Quantum Chemistry of Atoms and Molecules

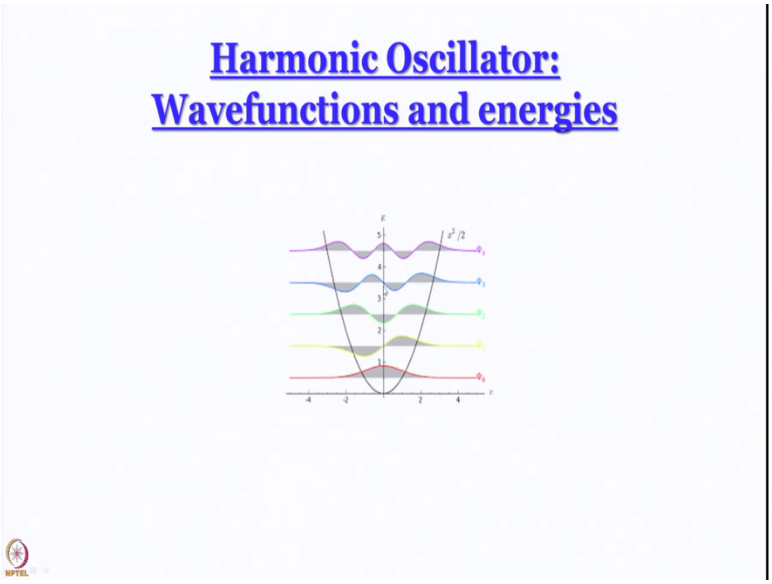
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-14
Harmonic Oscillator: Part 3

We continue our discussion of quantum harmonic oscillators today. What we will do in this module is at will talk about the energies of a harmonic oscillator and we will talk about actually one wave function will perform a more detailed discussion of the wave functions and how they are interrelated in the next module. Today we will talk about the lowest energy wave function. Let me start with spoiler what you see here? Well, we are seen this in the last module as well is a potential energy surface of a Quantum harmonic oscillator.

In which we have shown the different energy levels that are allowed remember energies quantized here and quantization arises out of the boundary condition that the wave functions must become 0 at x equal to plus infinity and minus infinity.

(Refer Slide Time: 01:14)

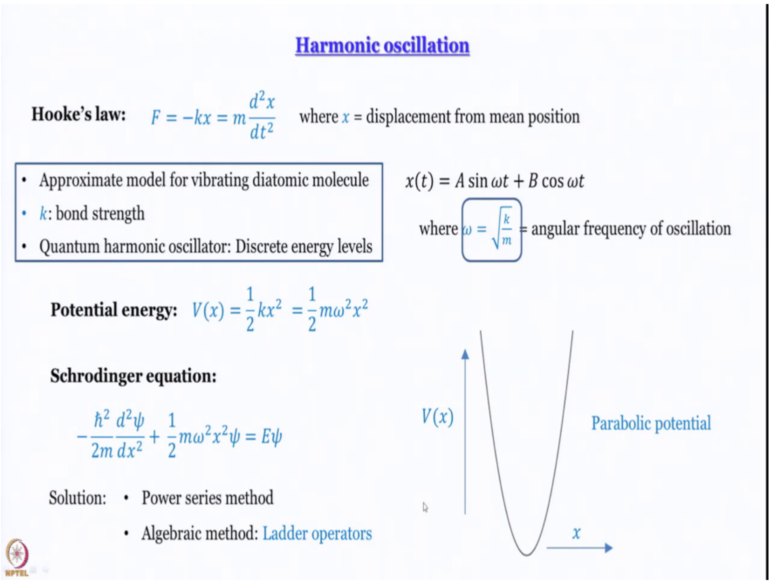


Harmonic Oscillator:
Wavefunctions and energies

As you can see wave function do not exactly terminate at the potential energy surface they go a little bit beyond and it was your homework to find out why this is a case how this is justified. Please read about this and a post on the forum. If look at the wave functions they look somewhat similar to the particle in a box wave functions. The lowest one is pretty much caution function without any this one node in the second one. Two in the third one and as you go higher up number of nodes in the wave function increases.

