**Engineering Chemistry - 1**

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**Lecture - 4**

**Module 1- Atoms and Molecules**

**Harmonic Oscillator and Molecular Vibration**

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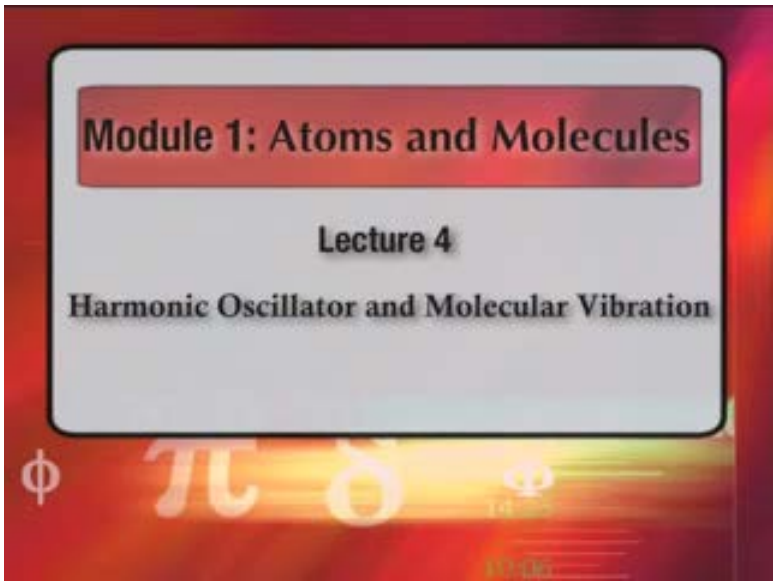


Welcome to the lectures series by the National Programme on Technology Enhanced Learning. This is the lecture series in Chemistry. Today it is the 4$^{th}$ lecture that we are going to discuss the Molecular Vibrations but more importantly the underlying quantum mechanical model namely the Harmonic Oscillator model.

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The last three lectures we have been going through a sequence of how to solve the Schrödinger equation with simple models like the particle in a one dimensional box and the particle in a two dimensional box. As quickly as possible we will try to assimilate the results rather than worry about the details of the Mathematics. As I told earlier that the importance of this approach or the reason for this approach is that we want to get the Chemistry part as quickly as possible. That is to deal with the atoms and molecules with the atomic orbitals and to understand the quantum mechanics behind that we must solve at least a few simple models. And today it will be another model the model of simple Harmonic Oscillator which is a very well known solved problem in mechanics in classical mechanics many of you might have to recall the classical solutions or the methods. We will go along the way and let me relate what that model has to do with Molecular Vibrations as we are interested in Chemistry.

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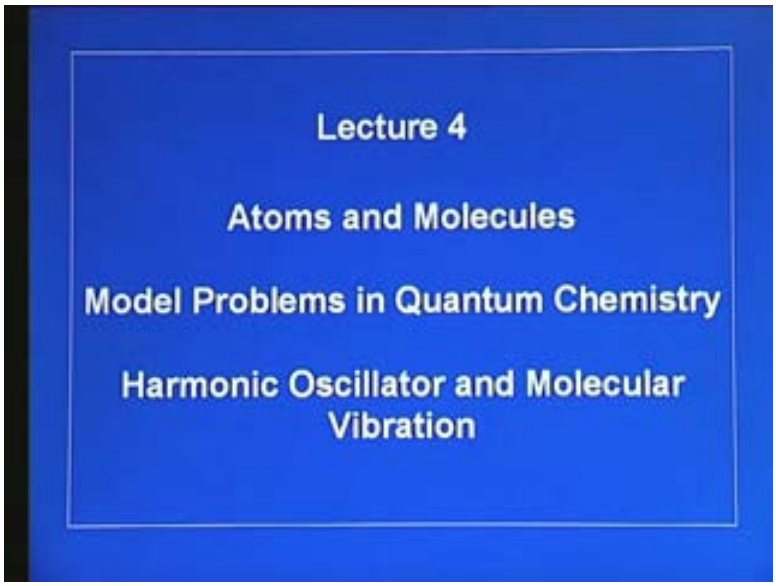


So the lecture today is on Harmonic Oscillator and Molecular Vibration that how we relate these two things is the subject of today‘s talk.

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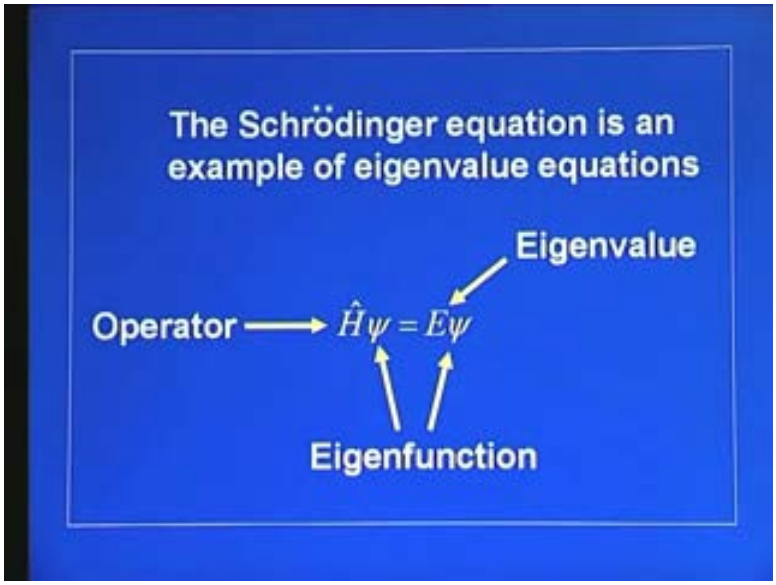


Let us recall the Schrödinger equation. you have solved the two simple equations $-\hbar^2/2m\ (d^2\psi/dx^2)+V(x)\ \psi(x) = E\ \psi(x)$ for a particle in one dimension we assumed that the potential to be 0 in certain region and infinity everywhere and we had simple solutions coming out of it the idea of quantization also coming out and the wave function. The solution gave infinite number of solutions which we marked as $\psi_1(x)$, $\psi_2(x)$ etc.

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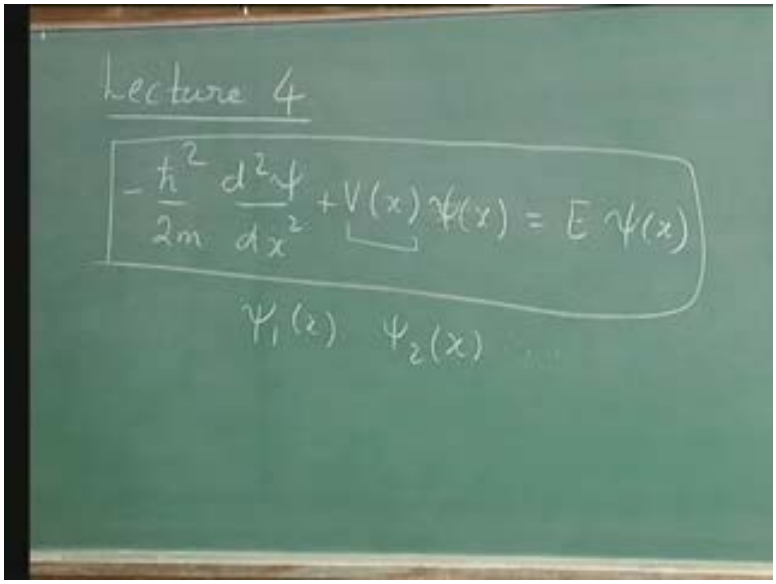


When we solve the differential equations of this kind the Schrödinger equation particularly the mathematical terminology associated with the Schrödinger equation is that an Eigenvalue equation.

