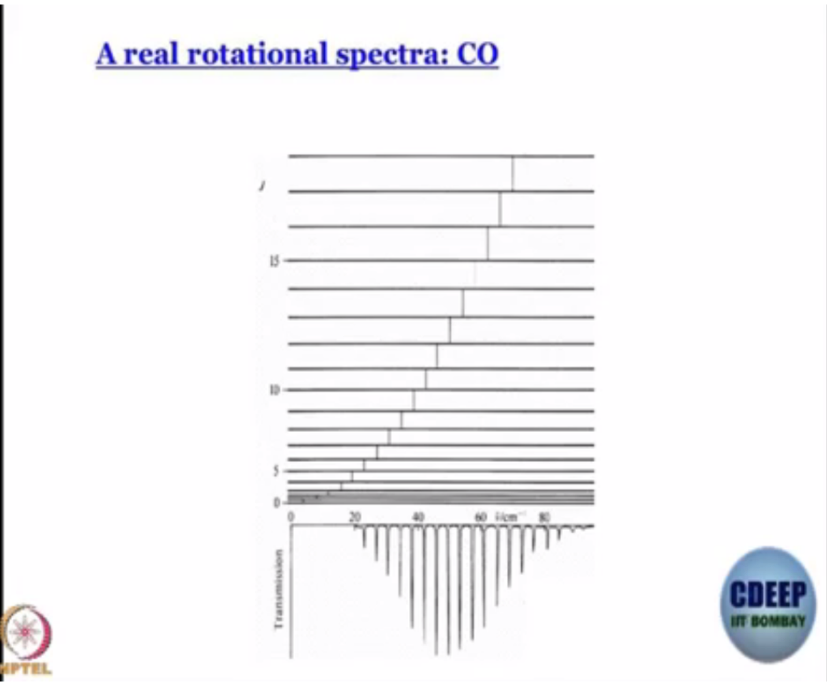


A real rotational spectra: CO

We have discussed how to determine bond by microwave spectroscopy. Today we move on and we talk about how to determine bond strength from IR spectroscopy. But before that I cannot go away from the discussion of microwave spectroscopy unless I show you at least one real microwave spectrum. So here it is. This is the rotational spectrum of carbon monoxide. Diatomic molecule, dipolar molecule, so it is microwave active and this is what the spectrum looks like. Now generally we are used to seeing spectra pointing upwards. Whatever I had drawn on the board had the peaks pointing upwards.

In this case you see it looks like a negative spectrum, pointing downwards, why is that? Yeah, why is that? Yes, please read the y-axis, it is transmission. So essentially, the way it has been plotted here is that you don't plot absorbance but you look at transmitted light, essentially y-axis is I-T, I-transmitted about which we had some questions yesterday after class.

So as you see the spectrum does go through a maximum, well a minimum in this case because it's a transmission. Lines are approximately equispaced and so you can understand from the spacing of the lines, you can figure out what is b and consequently you can figure out what is the bond length.

However, if you look very carefully, do you think this space is equal to this space? If you look at the two ends of the spectrum, the gap between two successive lines are they the same at the two ends of the spectrum? Of course, you have to look very, very carefully, I am talking about this one and this one. They are not exactly same; they are little different nad you see the difference when you compare the two ends of the spectrum. Why are they different? They are different because what you are supposed to do by yourself, I did not complete the discussion yesterday.

If you consider a non-rigid rotor, in a non-rigid rotor the spacing does not remain equal anymore. It keeps decreasing as you go to higher rotational numbers. That is why the spacing is not same on the two sides. We will have occasion to come back to this when we talk about high resolution infrared spectrum a little later today. In Banvil it is mentioned.

Those are polyatomic molecules, right? So you are talking about symmetric tops. Manthan is asking what about symmetric tops and all. Right now, we are not going to discuss in the same sequence as it is discussed in Banvil or any other textbook.

So the way we have organized this course is that first we are going to talk about diatomic molecules only. We'll complete the discussion of diatomic molecules, then go on to understand where your transition moment comes from. Once we are done, then it is very easy to work out the transition moment integrals for the diatomic molecules.