As a rule of thumb energy and number of nodes go hand in hand. More energetic wave function would have a greater number of nodes this is perhaps something that your study axiomatically at will in High School as well. Today let us go ahead and see how one can arrive at the expression of the energy and at least one of the wave functions.

(Refer Slide Time: 02:16)



Harmonic oscillation

Hooke's law: $F = -kx = m\frac{d^2x}{dt^2}$ where x = displacement from mean position

- Approximate model for vibrating diatomic molecule
- k: bond strength
- Quantum harmonic oscillator: Discrete energy levels

$x(t) = A\sin\omega t + B\cos\omega t$

where $\boxed{\omega = \sqrt{\frac{k}{m}}}$ = angular frequency of oscillation

Potential energy: $V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$

Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$$

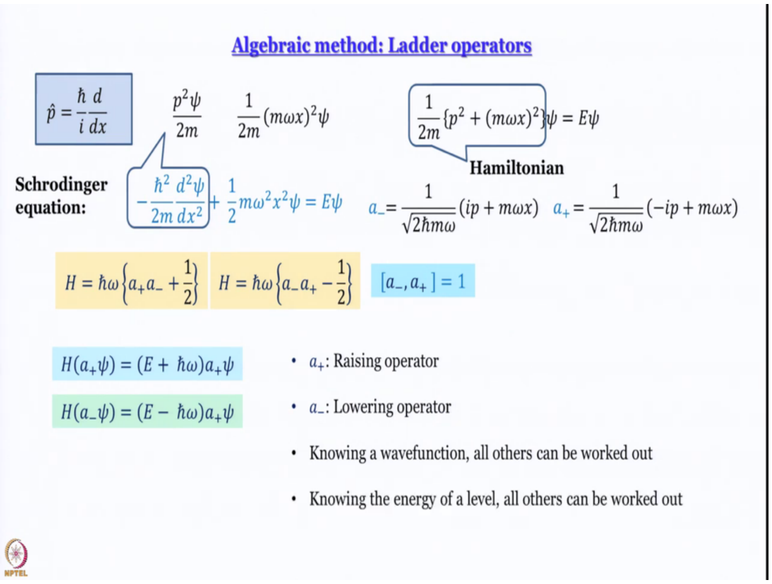
Solution:
- Power series method
- Algebraic method: Ladder operators

But before that we have brief recap what we have studied in the last couple of modulus. We have said that harmonic oscillators are those which obey Hook's law. So in the classical domain solution for x the displacement from mean position would be A Sin Omega t + B cos Omega t Omega is the angular frequency of oscillation. Please note the term angular frequency of oscillation by the time we close the discussion in this module will have to say about that.

So this angular frequency of oscillation is popular because it simply root over k by m where k is the force constant of the spring and m is the mass. So for harmonic oscillator from classical mechanics itself, we know from classical mechanics itself we know that the potential energy is parabolic. So what we do if we take this parabolic potential and we plug it into the Schrodinger equation in place of V the first term remains the same the kinetic energy, becomes half m omega square x square Psi equal E Psi as I said earlier the beauty of Schrodinger treatment of quantum mechanics is that you start with classical quantities.

And then when you try to interpret the wave functions the unique features of the quantum world manifests themselves automatically that is what happened here as well. So, this is your Schrodinger equation and we said that there are two ways of solving it first is a power series method which will come to later on and what are you doing right now is the algebraic method and the most important thing about algebraic method is ladder operators to which we have been introduced in the last module.

(Refer Slide Time: 04:06)



Algebraic method: Ladder operators

$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$

$\frac{p^2\psi}{2m}$

$\frac{1}{2m}(m\omega x)^2\psi$

$\frac{1}{2m}\{p^2 + (m\omega x)^2\}\psi = E\psi$

Hamiltonian

Schrodinger equation: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$

$a_- = \frac{1}{\sqrt{2\hbar m\omega}}(ip + m\omega x)$ $a_+ = \frac{1}{\sqrt{2\hbar m\omega}}(-ip + m\omega x)$

$H = \hbar\omega\left\{a_+a_- + \frac{1}{2}\right\}$ $H = \hbar\omega\left\{a_-a_+ - \frac{1}{2}\right\}$ $[a_-, a_+] = 1$