The Eigenvalue meaning there is a class of differential equations in Mathematics and here the $\hat{H}$ is Hamiltonian and that is what makes it the Schrödinger equation and the wave function $\psi$ as well as the energy E that we are looking for are called Eigenfunctions $\psi$ is called the Eigenfunction and the constants that we obtain are called the Eigenvalues. In this terminology for the particle in a one dimensional box you might associate with them the $\psi_n(x) = \sqrt{2/L} \sin(n\pi x/L)$ as the Eigenfunctions and the energy $E_n$ which you obtained as $h^2 n^2/8mL^2$ where the potential is 0 in the box of region of length L, this as the Eigenvalues. Thus you can call the operator $-\hbar^2/2m\ (d^2/dx^2)+V(x)$ as the Hamiltonian operator acting on a function $\psi(x)$ giving you a constant times the function itself and such solutions are called Eigenvalue, Eigenfunctions solutions and the equations are called Eigenvalue equations.

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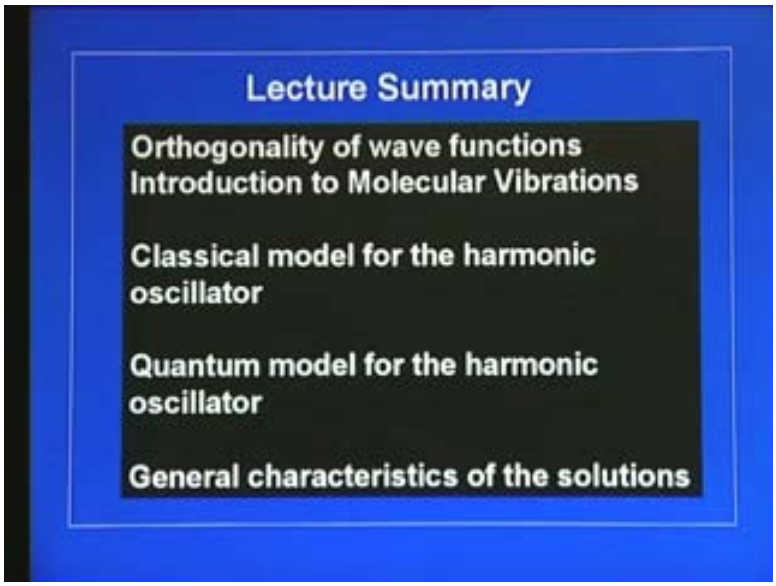


Also one important point which I did not stress in the last lecture is that the solutions that we obtain for the $H\psi = E\psi$ and the solutions corresponding to different E values for example here the solutions corresponding to n = 1 and n = 5 or n = 2 or n = 10 for example these solutions are orthogonal.

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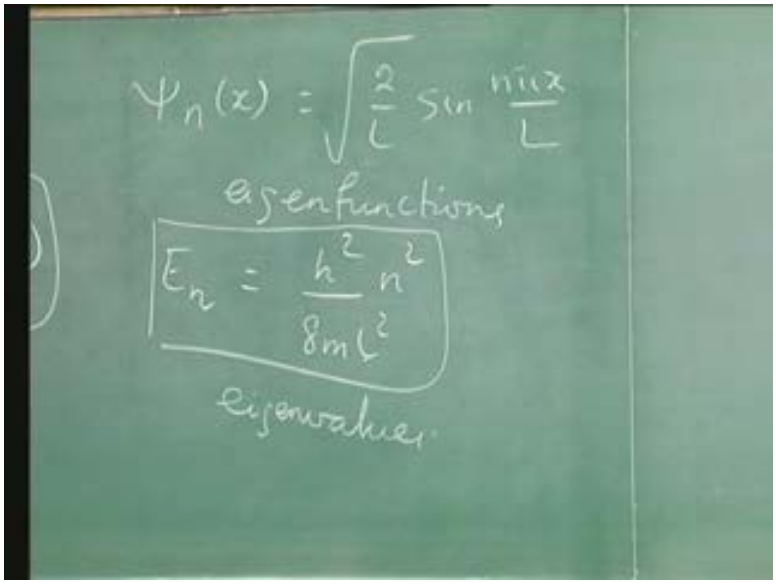


The definition in this case of the orthogonality is that the integral of a wave function $\psi_n(x)$ which is an eigenfunction of the Hamiltonian and for a particle in a box, the limits you might recall that x = 0 to x = L and $\psi_m(x)dx$ and then this integral is 0 if $n \neq m$. You might also recall that n and m are the same of course this gives you 1 and that is how we got the factor $\sqrt{2}/L \sin(n\pi x/L)$ that

is what is called the normalization. But the functions belonging to different eigenvalues of the Hamiltonian operator are orthogonal and that is something you have to remember. So in today's lecture we will introduce the ideas as follows: The Orthogonality of wave function, the molecular vibrations, classical model for the Harmonic Oscillator, Quantum model for the Harmonic Oscillator and some general characteristics of the solutions.

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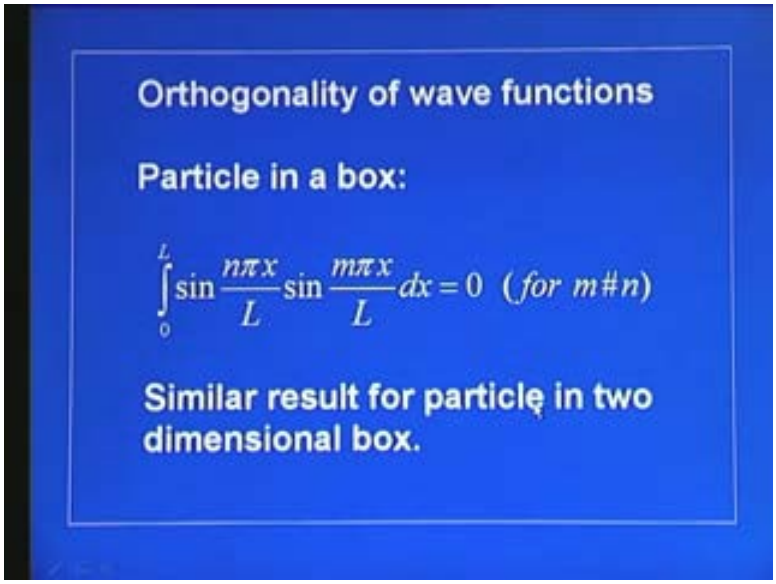


I have just described this you have seen that on the board. The orthogonality of wave functions for a particle in a box is that the integral of the two wave functions sin(nπx/L) and sin(mπx/L) are integrated over dx in between the limits of the particle in a box that is integrated overall the space available to the system where integral is 0 for the solutions which do not have the same Eigenvalue i.e. for $m \neq n$. You can also prove this in general for degenerate systems that are two solutions corresponding to two Eigenvalues both of which are the same can also be orthogonal but let us not worry about it now. Orthogonality is the term we would come across frequently.

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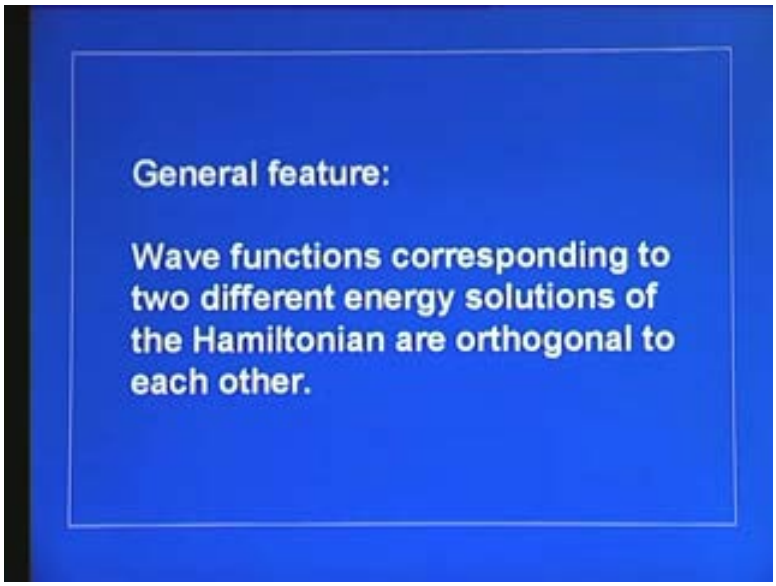


So the summary is that the wave functions corresponding to two different energy solutions of the Hamiltonian are orthogonal to each other, this point must be remembered. Now we will go to the solutions of the Harmonic Oscillator and Molecular Vibrations.