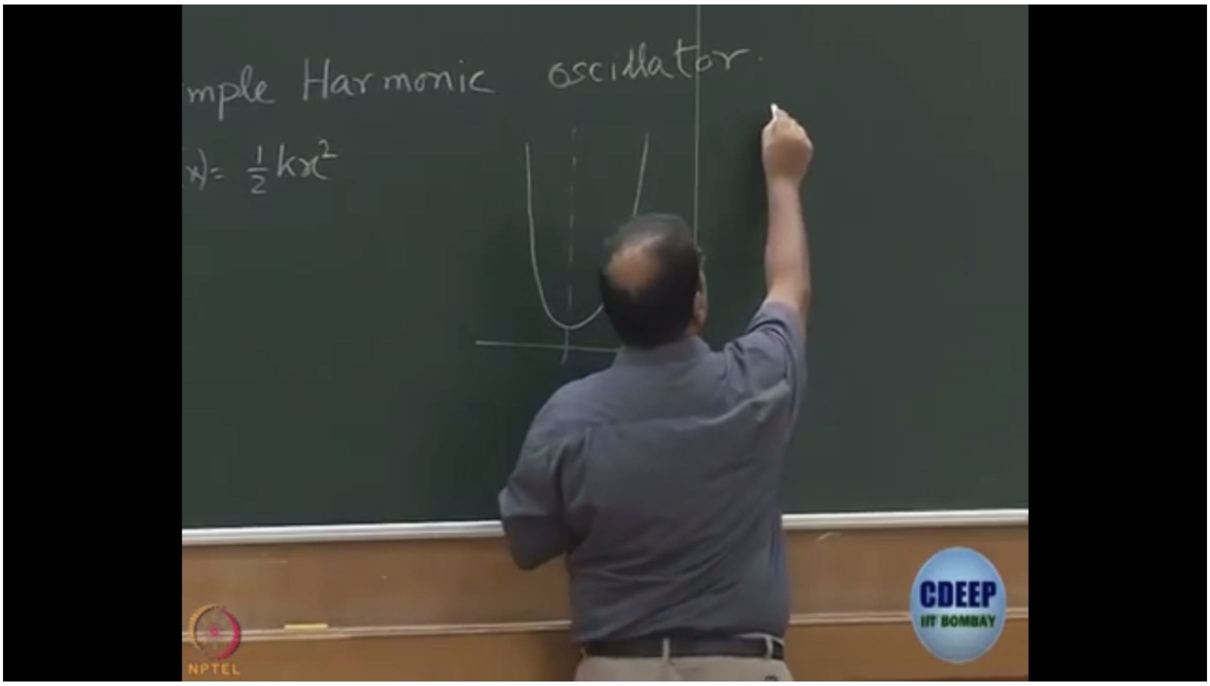
It's like studying hydrogen atom and multielectron atom. You want to do hydrogen atom first. So once we are done with diatomic molecules then only we'll go on to polyatomic molecules. That is why we are not talking about symmetric top and asymmetric top and all that right now. We'll come to that later. But the name says symmetric top. So the moment you go to polyatomic molecules, symmetry becomes important. Using symmetry you can simplify a more complicated, more complex problem.

So we will have to discuss symmetry as well a little bit and we are going to focus on IR and electronic spectroscopy from the point of your symmetry. But let that be the story for another day. Today we want to stick to our simple model, simple molecule, diatomic molecule. The only difference is we want to talk about vibration instead of rotation.

