# Quantum Mechanics and Molecular Spectroscopy
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## Lecture – 31
## Molecular Vibrations (Part 2)

Hello, welcome to the lecture number 31 of the course Quantum Mechanics and Molecular Spectroscopy. In the previous lecture, we were talking about the harmonic oscillator and its selection rules. So we will continue with the same topic.

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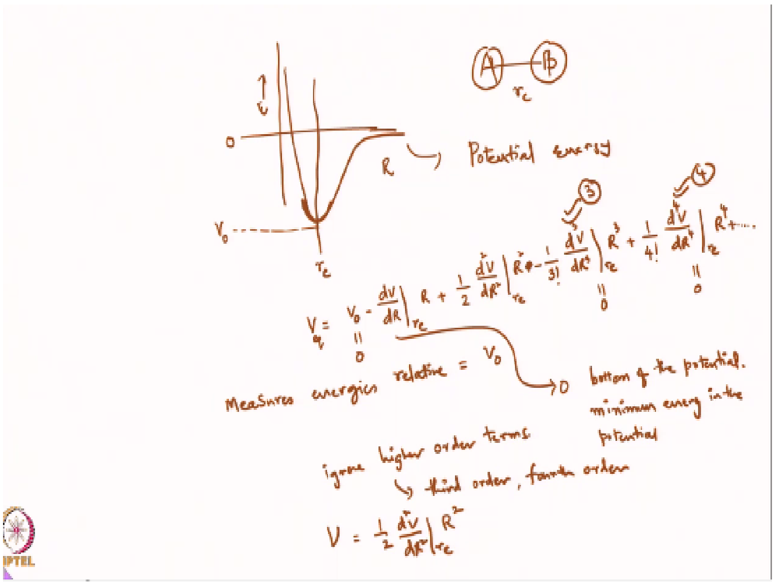

Potential energy

$$\underset{q}{V} = \underset{0}{\underset{\parallel}{V_0}} - \frac{dV}{dR}\Big|_{r_e} R + \frac{1}{2}\frac{d^2V}{dR^2}\Big|_{r_e} R^2 - \frac{1}{3!}\underset{0}{\underset{\parallel}{\frac{d^3V}{dR^3}\Big|_{r_e}}} R^3 + \frac{1}{4!}\underset{0}{\underset{\parallel}{\frac{d^4V}{dR^4}\Big|_{r_e}}} R^4 + \cdots$$

Measures energies relative = $V_0$

→ 0 bottom of the potential.
minimum energy in the potential

ignore higher order terms
↳ third order, fourth order

$$V = \frac{1}{2}\frac{d^2V}{dR^2}\Big|_{r_e} R^2$$

So, if you have a molecule or A, B molecule has a potential something like that. So this I will call it as 0 and this will be sum v 0 and there is equilibrium distance re that is if you construct bond A, B. The equilibrium distance is re and this is the potential energy function as a function of R this is nothing, but the potential energy. So at the bottom of this (()) (01:21) one can write the potential as a Taylor series expansion.

So your v is equal to at equilibrium is nothing but v 0 – d v / d R at re into R + 1 over 2 factorial is nothing but 2 d square v / d R square at re evaluated at re is R square – 1 over 3 factorial d cube v / d R cube evaluated re into R cube + 1 over 4 factorial d to the power of 4 v / d R to the power of 4 evaluated at re R to the power of 4 + etcetera. Now, one can always measure energies with respect to some value.

And if that value is v 0 so measure energies relative to v 0 that means if I measure energies with relative so I can equate this to be 0. Now the second thing is d v / d R we are at the bottom of the potential so when you are at bottom of the potential the first derivative will go to 0. So this will go to 0 because bottom of the potential are same as minimum energy in the potential.

Then you are left with and if I ignore higher order terms that means I will ignore third order higher order means third order which is this order 3 fourth order which is this. So if I ignore that okay ignore means basically going to 0. So, what I will do is I will also take this to 0 and this to 0. So what I am left with v = 1 / 2 d square v / d R square evaluated re R square where R is the intermolecular distance or interatomic distance in this case.