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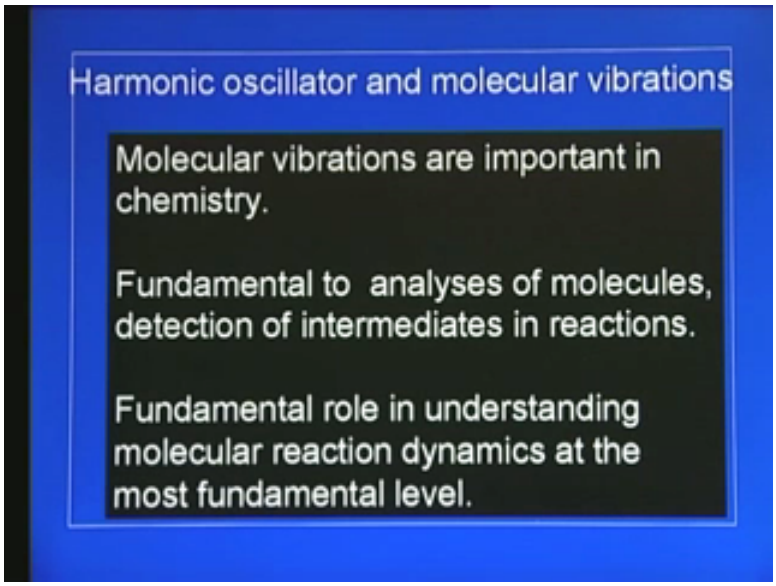


That idea was something that I did not stress in the last two lectures. So with that we sort of come to one model problem reasonably completely solved. Now we will look at the model problem of the Harmonic Oscillator and the Molecular Vibrations. The reason why vibrations are important of course is that vibrations play a fundamental role in the chemist understanding of how molecules dissociate, how molecules form, the dissociation energy of the molecule is

associated with what is called the bond energy and the bond energy is a concept that it comes out naturally when you assume molecules to vibrate about an equilibrium or as an harmonic spring. So the vibrational motion is fundamentally important in Chemistry and is of course used in many instances particularly in the field of spectroscopy molecular vibrational spectroscopy and those of you who have studied organic Chemistry have seen infrared spectra of many molecules, the basis for that is molecular vibrations.

In order to understand molecular vibrations one has to understand the model or one has to predict a model underneath such molecular vibrational concepts. The other thing is vibrations are extremely important in ones analysis of molecules, detection of intermediates and chemical reactions in the form of spectroscopy and also vibrations play a basic role in ones understanding of the details of molecular reaction dynamics at the most elementary or at the most fundamental level that is at the level of applying the Schrödinger equations to molecules. So it is not necessary to stress this beyond this basic level introduction that vibrations are fundamental to Chemistry.

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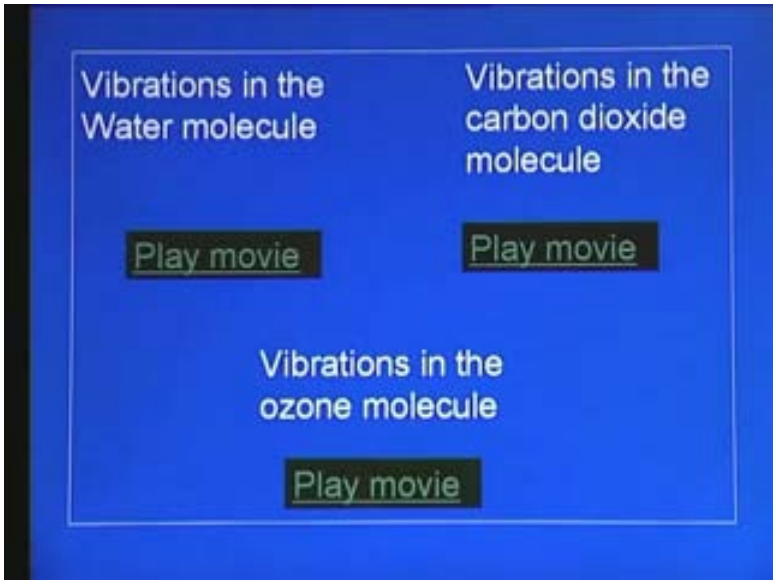


You can perhaps recall simple models of vibrations of simple molecules like water molecule or carbon dioxide.

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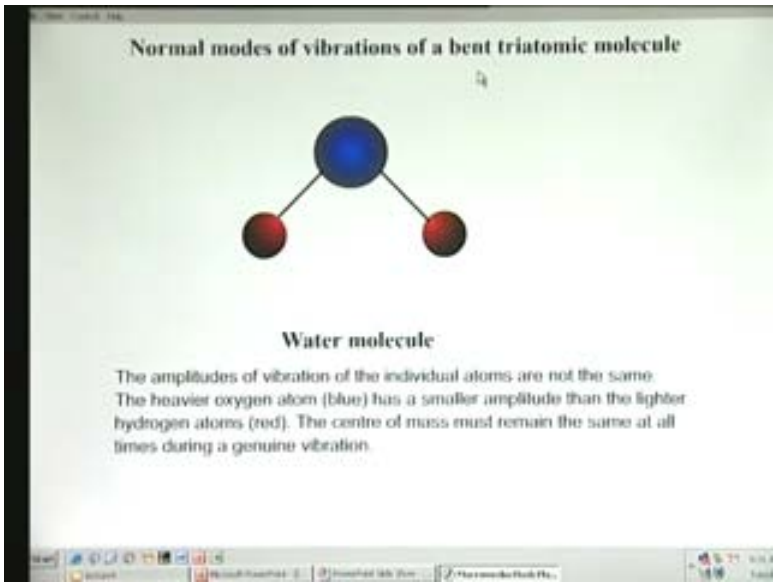


What are called normal vibrations of a bent tri atomic molecule, water molecule? Later on when we study spectroscopy we will see that such molecules have three modes of vibration and so on a simple illustration of what is meant by displacement of the atoms about their equilibrium positions. And what you see here is that the molecule vibrates about an equilibrium position and the centre of mass. And such modes are going to be studied using quantum mechanics.

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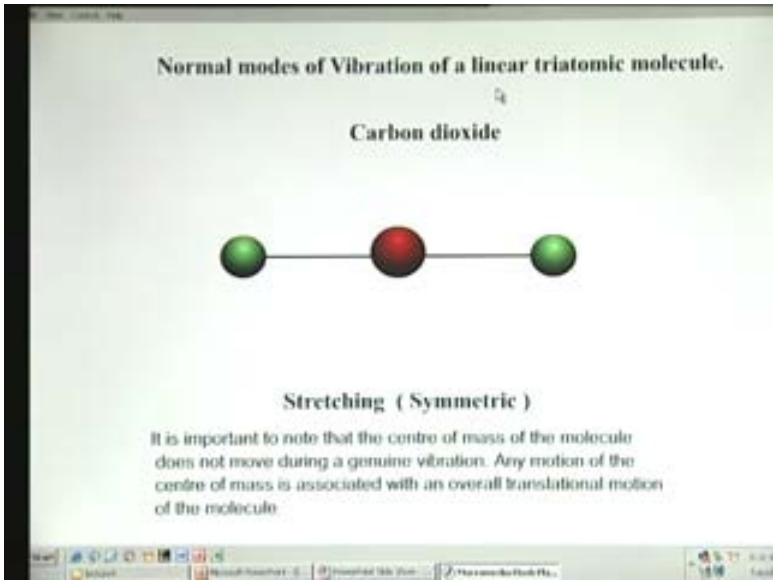


Another example of vibrations of a molecule is the carbon dioxide, a linear molecule and you can recall that the symmetric stretching of carbon dioxide about its equilibrium point and about its equilibrium position is another example of how we visualize molecular motions.