$H(a_+\psi) = (E + \hbar\omega)a_+\psi$

$H(a_-\psi) = (E - \hbar\omega)a_+\psi$

- a_+: Raising operator
- a_-: Lowering operator
- Knowing a wavefunction, all others can be worked out
- Knowing the energy of a level, all others can be worked out

So what the way we got to the ladder operator is that we wrote Schrodinger equation. And remember the operator for Linear Momentum h cross by i d dx we plug it in and we wrote the kinetic energy term as p square Psi by 2m remember you are not writing the hat here, but p is really an operator the momentum operator. It is not a number second term since it is 1 by 2 m here. We take 1 by 2m common for the second time as well. So that to get square of m Omega x operating on Psi.

So the Schrodinger equation becomes like this 1 by 2m then p square + square of m omega x for whole operator this is Hamiltonian, the Hamiltonian operate on Psi to give you E Psi. So, what we have done essentially is that we rewritten in the Hamiltonian in terms of the linear momentum operator? And then what we said is that this Hamiltonian here is sort of u square + v square kind of term. So if it was a number you could have written it as i u + v whole thing multiplied by –iu+ v but then this is a operators I will not be the case.

But let us see what happens when we take this iu + v, u here is p so ip + v is m Omega x ip + m Omega x and minus ip + m omega iu + v -iu + v. What we said is let us take these two quantities anyway work out the products and see how far we are from the Hamiltonian. And as you said this factor that is there that is because you already know what the solution going to be. The solutions to better if you have this 1 by root over 2 into h Cross m omega right a minus and a plus these 2 are operators in themselves these are our ladder operators.

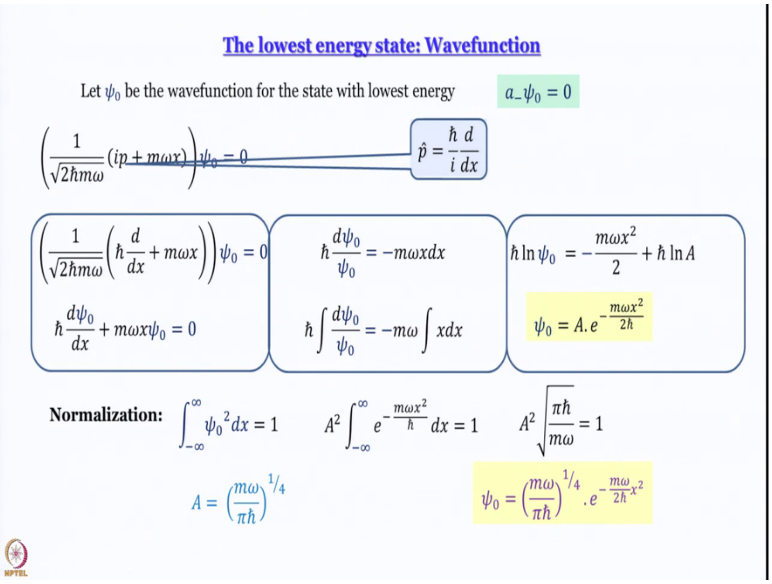
And we also asked you to work out that the commutator of a minus a plus is equal to +1 which means commutator of a plus a minus is -1 and since the commutator is not equal to 0 what happens if the Hamiltonian is not just a minus a plus or a plus a minus. What we get is that Hamiltonian is written as h cross Omega multiplied by a plus a minus plus half or you can write it as h cross Omega a minus a plus minus half both are valid forms.

We use the one that is more convenient given the situation we are in. So, this is how we rewrite the Hamiltonian in terms of ladder operators a plus and a minus. Then we came to this question why is a plus called a plus and a minus is called a minus because we prove that when a plus operates on Psi. It produces a wave function which has eigenvalue of E + h cross Omega, E is the energy of Psi the original wave function. So when a plus operates on the wave function energy of the resultant wave function is increased by h cross Omega which is one vibrational Quantum for this harmonic oscillator.