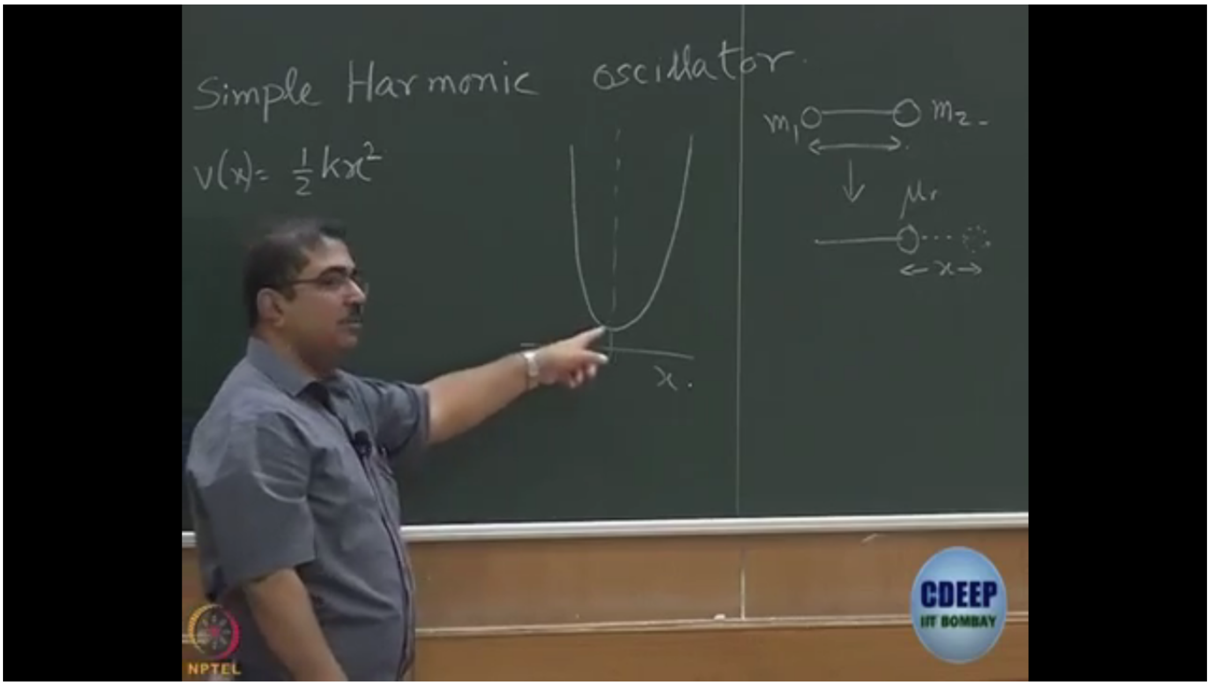
So you'll see instead of rotation is perhaps not a very fair comment. We'll elaborate upon that a little later in these two modules. So we go on to our model of diatomic molecules and the fist model that we want to use is simple harmonic oscillator.

Well, but we are talking about molecules. So when we talk about simple harmonic oscillator, it will not be enough, if we talk about a classical oscillator, we have to discuss a quantum harmonic oscillator and this is something that all of you have studied in some quantum mechanic scores or the other earlier.

So what we'll do is to start with, we are going to recapitulate the results. We are not going to do any derivation in that part. We'll recapitulate the results, we'll remind ourselves, what are the energies of simple harmonic oscillator. We are going to remind ourselves what do the wave functions of simple harmonic oscillator look like. Then we are going to talk about using these wave functions, we are going to talk about what the transition moment integral would look like and when the transition moment integral vanishes, when it does not. From there, we'll come to a discussion of which transitions are allowed and therefore, what do the spectra look like for simple harmonic oscillator.



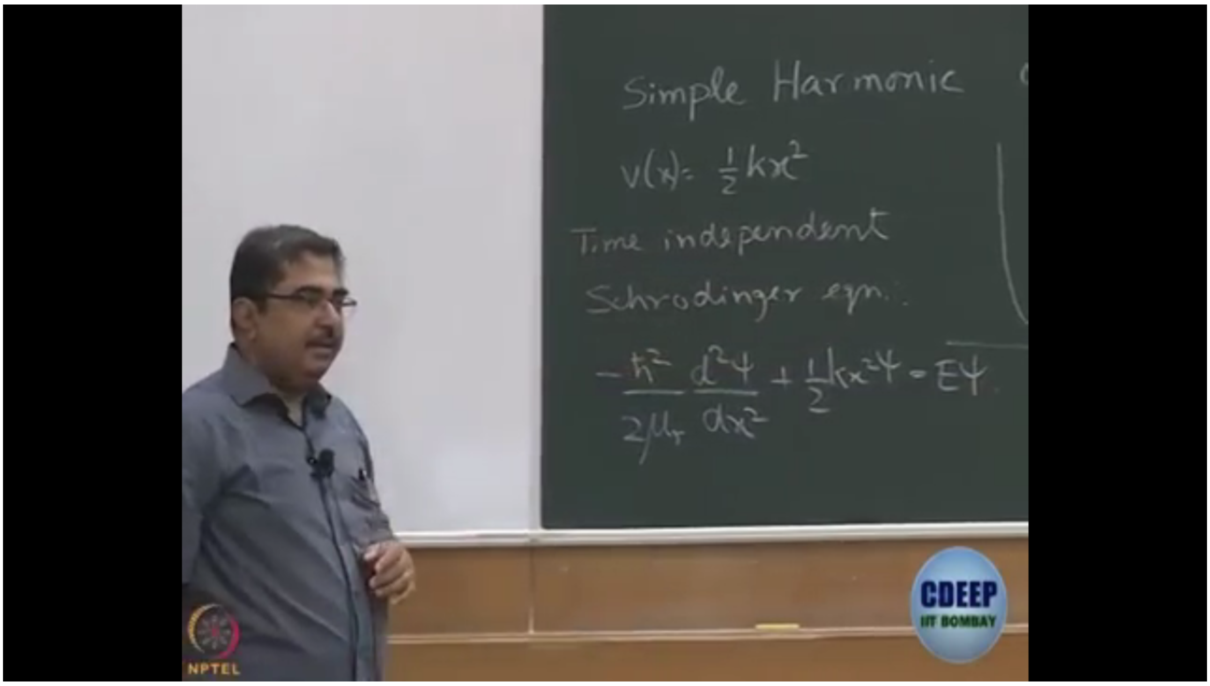
Then we’ll do something a little more complicated. But let’s start with this. Simple harmonic oscillator, first thing that we know is if it’s simple harmonic, what is the potential energy for the simple harmonic oscillator ½ kx^2. So potential energy I can write is ½ kx^2 and ½ kx^2 is the equation of a circle. Is that right? No? Then what is right? It’s the equation of parabola. Do not say yes to anything and everything I say. Sometimes I can make a mistake to see if you are away. Sometimes I can make a mistake because I made a mistake. So please don’t take everything for granted.