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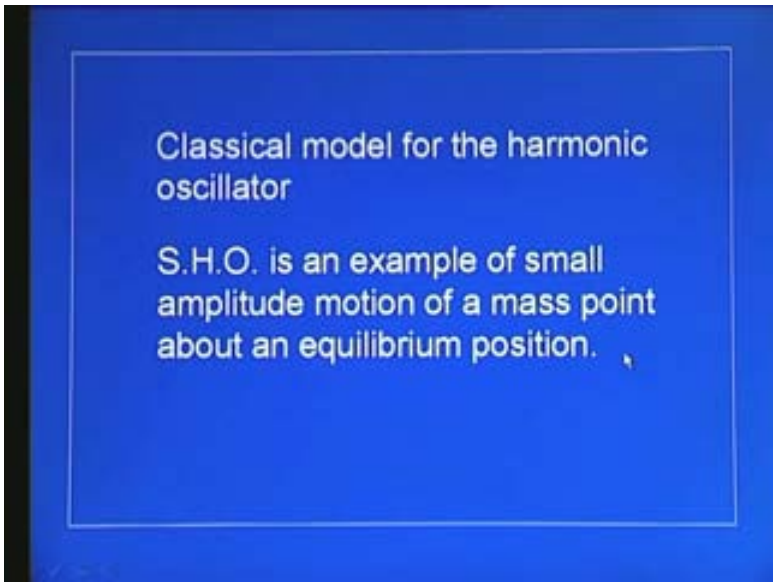


Vibrations at the level of what are called normal modes in molecules are analyzed or studied using the simple Harmonic Oscillator model. We will also look at the classical model and then on how we quantize and get the solutions and so on. Simple harmonic motion is something again is that a pendulum, a clock that a quartz clock and there are many examples of what are called simple Harmonic Oscillators. This is basically an oscillation about an equilibrium position such that the force that is responsible is proportional to the displacement from the equilibrium. And the force and the displacement are in opposite direction to keep the motion continued.

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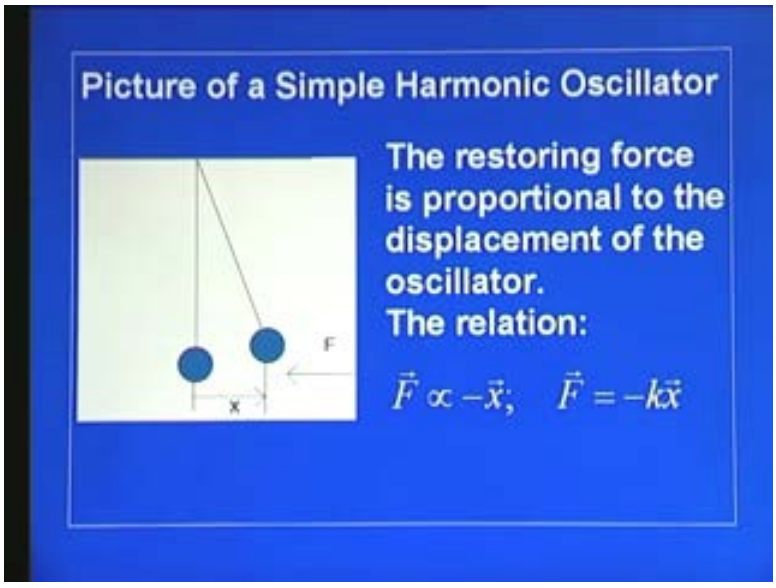

A picture of a simple Harmonic Oscillator, you recall a pendulum, it keeps on moving back and forth. And obviously the back and forth motion in the absence of any other frictional energy loss is that you can express by a simple equation namely the force that is responsible when you displace the atom from its equilibrium position or you displace the clock from its equilibrium position.

You have given a certain force to it and when you release it with the force that is responsible makes the pendulum go back to its equilibrium position but by then it has picked up some kinetic energy in and this kinetic energy keeps the pendulum oscillating back and forth. The relation is that the force and the displacements are vectors and are in opposite directions and the force is equal to the vector with a force constant k which expresses the strength of the oscillation or the frequency of the oscillation, i.e. F= −kx.

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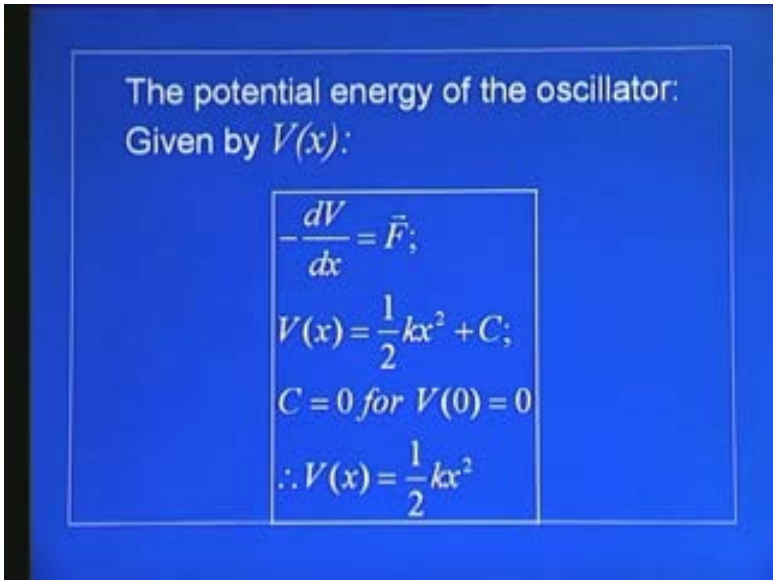


With this model for simple Harmonic Oscillator one can write the total energy of the oscillator. When we write the force is proportional or equal to the F= −kx and the force itself is the negative derivative of a potential field associated with the Harmonic Oscillator motion and that is −dV/dx = −kx. Then the integration leads to V(x) = ($kx^2$/2)+C, where C is a constant. The constant refers to the value of the potential when the displacement is 0. If the displacement is 0 let us assume that the species is in equilibrium and has the minimum potential energy and that minimum potential energy being a constant is usually set to 0 as a scale that is the scale which respect to which the potential energy is referred for displacements not equal to 0. So when you do this the potential energy has a simple expression V(x) = 1/2 $kx^2$.

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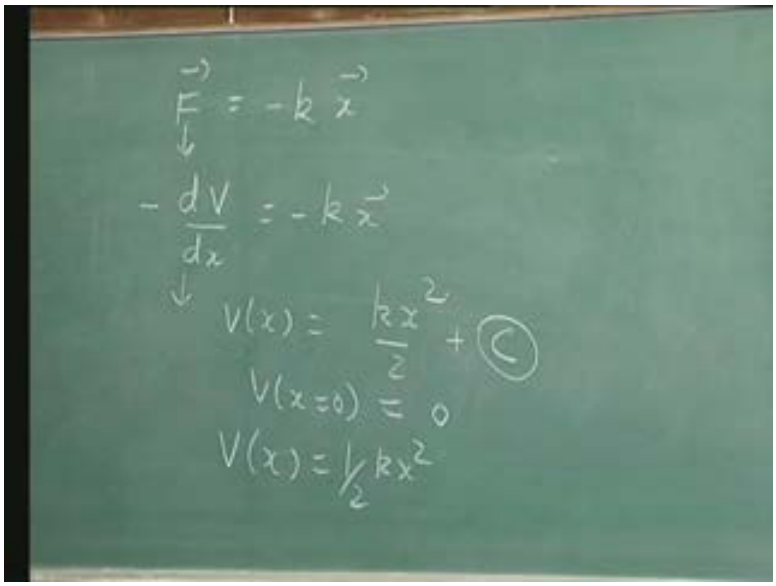


And if the oscillator is displaced by x and has been associated with motion then its kinetic energy is obviously the mass of the oscillator and the derivative of the displacement square that is the velocity $\mu v^2/2$ as its kinetic energy or in terms of momentum. The kinetic energy KE as $P^2/2\mu$ where $\mu$ is the mass of the Harmonic Oscillator associated with the motion.