That is why a plus is called raising operator. It takes us up by one step in the energy ladder of quantum harmonic oscillator. Similarly when a minus operates on Psi the eigenvalues that we get for the new wave function a minus Psi again, unfortunately have repeated the error of last module sorry about that. This is a minus of course, but the wave function the eigenvalue is E - h cross Omega a - Psi. This is a minus please correct it in your notes a minus.

So, this is called the lowering operator and good thing about this is that in principal if you know one wave function we should be able to work out the others by going up and going down the ladder using the appropriate ladder operator. If you know the energy of one Level we can work out all others and this is something will do in the next 15 - 20 minutes.

(Refer Slide Time: 08:34)



The lowest energy state: Wavefunction

Let ψ_0 be the wavefunction for the state with lowest energy $a_{-}\psi_0 = 0$

$$\left(\frac{1}{\sqrt{2\hbar m\omega}}(ip + m\omega x)\right)\psi_0 = 0 \qquad \hat{p} = \frac{\hbar}{i}\frac{d}{dx}$$

$$\left(\frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{d}{dx} + m\omega x\right)\right)\psi_0 = 0$$

$$\hbar\frac{d\psi_0}{dx} + m\omega x\psi_0 = 0$$

$$\hbar\frac{d\psi_0}{\psi_0} = -m\omega x dx$$

$$\hbar\int\frac{d\psi_0}{\psi_0} = -m\omega\int x dx$$

$$\hbar\ln\psi_0 = -\frac{m\omega x^2}{2} + \hbar\ln A$$

$$\psi_0 = A.e^{-\frac{m\omega x^2}{2\hbar}}$$

Normalization: $\int_{-\infty}^{\infty}\psi_0{}^2 dx = 1 \qquad A^2\int_{-\infty}^{\infty} e^{-\frac{m\omega x^2}{\hbar}}dx = 1 \qquad A^2\sqrt{\frac{\pi\hbar}{m\omega}} = 1$

$$A = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}.e^{-\frac{m\omega}{2\hbar}x^2}$$

So this is what we had said and now with this background let us to try to find out the wave function of the lowest energy state of course the question that should arise here is that is there a lowest energy state or is it a bottomless pit? I mean can you go down further and further? Can you go down to minus infinity energy, can you go down to plus Infinity on the higher side. Can you do at to stop at 0 well minus infinity and all might be stretching things little bit.

What is the meaning of negative vibrational energy, but then if you think of the classical harmonic oscillator, then we can expect that the lowest energy state should have energy equal to zero. As we touched upon briefly in the module before last for classical harmonic oscillator it can come to rest right it does not have to vibrate all the time. Does not have to oscillate all the time what happens here, so to do that we use a clever trick and once again I am using the treatment used in Griffith quantum mechanics book.

Let us say Psi 0 is a wave function for the state with lowest energy if there is 1, well there will be 1. So, Psi 0 is a wave function of the state with lowest energy. See, if I apply a plus on Psi 0 what happens I go up higher up the ladder. I get the wave function or I get the function that is proportional to the wave function that has energy which is higher than the lowest energy wave function by one step one Quantum h cross omega what happens when I apply a minus on this supposedly lowest energy wave function it is nothing below it.

So, when a minus operates on this wave function. Let us say whatever we call it I call it Psi 0 when a minus operation Psi 0 will you agree with me that I should get zero. Not because the energies is 0 not because eigen value is 0 but because the resultant wave function itself should be 0 everywhere other words it should not exist because its Psi 0 is the lowest energy wave function to operate a minus on it where do you go to go? Nowhere to go that state does not exist, so wave function cannot be there for it so wave function has to be 0 at all values of x.

In other words we can think the probability of finding the state is 0 everywhere. So, Psi Psi star probability density is 0 everywhere therefore Psi also has to be 0 everywhere. Psi has to be 0 everywhere. Ok. So a – Psi 0 produces a wave function that is 0 everywhere. That is why we write a – Psi 0 is equal to 0. I hope you understand this. This is a very crucial step see mathematics and all we will work out but it is important to get the logic.

And the logic is quite subtle. Sometimes if you miss it, then we might not get it in a lifetime a – Psi 0 equal to 0. Now, we know what a minus is. This is a minus, 1 by root over 2 h cross m Omega x ip + Omega x when this operates on Psi 0 I get 0. We know what x operator is, is just multiplication by the value of the position x? What is p operator? This is p operator h cross by i d dx so what will do now is that what are you trying to do?