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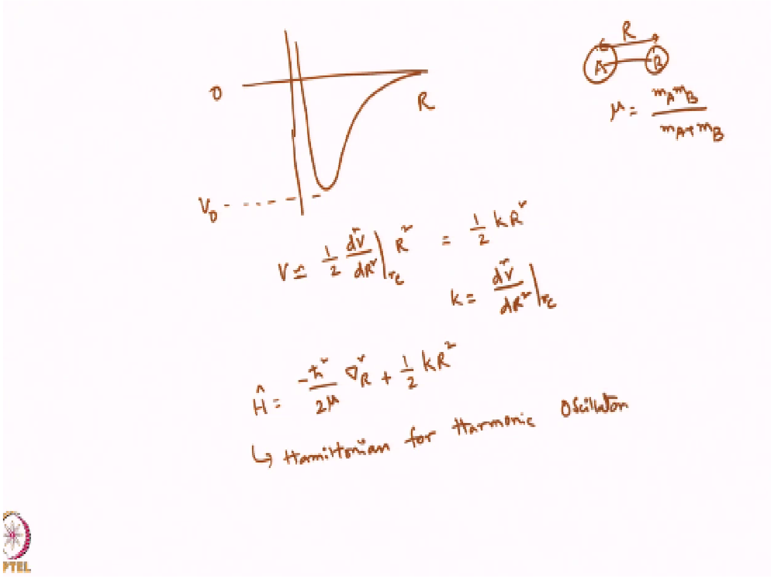

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$V \simeq \frac{1}{2} \frac{d^2V}{dR^2}\bigg|_{r_e} R^2 = \frac{1}{2} kR^2$$

$$k = \frac{d^2V}{dR^2}\bigg|_{r_e}$$

$$\hat{H} = \frac{-\hbar^2}{2\mu} \nabla_R^2 + \frac{1}{2} kR^2$$

↳ Hamiltonian for Harmonic Oscillator

So, if you have a potential where R is the interatomic distance then what you have is the v equals to 1 / 2 d square v / or approximately = d R square at evaluated re R square. This I will write it as 1 / 2 k R square where k is nothing, but d square v / d R square evaluated re and now if you write the total energy Hamiltonian H is equal to – h bar square / 2 mu del square R where if you have A and B connected and mu is nothing, but m A m B divided by m A + m B.

And R is the coordinate so this R is nothing but internal coordinate + 1 / 2 k R square. So this is my Hamiltonian for harmonic oscillator. Now harmonic oscillator is just a model that represents a A, B bond.

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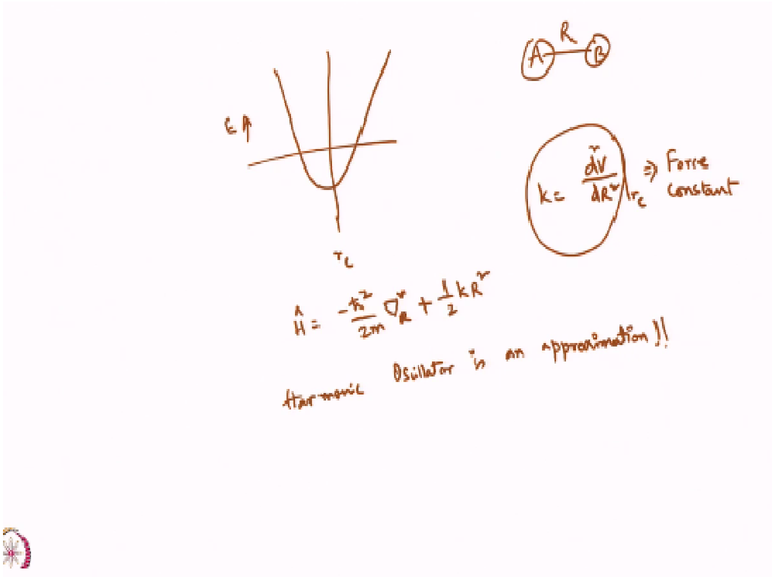

Now one of the problems with harmonic oscillators is that so when I draw harmonic oscillator, harmonic oscillator is with respect to sum re and it should something like that. So harmonic oscillator never breaks the potential can raise up to infinity, but all chemical bonds between molecule atom A and B they will break eventually if you keep stretching they will break.