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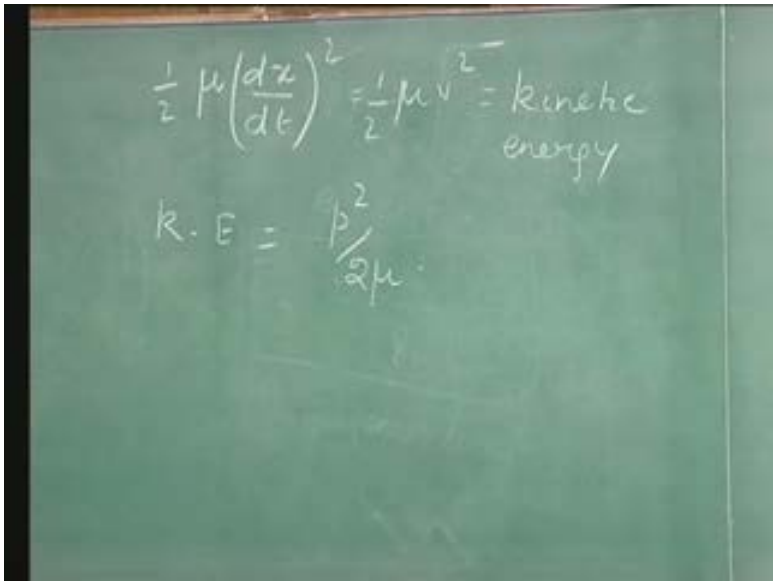


This kinetic energy and the potential energy of the harmonic oscillator represents the total energy of the Harmonic Oscillator. And one can write the total energy or the Hamiltonian in classical mechanics for the Harmonic Oscillator as $p^2/2\mu + 1/2\ kx^2$. As has been done earlier now you go to the process of quantizing and solving this as a quantum mechanical problem then the

prescription that was given to you in the first or second lecture was that the p the momentum has to be associated now with the operator called –iħ d/dx and then you convert this into a quantum mechanical Hamiltonian then solve the Schrödinger equation that $H\psi = E\psi$.

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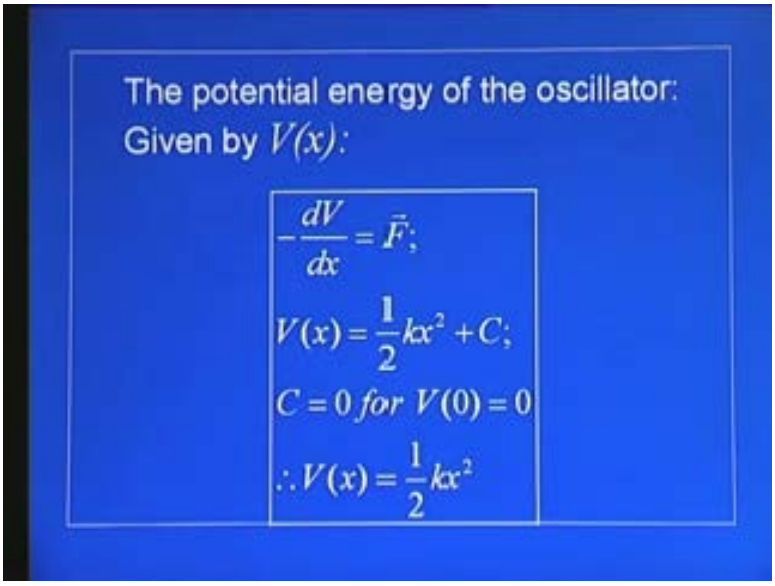


That is the quantum problem associated with the classical Harmonic Oscillator. So what you see here is essentially the summary of that namely the potential energy is a function of the square of the displacement and for the constant set to 0 for the lowest value of the potential. This $V(x) = ½kx^2$ is parabolic. If you plot the potential energy as a function of x then what you have is a parabola. You plot the potential energy as a function of x = 0 and x can be both negative and positive because if you choose one direction as the positive direction the other side the opposite direction is obviously the negative direction. The positive or the negative value of the potential energy, $V = 1/2\ kx^2$ is a parabola if x = 0. Depending on the value of k the parabola can be this way or the parabola can be even other way or the parabola is that depending on various values of p and k. (Refer Slide Time: 20:02 min). And I will leave it you to decide whether k, here $k_1$, $k_2$, $k_3$ each represents one of these graphs for you to decide whether $k_3$ is greater than $k_2$ or $k_1$or $k_1$ is greater than $k_2$ greater than $k_3$. The potential energy is given by a bounded curve.

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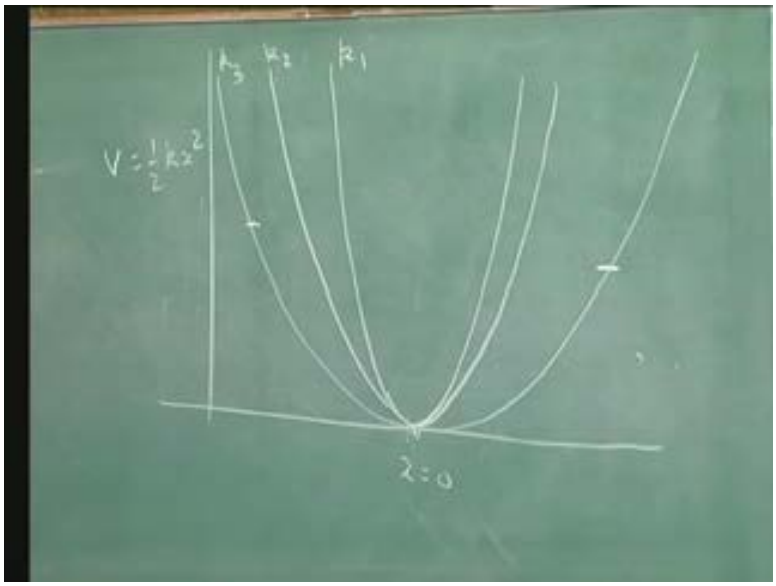


And if this is the maximum displacement for any value of k, for example let us take $k_3$ as the Harmonic Oscillator potential energy what does this maximum displacement mean? The maximum displacement means that the potential energy is maximum at that point that is the turning point of the oscillator and then the oscillator comes back again to go to the other side of the x. At the turning point it has no kinetic energy therefore what it means is that the Hamiltonian when you write $H = p^2/2\mu + 1/2\ kx^2$. Here the kinetic energy is 0 therefore the potential energy represents the total energy at a point of the either of the extremes of parabola at this point or at this point. (Refer Slide Time: 20:46 min) What about the value at middle of these points? At this point the potential energy is zero because there is no displacement the oscillator has come back to its exact equilibrium position.

Therefore what you have is there is no potential energy associated with it but what you have is all the energy H is $p^2/2\mu$ there is no potential energy involved. So what you see as a Harmonic Oscillator with a constant energy is that it is oscillating in such a way that the energy is transferred between a kinetic energy and a potential energy such that the total remains the constant but at the extremes the potential energy is maximum, right at the middle kinetic energy is maximum and everywhere in between it is possible for the oscillator to have a combination of energies such that the total is a constant value. Now, that is one important point.

The second important point is that the oscillator can have a constant energy like this or the oscillator can have a constant energy like this. Classically any energy is possible depending on how much of it the maximum displacement is. Assuming those things are harmonic. Now, when the displacement is very large you do not except the motion to be harmonic and this graph may not be satisfied then the former expression may not be the right expression for the potential energy. But assuming things are harmonic any value for the displacement is possible and any value for the energy is possible. Let us restrict such things in Quantum Mechanics.