This then is the potential energy surface, this is x. While drawing this it makes sense to remind ourselves what the meaning of x is. What is the meaning of x? You are talking about an oscillator and we are going to use this model for a diatomic molecule. So once again, like a rigid rotor it is a two-body problem. We have two atoms connected by a bond and they are vibrating.

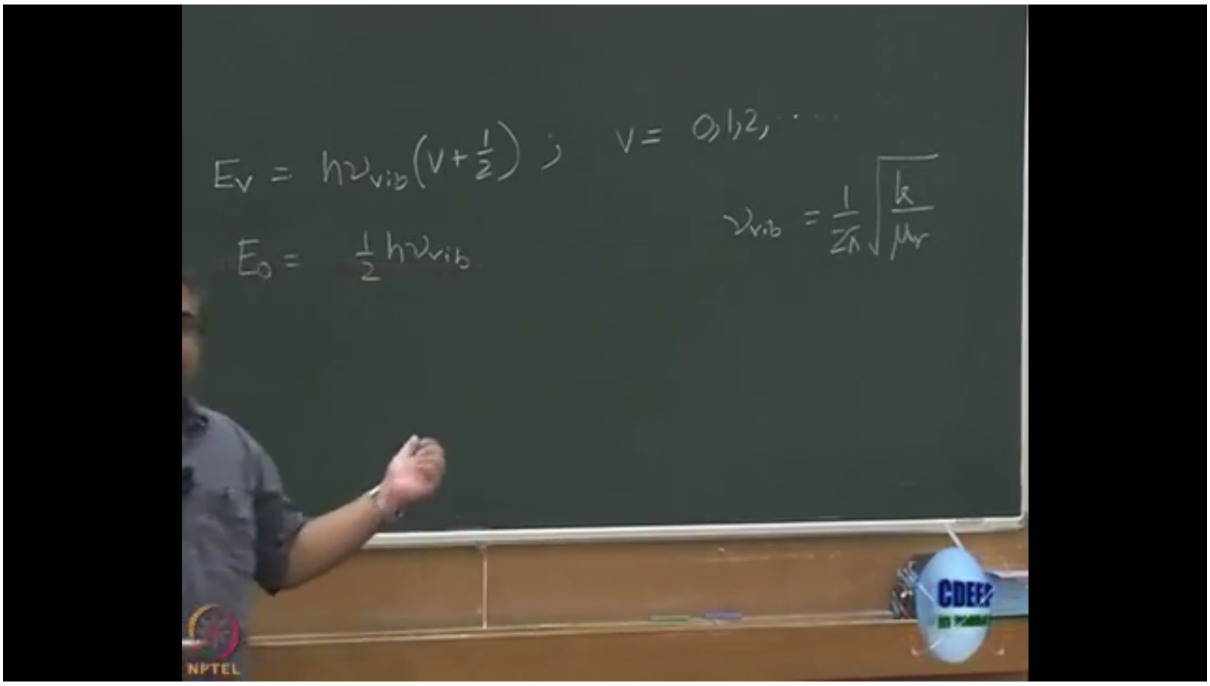
As you know as we have discussed several times in the previous classes you don't want to handle two-body problems. Wherever possible, you want to reduce two-body problems to ta one-body problem. So what does this reduce to? Say let's say this is m_1 mass, this is m_2 mass. It reduces to one mass of reduced mass μ, I'll just write μ_r here because again I am going to use μ for dipolar moment. I don't want you to get confused. So let us say μ_r reduced mass and it is attached to a massless centre. It's vibrating with respect to that.