So, harmonic oscillator in some sense is not a good representation for a chemical bond. However, at the bottom of the potential that means around the equilibrium geometry harmonic oscillator is a reasonably good model and we use harmonic oscillator to represent bonds when they are at the equilibrium position.

Now if you have this harmonic oscillator then of course your Hamiltonian as I just said is nothing but – h bar square / 2 m del square R + 1 / 2 k R square and where k is nothing but d square v / d R square evaluated at re. This is nothing but your force constant. Now the problem here is the following. The thing is that this force constant is only the second order term.

And in such case we are ignoring the higher order terms the third order and the fourth order terms which in normal molecule or in normal diatomic molecule A B would have or harmonic oscillator is an approximation. Now, if a harmonic oscillator in approximation and we know R is just a dummy variable. So, I am going to rewrite this whole thing in some other variable x.

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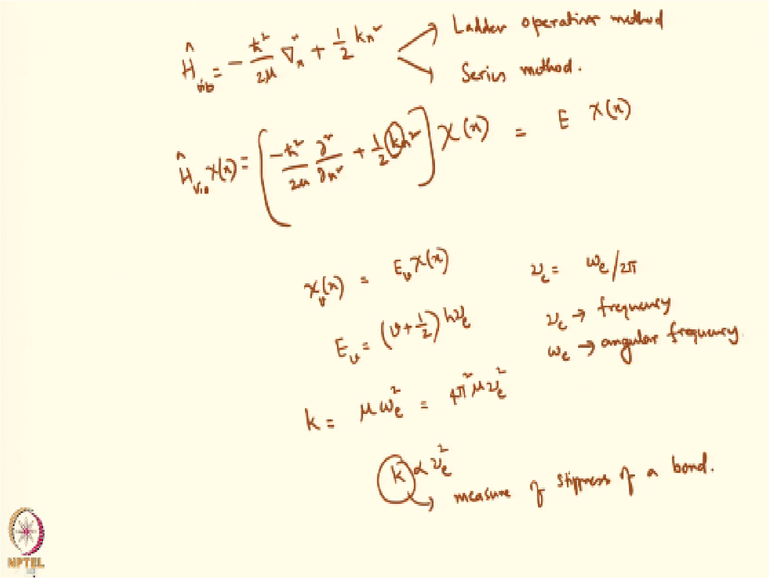

$$\hat{H}_{vib} = -\frac{\hbar^2}{2\mu}\nabla_x^2 + \frac{1}{2}kx^2 \xrightarrow{} \text{Ladder operation method}$$
$$\xrightarrow{} \text{Series method.}$$

$$\hat{H}_{vib}\chi(x) = \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}\boxed{k}x^2\right]\chi(x) = E\,\chi(x)$$

$$\chi_v(x) = E_v\chi(x) \qquad \nu_e = \omega_e/2\pi$$

$$E_v = \left(v+\frac{1}{2}\right)h\nu_e \qquad \nu_e \rightarrow \text{frequency}$$
$$\omega_e \rightarrow \text{angular frequency}$$

$$k = \mu\omega_e^2 = 4\pi^2\mu\nu_e^2$$

$$\boxed{k} \propto \nu_e^2$$
$$\rightarrow \text{measure of stiffness of a bond.}$$

So instead of R I can always use another variable x and that would be – h bar square / 2 mu del square x + 1 / 2 k x square this is going to be my Hamiltonian H vibration. Now you have this Hamiltonian one can solve for it there are two methods to solve this. One is called ladder operator method and other is the series method. So, essentially you are going to solve a second order differential equation.

So this can be written as – h bar square / 2 mu d square / d x square + 1 / 2 k x square this into some function chi of x H vibration on into chi of x = E chi of x that is going to be a solution for it, but when you solve by either of the method whatever one can solve by whichever is convenient method and there are textbook like molecular quantum mechanics by Atkins or quantum chemistry by Ira N. Levine where you can find the solutions.