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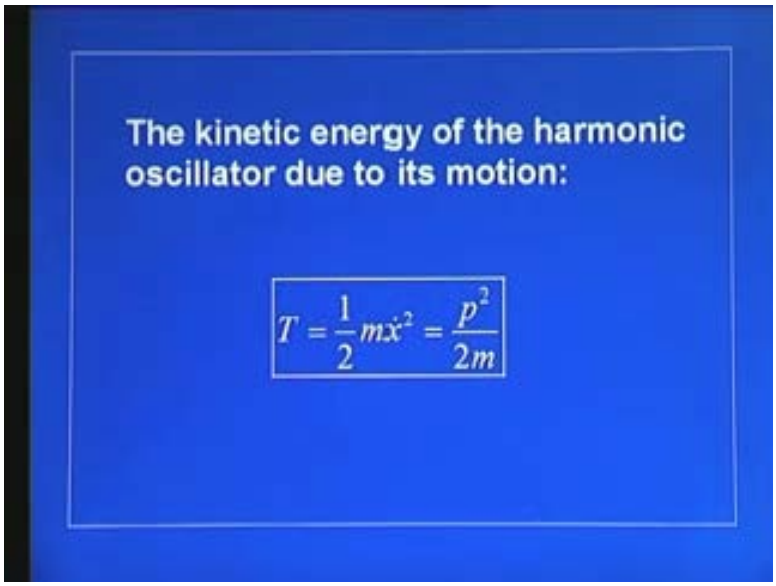


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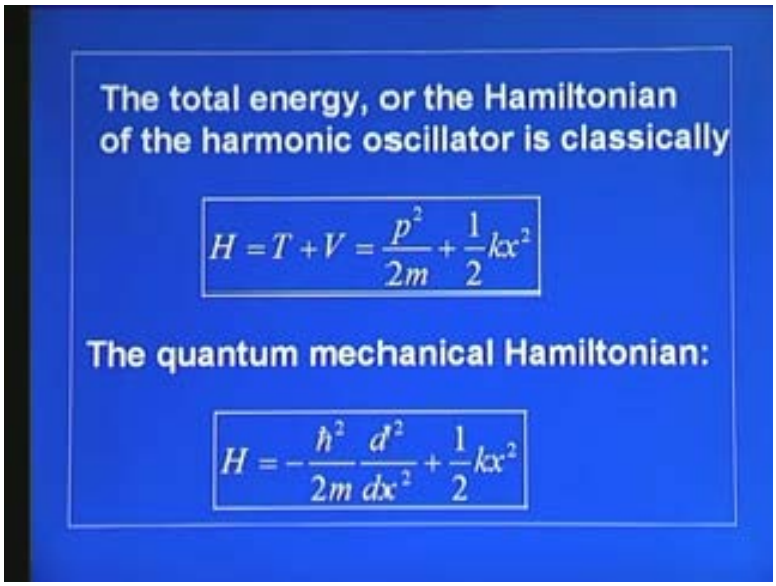


So the Quantum Hamiltonian, now when we quantize the classical Hamiltonian for the Harmonic Oscillator $p^2/2\mu + 1/2\ kx^2$ when p is replaced by $-i\hbar(d/dx)$ the Hamiltonian is $-\hbar^2/2m\ (d^2/dx^2) + ½kx^2$ the symbol miu is used where m is mass of the oscillator so the symbol m and μ are often used interchangeably. You will also know what this μ represents. It is –s h bar square/2m or 2miu d square/d square + 1/2 kx square.

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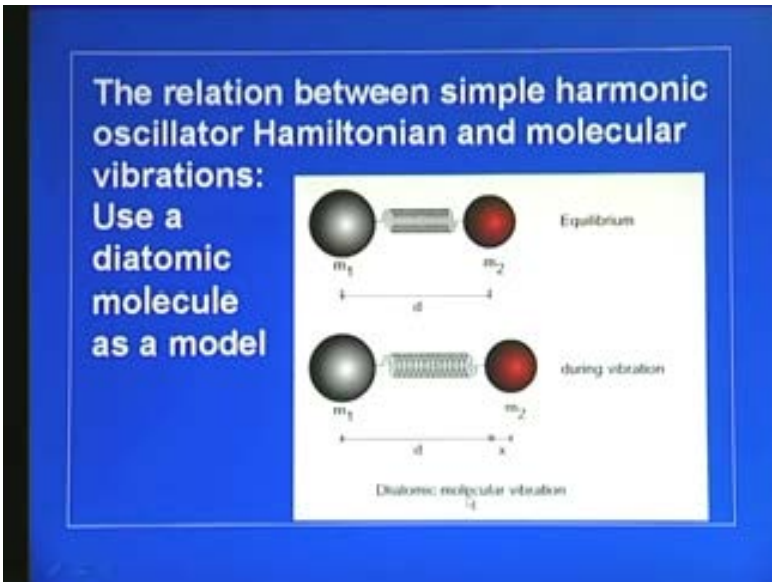


What is the relation now between this and the molecules vibration that I have been talking about? Now, if you think about a diatomic molecule as two atoms with mass $m_1$ and $m_2$ connected to each other by a bond which you can imagine to be a spring and if the molecule does not vibrate, it has no vibrational energy you call this as the equilibrium the position of the molecule, then the bond distance or the bond length between the centers of masses of the two atoms $m_1$ and $m_2$ is d, during vibration the spring is extended or compressed as the molecules undergo vibration, the length d changes by x, it is positive or negative and the spring motion for small values of x relative to the value of d is modeled as a Harmonic Oscillator.

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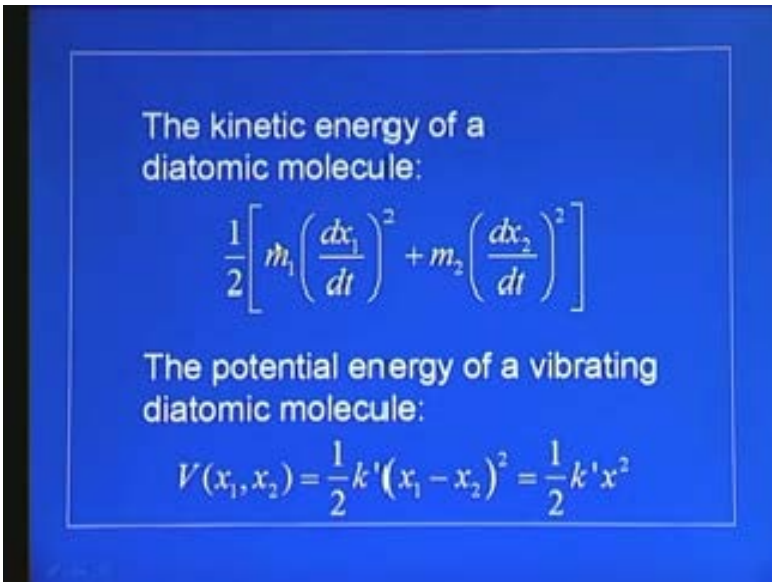

The kinetic energy of the diatomic as the two atoms vibrate about their equilibrium positions as the two atoms are going away from their equilibrium positions each displacement of the atoms 1 and 2 namely $x_1$ and $x_2$ lead to the individual kinetic energies $\frac{1}{2}[m_1(dx_1/dt)^2 + m_2(dx_1/dt)^2]$ where first term is the velocity of the atom 1 and the other is the velocity of the atom 2 with the masses $m_1$ and $m_2$ and the potential energy of a vibrating diatomic molecule is essentially the potential energy due to the separation between the two atoms in the molecule. If they are farther apart the interaction between the two is less and if they are closer the interaction between the two is more and so on.