And then let us say this is the displacement. So this is the mean position. x is this, displacement from mean position that is x. of course, x can be positive, x can be negative. So that's what we are doing here. It's important not to forget something that we might think is obvious. This is x.

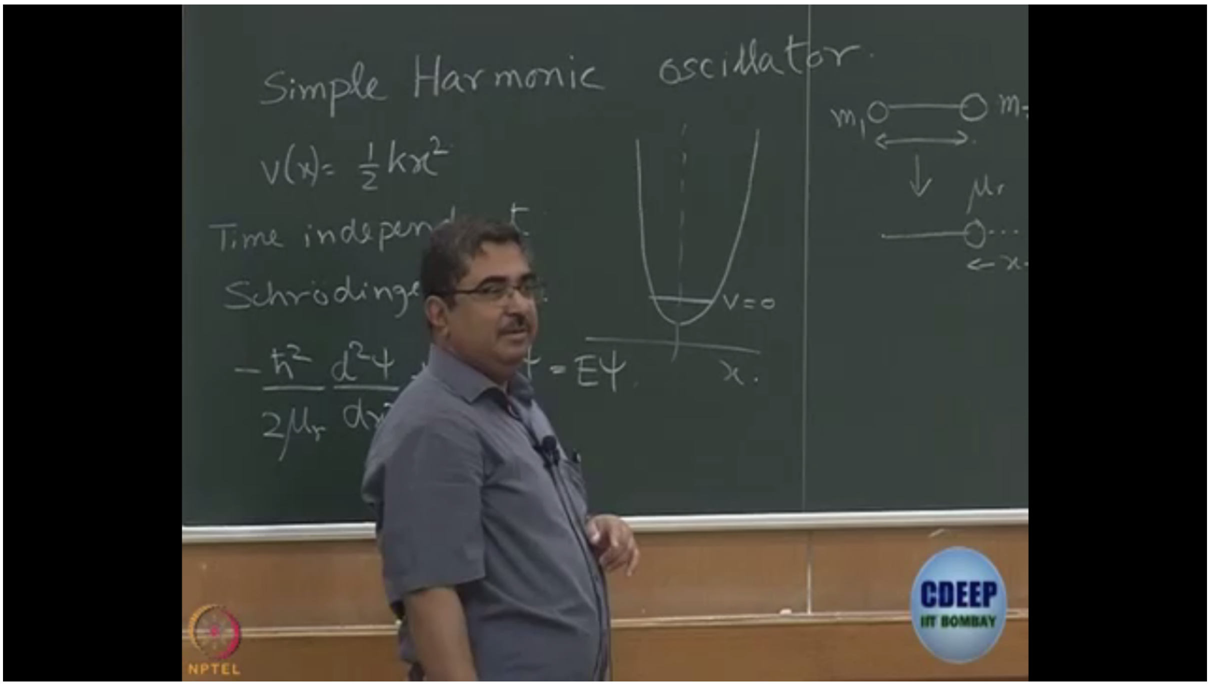


If this is v, and since we have defined x, what would the time-independent Schrodinger's equation be? $\frac{-h^2}{2\mu r}\frac{d^2\Psi}{dx^2}+\frac{1}{2}kx^2\Psi=E\Psi$. Once again it is important to remember, x is not cartesian x. x is displacement from mean position here. And you know that if you solve the Schrodinger's equation using the boundary conditions, what are the boundary conditions used in case of simple harmonic oscillator?

See, for that φ part I remember the boundary condition very well, periodic boundary condition. What is the boundary condition used for a simple harmonic oscillator? Yes, so what she is saying is the way function must vanish at -∞ and ∞.



So when you use appropriate boundary condition and all, you get this energy expression, I'll write it in the form that I find to be very convenient. $E_v = h\nu_{vib}(V+1/2)$ where V is the vibrational quantum number and it varies from what to what? What is the value of V? 0, 1, 2, so on and so forth. We'll come to the wave function shortly. But even before we go there we can see that the lowest energy that I have is E_0 which is $1/2h\nu_{vib}$. By the way what is ν_{vib}? ν_{vib} is the frequency of vibration. We are not talking about light yet. ν_{vib} is frequency of vibration and how is it related to this k and μ_r? $1/2\pi(k/\mu_r)^{1/2}$.