If someone trying to find what Psi 0 is, to do that we need to set up some equation in Psi 0 so that becomes easy when we take this expression for the momentum operator h cross by i d dx plug it into expression for a minus and we get 1 by root over 2 h cross Omega multiplied by h cross d dx + m Omega x Psi 0 equal to 0 is a differential equation, first order differential equation. First thing I can do is I can get rid of this factor 1 by root over 2 h cross Omega because that will be equal to; of course that will not be equal to 0.

So rest of it has to be equal to 0. So, what I get is h cross d Psi 0 dx + Omega x Psi 0 equal to 0. Simple first order equation I think most of you would be able to solve it without me doing it, but will do it anyway. Now let us rearranges in which I have everything in Psi 0 on one side and everything in x on one side. So this is what I get h cross d Psi 0 by Psi 0 is equal to - m Omega x dx what would the next step be?

Pretty obvious next step would be to integrate it yeah h cross integral d Psi 0 by Psi 0 is equal to -m Omega integral x dx same. What is the dPsi 0 by Psi 0? Everybody knows it is ln Psi 0. What is integral x dx? It is x square by 2 and let us keep it indefinite for the time being so will get h cross ln Psi 0 – m omega x square by 2 plus some constant of integration. Ok pretty simple now for the sake of convenience what I do is and write the constant in logarithmic form as well.

Because they can somehow bring it here inside this log then I can just take antilog on both sides rise both sides to the power of e and I will get a nice expression. So what I do is I will write this constant as h cross lnk then it will become simple you just take it to the other side it will become h across ln Psi 0 by a then rise both sides e. We will get Psi 0 equal to A multiplied by e to the power - m Omega x square by 2 h cross, right simple.

So you have got Psi 0 is it not already found what this lowest energy wave function is well almost but not quite because still have to find out A and if you remember the properties of wave function is wave function has to be normalised. So, we can treat A as a normalisation constant and when we consider normalisation what it means is that integral for values of x from minus infinity to plus Infinity of Psi 0 squared dx has to be equal to 1.

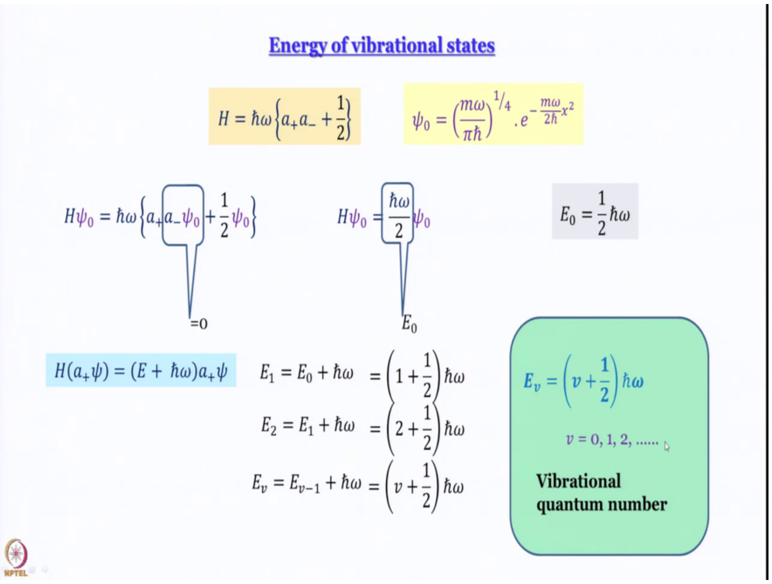
So, we write like that A square ideally I should have written Mod A square but I know in this case we are going to get real value of A so I have been little lazy and we have written just A not mod. So, A Square is a constant comes out of the Integral sign integral minus infinity to plus Infinity e to the power –m omega x square by h cross. So, here we had e to the power –m omega x square by 2 h cross take square of that this 2 in the denominator would go simple. So e to the power –m omega x square by h cross integrated for x equal to minus infinity to x equal to plus Infinity that should be equal to 1.