You can use either of the method and of course it is only one differential equation so depending on which method you use or the solution that come out should not depend on the method that you use. Now I am just going to write the solution so when you solve this using one of these two methods what you get is the following. Your chi of x will depend on a quantum number v that is a vibrational quantum number = E v chi of x.

So that is going to be your quantum number where it can show that E v = v + 1 / 2 h nu e where nu e is nothing, but 2 pi omega e where nu e is frequency and omega is angular frequency, but there is one thing that you must understand that there is this value k and this value k and this nu e should be related in some way. Sorry this is not that should be a right one.

So how is it relate so the k that is the force constant is related to mu omega e square or this is nothing but 4 pi square mu nu e square. So the force constant k is proportional to nu e square. So that means the vibrational frequency is proportional to square root of the force constant that means if you increase the force constant vibrational frequency will increase. So that is what we already know so if the bond becomes more stiffer the vibration frequency will increase. Stiffness is measured by the force constant. So this is a measure of stiffness of a bond.

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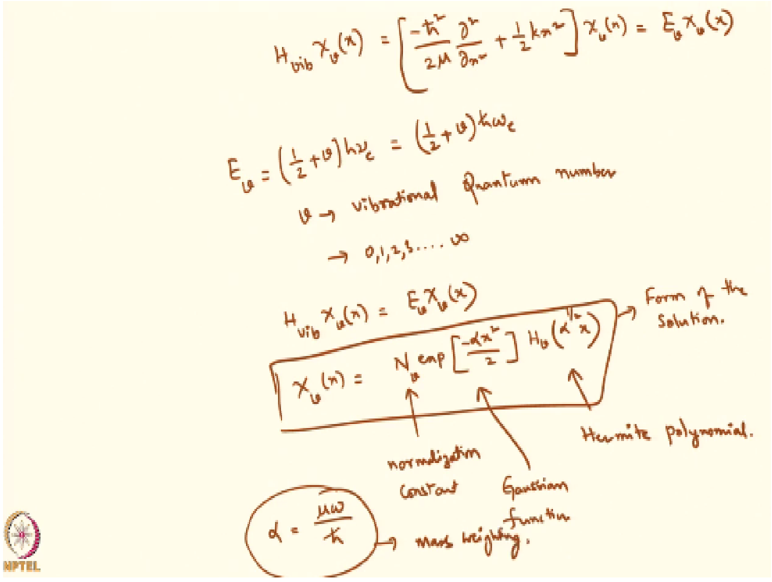

$$H_{vib}\chi_v(x) = \left[\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\chi_v(x) = E_v\chi_v(x)$$

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

$v \rightarrow$ vibrational Quantum number

$\rightarrow 0,1,2,3.\ldots \infty$

$$H_{vib}\chi_v(x) = E_v\chi_v(x)$$

$$\boxed{\chi_v(x) = N_v \exp\left[\frac{-\alpha x^2}{2}\right] H_v(\alpha^{1/2}x)} \rightarrow \text{Form of the Solution.}$$

normalization constant

Gaussian function

Hermite polynomial.

$$\alpha = \frac{\mu\omega}{\hbar} \rightarrow \text{mass weighting.}$$

So what we are going to solve the Schrodinger equation at hand for the vibration H vib chi v of x = - h bar square / 2 mu d square / d x square + 1 / 2 k x square into chi vibration of x = E vibration into chi vibration of x so that is your chi means I just said that E v equals to 1 / 2 + v h nu e this also = 1 / 2 + v h bar omega e and here v is the vibrational quantum number and that goes from 0, 1, 2, 3 up to infinity.

Now the solutions for this would be so you have what you have H vibration of chi v of x = E v of chi v of x and your chi v of x will be sum normal (()) (16:13) N of v exponential – alpha x square / 2 H v alpha to the power of 1 / 2 x. This is the form of the solution. Now where this one is the normalization constant and this is your Gaussian function and this is the Hermite polynomial.

Now one thing that I have written is your alpha which I have not written = mu omega / h bar. Alpha is some kind of a weighted coordinate so because you are multiplying with x so it is kind of a weighting of the coordinate. So this is actually is called mass weighting or mass weighing.