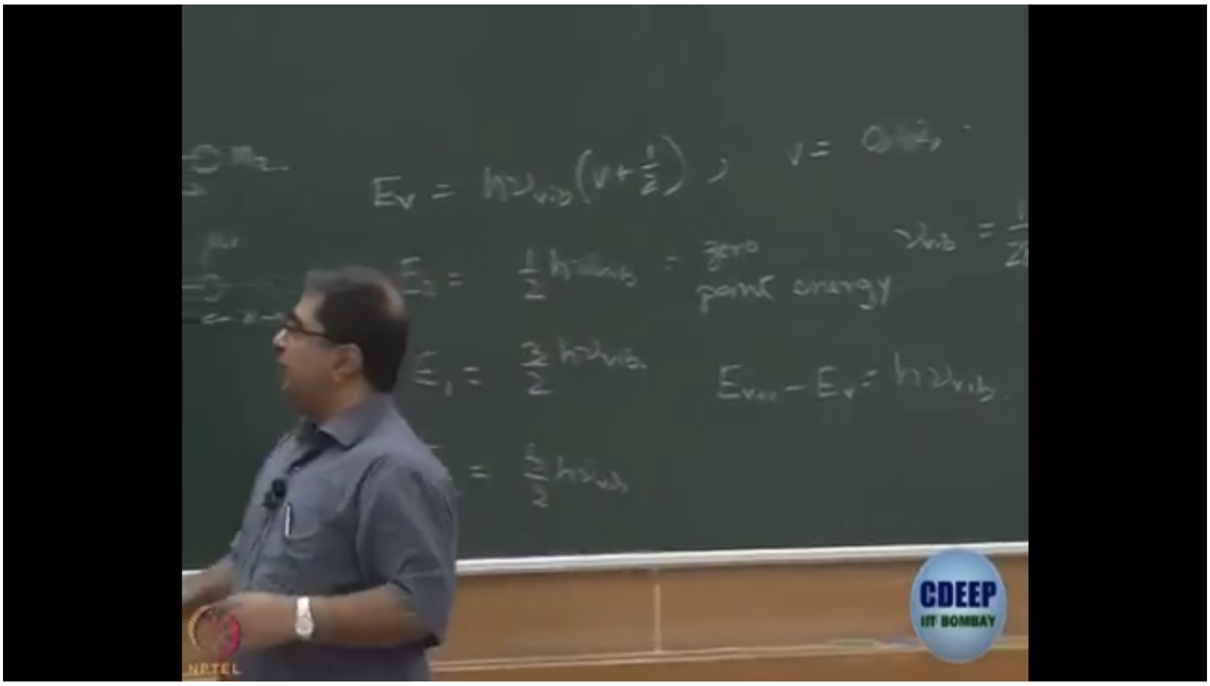
So if we can determine this frequency of vibration, knowing the reduced mass, we can find out what is k, the spring constant and if we know what the spring constant, k, is then we essentially know how strong the bond is. That's the basic idea of this whole exercise.

Now coming back to E_0. This is the minimum energy. So what we see is a very major difference between a classical harmonic oscillator and quantum harmonic oscillator is that energy can never be equal to 0. Minimum energy that we have is for V=0 which is $1/2h\nu_{vib}$. Since you have studied this problem in some other course already, can you tell me why? Why is it that for a quantum harmonic oscillator, energy can never become 0.