Now this minus infinity to plus Infinity integral, this is a standard integral the value is known you can look up a compendium of standard integrals and you can find out for the value is. Generally if you are asked to work this out in exam, the value of this integral has been given. So, will do that and believe me when I say that this value is root over Pi h cross divided by m omega x square multiplied by root h cross by m omega is equal to 1 rest is simple square root of m Omega by Pi h cross is equal to A square, A is equal to m omega Pi Pi h cross raise to the power 1 by 4 of course, you can ask why not taken the negative root I could have does not matter.

For wave function actually you have to define one wave function and work with respect to it. So you want to write minus might be my guest but generally wherever possible we keep the positive value does a convention. So A is there now we can say that we are found the wave function Psi 0 and it is well m Omega to the power Pi h cross raise to the power 1 by 4 multiplied by e to the power -m omega by 2 h cross x square. What kind of function is this? Gaussian function remembers the diagram I had showed you at the beginning of this module.

The lowest energy wave function was Gaussian right this is A so we have been able to work out the wave function of the lowest energy state. What is the next step? Next step is to find the energy.

(Refer Slide Time: 18:03)



Energy of vibrational states

$$H = \hbar\omega\left\{a_+a_- + \frac{1}{2}\right\}$$

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} . e^{-\frac{m\omega}{2\hbar}x^2}$$

$$H\psi_0 = \hbar\omega\left\{a_+\underbrace{a_-\psi_0}_{=0} + \frac{1}{2}\psi_0\right\}$$

$$H\psi_0 = \underbrace{\frac{\hbar\omega}{2}}_{E_0}\psi_0$$

$$E_0 = \frac{1}{2}\hbar\omega$$

$$H(a_+\psi) = (E + \hbar\omega)a_+\psi$$

$$E_1 = E_0 + \hbar\omega = \left(1 + \frac{1}{2}\right)\hbar\omega$$

$$E_2 = E_1 + \hbar\omega = \left(2 + \frac{1}{2}\right)\hbar\omega$$

$$E_v = E_{v-1} + \hbar\omega = \left(v + \frac{1}{2}\right)\hbar\omega$$

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega$$

$v = 0, 1, 2, ...$

Vibrational quantum number

Since you know the wave function what will do is will take that wave function and we will make the Hamiltonian operate on it energy should come as the eigen value of this the wave function that will be the lowest energy. So what will do is will use a convenient form use the differential form also. But since we are using ladder operators and since ladder operators are so convenient we will use the form of Hamiltonian with the ladder operator we could have used other one as well.

This is actually more suitable in this case you seen the moment why it is so. So H equal to h cross Omega multiplied by a plus a minus plus half this is the form of Hamiltonian we will use. So H Psi 0 then becomes h cross Omega multiplied by a plus a minus Psi 0 + half Psi 0, that should be equal to e Psi 0. Now one thing to remember from the last slide is that we know very well that a minus Psi 0 is equal to 0. We started with that consideration. The Psi 0 is the lowest energy of a lowest energy wave function. If you try to lower it is nothing to go nowhere to go.

So the wave function that we will get is actually 0 everywhere. So this is very convenient a – Psi 0 is 0 so even if you apply a + to that a + 0 is also 0 there is 0 everywhere you do not know what to do with that. So conveniently for the first term it becomes 0 only the second term servives. So what you get then is that second term is half h cross Omega multiplied by Psi 0. For Schrodinger equation reduces to H Psi 0 equal to h cross omega by 2 Psi 0. What is the eigen value here? H cross Omega by 2 and that then is E0 the energy of the lowest energy vibration state.

Psi 0 has an energy of half h cross Omega this if you remember from our introduction is called 0 point energy. This is the smallest energy a Quantum harmonic oscillator can have it can never be 0 because it was 0 then it would have violated Uncertainty Principle. So, even if you take the oscillator down to 0 Kelvin it will oscillate with the frequency of half h cross omega. This Psi 0 will be the only state that will be occupied that case.

In fact for most of the molecular harmonic oscillators this is the only state that is occupied in room temperature. In any way to know further please look up our NPTEL course on molecular spectroscopy but let us proceed from here. E0 is half h cross Omega great now, what can we do?