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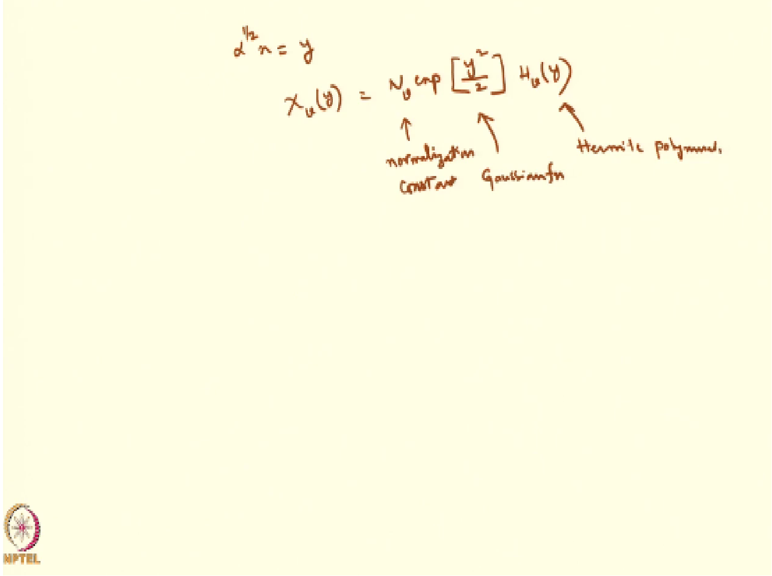

$$\alpha^{1/2} x = y$$

$$\chi_v(y) = N_v \exp\left[\frac{y^2}{2}\right] H_v(y)$$

normalization constant

Gaussian fn

Hermite polynomial,

So one can always write or generally in the textbook it is written that alpha to the power of 1 / 2 x = y if I make that transformation then what happens your chi v will now become function of y. By the way x and y are not different functions like orthogonal variables like what we have used in Cartesian coordinate axis y is just a transformation of x. Chi of y = N v exponential y square / 2 exponential y square / 2 H v of y.

So just trying to become more easier to represent or write and I told you this is nothing but your normalization constant and this is nothing, but your Gaussian function and this is the Hermite polynomial. When you solve it turns out that the Hermite polynomials have a dependencies that means that is generating function.

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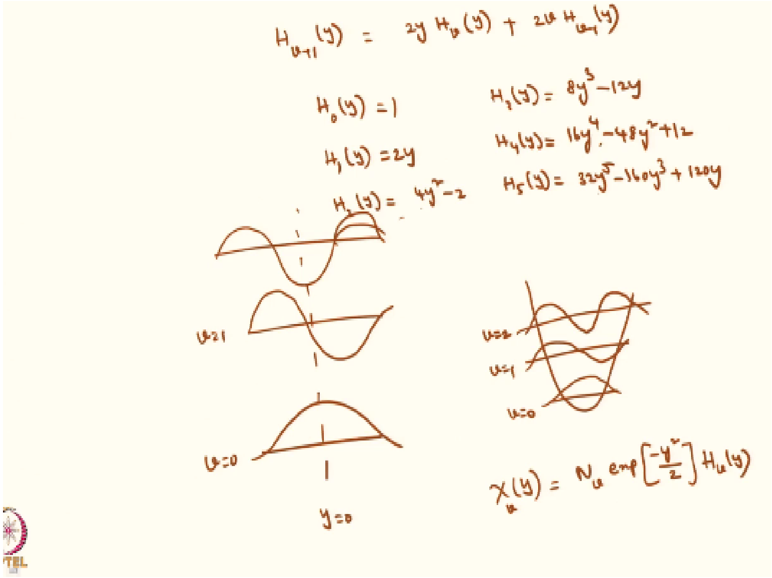

The recursion solution should be H v + 1 of y = 2 y H v of y – 2 mu so let me rewrite H v + 1 of y = 2 y H v of y + 2 v H v – 1 of y and I can get the generating functions so what I get is H 0 of y = 1 H 1 of y = 2 y H 2 of y = 4 y square – 2 H 3 of y = 8 y cube – 12 y H 4 of y will give me 16 y to the to the power of 4 – 48 y square + 12 H 5 of y = 32 y to the power of 5 – 160 y cube + 120 y.