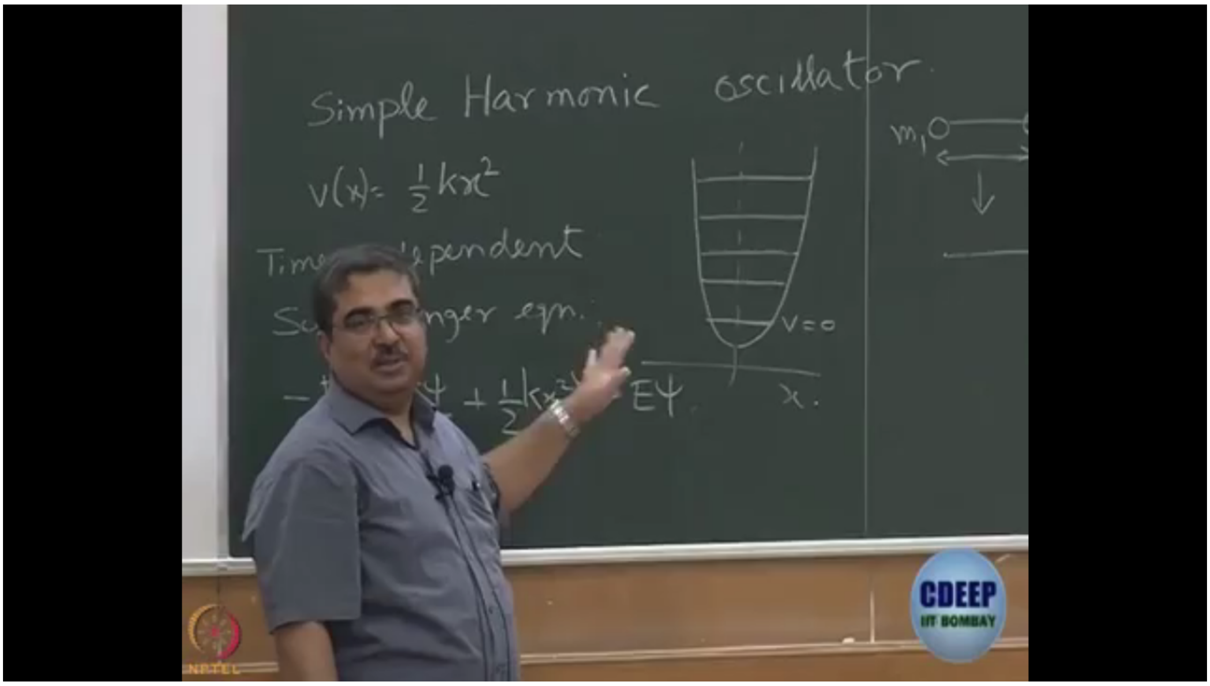
Tell us Vishnu. Rajdeep? Why is it that for a quantum harmonic oscillator, I cannot have 0 energy? 0 energy means what? The oscillator is not oscillating anymore. The vibration has stopped, right? Stopped completely. x is 0 mean it's at equilibrium position. Well, you are going one step forward perhaps. Easier. Well, that's a right answer but perhaps to a little different question. Yes, Sushnatu. Sushnatu is saying then it violates the answer, that's the answer I was looking for.

I am not talking about one simple harmonic oscillator; I am not talking about a collection of -- so when you talk about a collection of operators, then that residual entropy business comes in. But here, the answer I am looking for is answer -- see if it not vibrating at all, that means what? x=0. Position is completely well-defined. No uncertainty in position. Also, since it's not moving, momentum is also equal to 0, 0±0. So no uncertainty in position, no uncertainty in momentum.

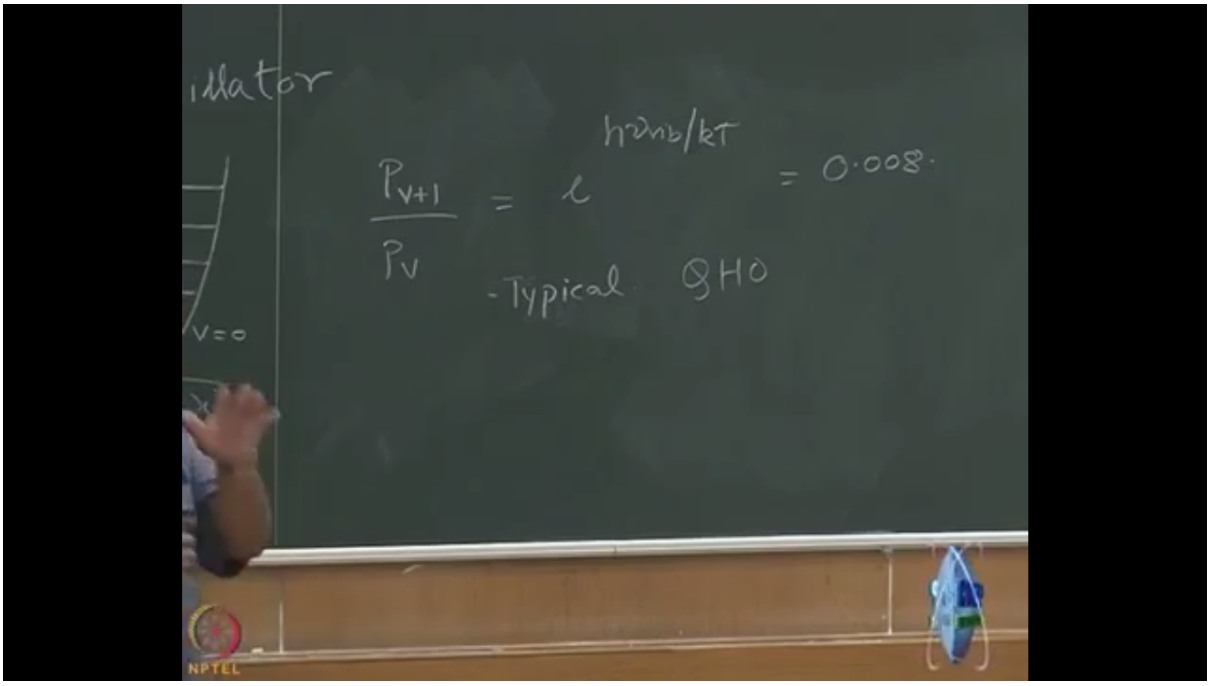
That is what would violate uncertainty principle. An uncertainty principle is something, remember, which cannot be violated. It is nature's threshold beyond which you cannot go. It's not a question of making a better instrument or anything. So if quantum harmonic oscillator stopped completely, then it would have violated uncertainty principle and here in lies a major difference between a quantum harmonic oscillator and a quantum rigid rotor that we discussed yesterday.