If you remember if we use this step up operator a plus operator on Psi then Schrodinger equation of a wave function becomes E + h cross Omega.

So what I am saying is this is just keep on applying a plus, let us apply a plus to Psi 0. What will I get? I should get Psi 1 the wave function that is that has energy that is just one step above that of Psi 0. So that E1 will be equal to E0 energy of Psi 0 that is half h cross + h cross Omega from here. What will E2 be it will be? E2 will be; sorry E1 will be then I can take; I can write this E0 as half h cross Omega I can take h cross omega common outside the bracket.

So I will get 1 + half h cross omega C by 2 h cross omega let me write it in terms of; in the form 1 + half because that leads us to general form of the energy any way so what will E2 be? I can again get E2 by making a + operator on Psi 1 then it should be E1 + h cross Omega E2 should be E1 + h cross omega. What is E1? E1 is 1 + half h cross omega add 1 to that what you get? Simply you get 2 + half; whole thing multiplied by h cross Omega and so on and so forth.

What to see in is that even though we are not really work out the wave functions for the higher energy states we have been able to work out the energies. So, what happens for E V? E V would be E V - 1 + h cross Omega that would be V plus half h cross Omega. What is V here what is the range of V? V ranges from 0 and it increases by an integer each time 0, 1, 2, 3, 4 right this is the vibrational quantum number and what we see here is the most general form? Of the energy of a Quantum harmonic oscillator Ev equal to V + half multiplied by h cross Omega where V equal to 0, 1, 2, 3 etcetera can go upto Infinity these are the vibrational quantum numbers.

So, what we have been able to do is we have been able to find out the expression of energy of not only the lowest energy state but all energy states of the quantum harmonic oscillator simply by using ladder function Ev equal to V plus half h cross Omega and V is equal to 12 etcetera, right. Now before going further I like to say one thing since I am Spectroscopist I like to rewrite this equation somewhat. Remember Omega is angular frequency.

Spectroscopist usually like frequency better than angular frequency particular reason is convention. So what I can do is I can write h cross as h by 2 Pi and omega 2 Pi multiplied by nu

Omega is angular frequency Radian per second and nu is frequency per second is a dimensionally consistent and this 2 Pi and that 2 Pi will cancel and you will be left with h nu. So, what I could do is; what I like to do is I like to write E V equal to V plus half into h nu. What is a h nu? 1 quantum of vibrations and I like this because when there is a transition from one state to the other what you have left with is h nu.

And its frequency of vibration turns out to be the frequency of light that it absorbs as well if it undergoes V to V+1 transition and as it happens for simple harmonic oscillator Quantum harmonic oscillators only V to V + 1 transitions are allowed something for selection rule just because your energy levels in a system does not mean that one can absorb; it can absorb light and go from any energy level to another.

Only certain transitions are allowed others are disallowed. I am well; one selection rule that I think most of us are familiar with Laporte selection rule remember d-d transitions are not allowed. So, similarly in Quantum harmonic oscillators only V to V+1 transitions are allowed others are not. For such transitions the energy difference simply turns out to be h nu where nu is the frequency of vibration of the oscillator. And then that will equal to h nu, when nu is the frequency of light also.

So, interestingly Quantum harmonic oscillator absorbs light whose frequency matches its own vibrational frequency we deal with this a little more detail in the molecular Spectroscopy course. Ok. So this is our expression where we wanted to get E V equal V + half h nu. We can; we know the expressions for the expression for the energy of all the vibration energy levels of the quantum harmonic oscillator, but until now we know only one wave function Psi 0 equal to m Omega to the power Pi h cross rise to the power 1 by 4 multiplied by e to the power -m omega by 2h cross x square.

What should the next goal be? Next goal obviously should be to find Psi 1, Psi 2, Psi 3, Psi 4. How can we do it? You can do it by using ladder operator, but then will also use is analytic technique which will allow us to arrive at some very beautiful relationship among the wave functions in vibration manifold and in fact got least the selection rule. So what will do in the next module is that will try and understand.

How to find out the expressions for Psi V the wave functions for the vibrational levels other than V equal to 0, V equal to 0 you already know. So, that will require maybe two modules after this. Today for this module we close our discussion.