Therefore it is a separation between these two and that is essentially the difference between the two displacements so the potential energy depends on what is called the relative displacement x for the diatomic molecule and it is exactly in the same form as that on the Harmonic Oscillator with of course a different constant k′ characteristic of that molecule. The potential energy is only a function of the relative displacement of the two atoms.

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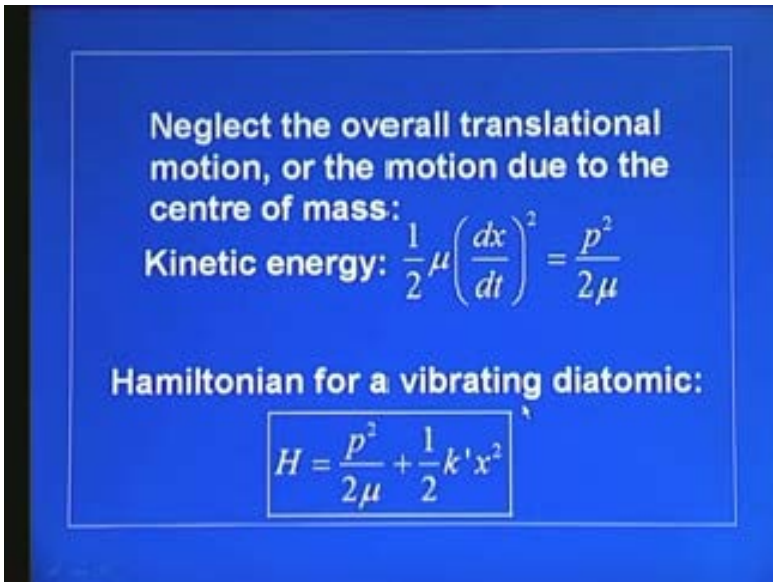


If we neglect the molecule as a whole when it is vibrating as a whole if the molecule is translating if we neglect that motion we neglect the motion of the molecule as it vibrates its translation then it is possible for you to rewrite the kinetic energy of the molecule in the form of a reduced mass times a velocity associated with the relative displacement. This is elementary classical mechanics. The answer is, when you neglect the overall translation motion or the motion due to what is called the centered mass the kinetic energy is no longer a sum of two terms but it is given by a reduced mass μ and the velocity dx.

Therefore V(x) for a molecule is that it is ½ k′ $x^2$ where x is $(x_1 - x_2)^2$ and $p^2/2\mu$ is the kinetic energy of the diatomic molecular vibration where p is $m(x_1 - x_2)$ where $x_1$, $x_2$ are velocities, it is a relative displacement or relative velocity. So what you have is, in the diatomic molecular Hamiltonian you have only one coordinate namely the displacement from equilibrium then the overall displacement from equilibrium determining the Hamiltonian as $p^2/2\mu + \frac{1}{2}$ k′ $x^2$ where μ is

now the reduced mass it is not the mass of the Harmonic Oscillator like you had earlier but this reduced mass is given by the expression $m_1m_2/(m_1 + m_2)$. So the analogy to Harmonic Oscillator with this Hamiltonian being the molecular Hamiltonian that is what we derived now and the other being the Hamiltonian of a simple Harmonic Oscillator that is $p^2/2\mu + ½ k x^2$ the analogy is very clear that, whatever was the mass of the oscillator is now replaced by a case of the diatomic molecule by a reduced mass, here $\mu$ is called reduced mass.

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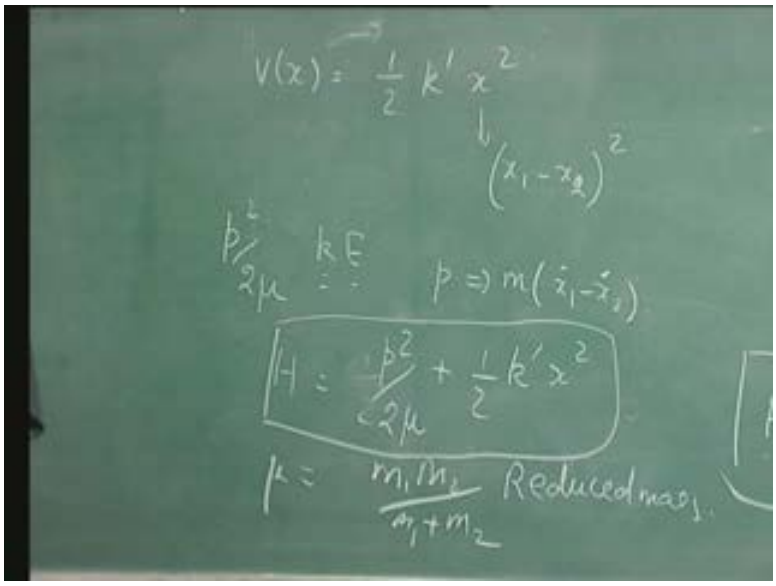


And the k′ is a force constant that is associated with the bond strength between the two atoms in the molecule how quickly they vibrate or how slowly they vibrate and what is the relative strength between the two atoms and so on. So, when you solve this problem there is information that you will obtain about the strength of the bond or the strength of the harmonic force constant of the oscillator.

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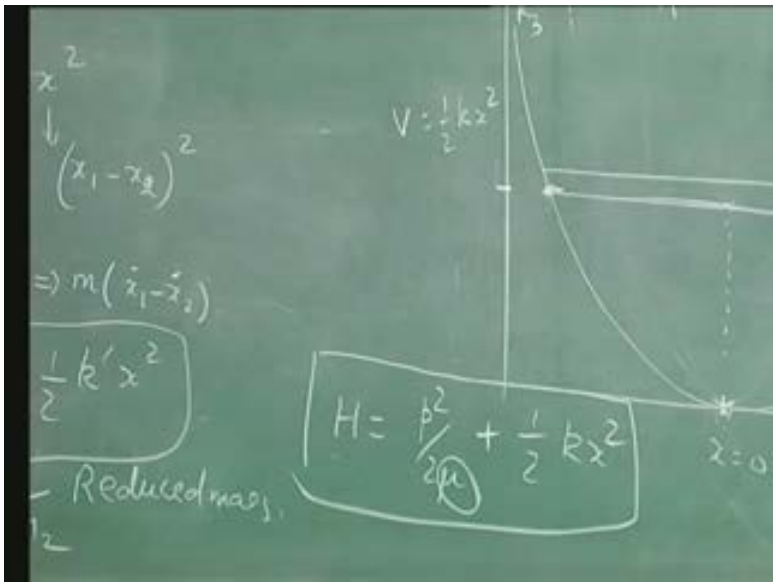


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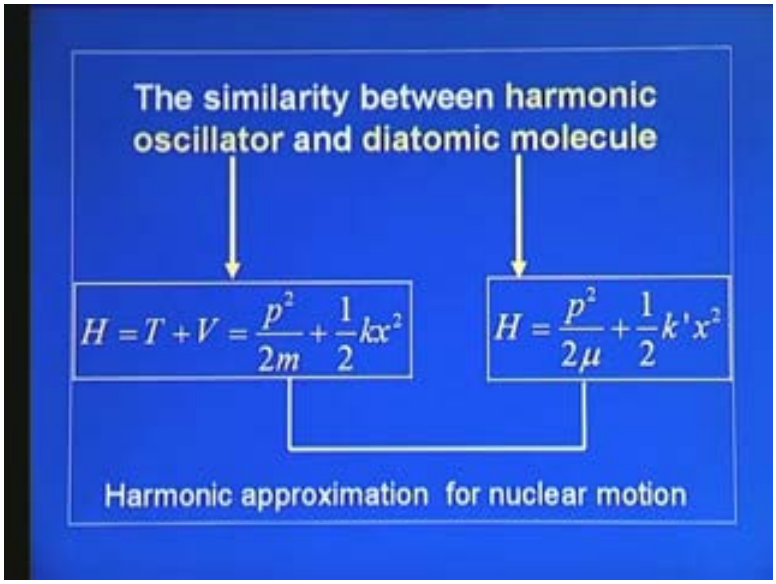


Thus if you compare the two problems, the Harmonic Oscillator problem with the kinetic energy $p^2/2\mu + ½ k x^2$ and that of the diatomic molecule with no translation energy in place then we neglect that and also no rotational energy so we do not consider the molecules to be rotating. Let us assume that the molecules only undergo vibrational motion you see there is already a relation between the two.