Remember, rigid rotor could have stopped. Why? Because when it stops it can take up any value of θ, it can take up any value of φ. So uncertainty in position is ∞. Here, if it stops uncertainty in position also would become 0 and thereby, uncertainty principle would be violated. That is why quantum harmonic oscillator cannot have 0 energy. Minimum energy, even if you go down to 0 kelvin and 0 kelvin is what prompted Manthan to give that answer, residual entropy, then also you get this $h\nu_{vib}$ energy. So this is called, I know you think, what is it called zero point energy. Where is the next one? Where is E_1. If you put V=1, 3/2 $h\nu_{vib}$. Where is E2? 5/2 $h\nu_{vib}$. In fact, if you just write the general expression for E_{v+1}-E_v, what do you get? $h\nu_{vib}$.



So we learn that allowing for my poor artistic skills, the energy spacings are all equal for a quantum harmonic oscillator and the spacing between two successive levels is $h\nu_{vib}$. Now that we have talked about energy, let us talk about populations quickly and then we move on to the wave function.



Again, we use a concept that we have discussed for your rigid rotor. It is your Boltzmann distribution. Using Boltzmann distribution, you understand that P_{v+1} or maybe I'll even like, well it doesn't matter. P_v what would that be equal to? Now degeneracy of each of these levels is actually 1. In case of rigid rotor you have degeneracy of 2_{J+1} because the same angular momentum vector could have been pointed in different directions. Here, there is no such thing. So degeneracy of every vibration level is 1 and only 1.

So degeneracy factor is 1 and then you have Boltzmann factor, what is that? $e^{-\Delta E/kT}$. What is ΔE for two successive levels? $h\nu_{\text{vib}}/kT$. Now, of course, I am jumping a few steps at this moment but let me just tell you that if you use, say, $\bar{\upsilon}_{\text{vib}}$ this is what I remember, $\bar{\upsilon}_{\text{vib}}$, or ν_{vib}. How is $\bar{\upsilon}_{\text{vib}}$ related to ν_{vib}? By factor of c. So if it is 1000 centimetre inverse, well for typical vibrational levels, let us say, typical quantum harmonic oscillator, this ratio trans out to be something like 0.008. Well, I am using an energy gap, the wave number equivalent of which is 1000 centimetre inverse and I am using a temperature of 300 kelvin.

If I use those numbers the ratio becomes 0.008. What does that mean? Start with the 0th level. If there are 1000 molecules in the 0th level, how many molecules should be at $v=1$ level? 8. And how many would be in $v=2$ level? Well, 0 because you cannot really have factional molecules.

So for all practical purposes, for that kind of energy gap the only populated level is $v=0$. So all upward transition will actually begin here. Is that point made? This becomes more important when we talk about an un-harmonic oscillator because in un-harmonic oscillator the energy gaps are not one and the same. Here see, if there is a transition between these two, and if there is a transition between these two, would you be able to differentiate? No, because energy gaps are all the same. If there is a transition from here to here, of course, it will be different. But as we'll see, that is not allowed. The only allowed transitions are $\Delta V=\pm 1$.

So for $\Delta V=\pm 1$ all energy gaps are same. So even if a transition originated in one of the higher energy levels, you would not be able to tell, but the issue is it doesn't. The only populated level for all practical purposes, for 1000 centimetre inverse kind of energy gaps is $V=0$. Are we clear about this?

Then we move on to the wave function.