Now you can see H 0 of y is only 1 H y of y is 2 y so when y = 0 it will go to 0 so this will have 1 node this will have 2 nodes because it is a quadratic equation this will have 3 nodes because it is a cubic (()) (21:27), it will have 4 nodes it is a (()) (21:29) and this will have 5 nodes. So when I draw but all of them are the Hermite polynomials which are riding over your Gaussian function. So, when I draw them so v = 0 I will get a Gaussian function.

Now for v = 1 so one can imagine so this is y = 0 or equilibrium so we will get this function and the third case we will get so if we look at the functions they will look at particle in a box function. So they can always be represented like this something like that. They look like particle in a box function, but particle in box functions are sinusoidal functions here there are Gaussian functions that are modulated by the Hermite polynomials.

So this is v = 0, v = 1, v = 2. So you can always see that the functions become odd and even as the quantum number. So this v = 0 is a even function v = 1 will be odd function v = will be even function and so on. So for the even quantum numbers the function is a even function and for odd quantum number it is a odd function. So if I look back my H not H but chi of y or v = sum constant v that is normalization constant exponential – y square / 2 I am not sure oh this should have been a negative sign here.

I am sorry about that so there should have been a negative sign here okay there is negative sign already there so I just missed so – y square / 2 H v.

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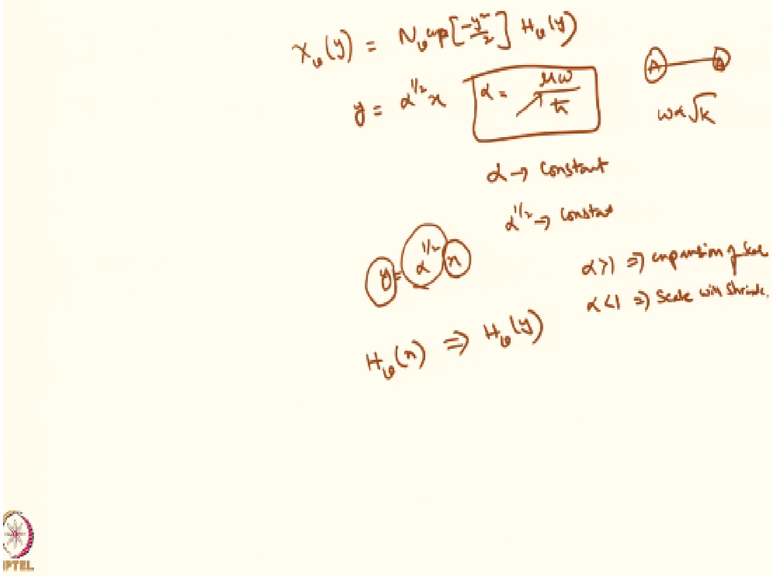

Now one thing that I want to tell you is very simply is that when you have the Hermite wavefunction chi of v now I am writing in terms of y this is nothing but some normalization constant N of v exponential – y square / 2 H v of y, but we said y is nothing but alpha to the power of 1 / 2 into x where alpha is equal to what was the value of alpha mu omega / h bar yeah that is what it is alpha is this.

Now mu is the if you have A and B masses mu is a constant omega is also constant because omega is nothing is related to omega is related to square root of k and k is related to the potential so this also is a constant h bar is a constant. So alpha is a constant so alpha to the power of 1 / 2 will also be a constant that means when you have y to the power of alpha x the behavior of y or the shape of the function of y will be variable y will be same as the variable x.

So H v of x transform to H v of y will have a same shape except that the y will get multiplied by so that means the depending on the value of alpha the scale will either elongate or shrink. If alpha is greater than 1 then the scale will expand and alpha if so this will lead of expansion of the scale and alpha is less than 1 this will be instead of expansion the scale will shrink, but it will not change the way the function will look like.

The shape of the function will remain constant. So you have the functions of Eigen value of a harmonic oscillators as Gaussian functions multiplied by the Hermite polynomials and will look like oscillator is a representation of vibrational wavefunction which we will continue in the next lecture. Thank you.