The Hamiltonians look exactly the same and therefore the solution of the Harmonic Oscillator problem throws light on the vibrational motion molecule and that is the reason why we are interested in it as a physics problem, no, Quantum Mechanics as a physics subject is not of

interest to us. Here, we are looking at how to apply these two chemical systems and therefore our solutions will be directly involved or will be only those which are of interest to extensions to molecule.

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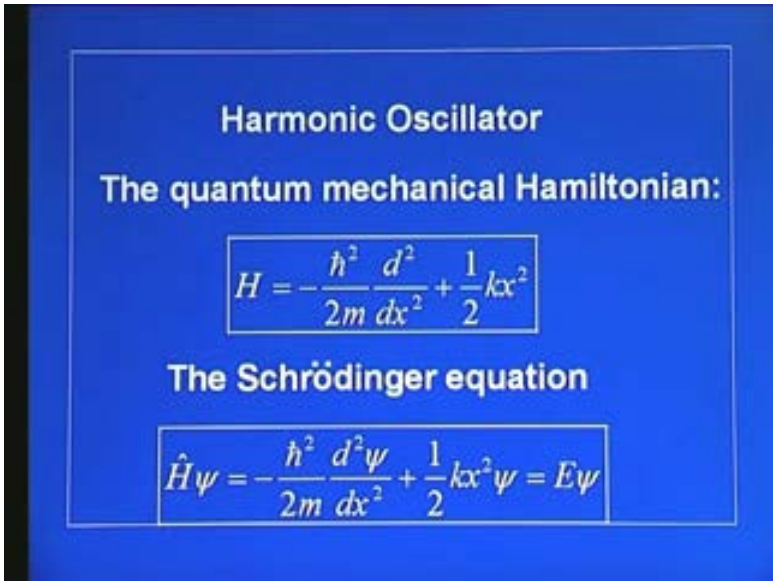


The Schrödinger equation now is having written the Hamiltonian, the Schrödinger equation $H\psi = E\psi$ can be written rather immediately with $[-\hbar^2/2m\ d^2/dx^2 + ½\ k\ x^2\ ]\ \psi(x) = E\ \psi(x)$, let us use 2m for the mass of the oscillator and we know that we have to replace m by μ in the case of a diatomic molecule times or acting on si of x = E si of x. Since we have not imposed any boundary on what energy or what the x value of the oscillator is, that is how far away it is from equilibrium. The theoretical limit does not make any sense but still we will write it, the theoretical limit for the x is from $-\infty$ to $+\infty$. We know very well that it is not going to be harmonic when x is very large away from equilibrium.

You try to swing a pendulum far away from it I do not think it ever comes back its equilibrium position, it loses may be it will even break if the energy is associated with is the pendulum is very large. But for a model let us assume that the x values or either extremes of the x values and when that is not true then we will say the Harmonic Oscillator is not a Harmonic Oscillator the oscillator is an Anharmonic Oscillator and so on. For a theoretical model let us fix the value of x from $-\infty$ to $+\infty$, and this as the boundary and x is all the way from the $-\infty$ to $+\infty$.

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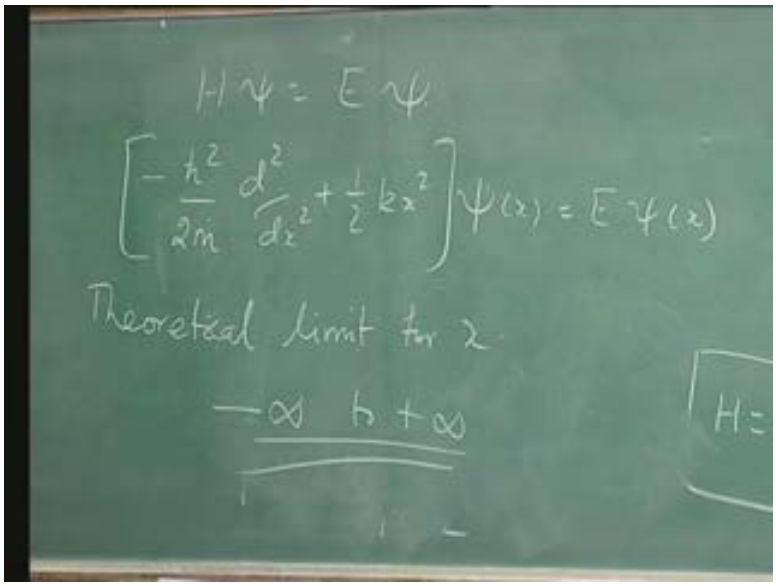


And with this boundary we want to solve this equation. I cannot give you the method of solution of this equation in half an hour it is not possible and the method is also complex. If you have not understood or studied solving such differential equations using what are called infinite series method or power series method. Such methods are usually thought on the second or third level of Mathematics courses and we are not going to worry about how to solve this equation but rather concentrate on what are the solutions and how do we understand the solutions.

If you do not know how to solve a differential equation and are given a solution for the differential equation what you will do? All you have to do is substitute that solution in the differential equation and see that it satisfies and try and at least convenience yourself that the solution makes sense even though we may not be able to write it down immediately.

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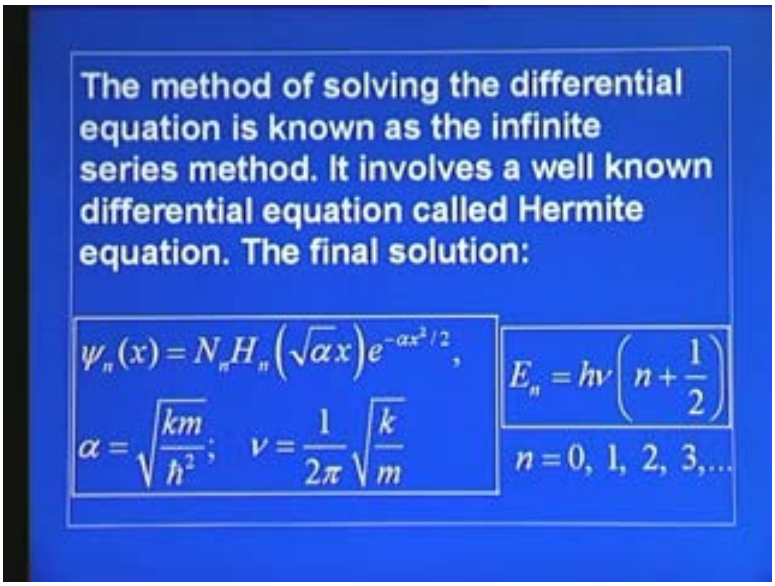


The solution is rather complex so let me write down parts of it one by one. Like the particle in a box, this equation also gives many solutions. That is many ψ's and many E's. How many in principle, infinity of the solutions? what is also interesting is that E does not turn out to be any possible value but E is given by a certain number called the quantum number just like the particle in a box where the n turned out to be a quantum number because we imposed the boundary conditions on the particle in the box, E is infinite number but not any possible value of E.

The value of E turns out to be $E_n = h\upsilon(n + ½)$ where, h is already in the differential equation, –ħ is h/2π so when you solve, the h come out, what is υ? Here υ is $^1/_{2\pi}\sqrt{k/m}$, k is the force constant associated with the potential and m is the mass of the particle of the oscillator associated with its kinetic energy term. What are the values of n? Here to our surprise n = 0, 1, 2, 3 etc only integral values but including 0. In the particle in a box n = 0 was not an acceptable solution because you know that left to a wave function which is 0 everywhere. And all these solutions have is a solution ψ = 0 as a trivial solution. But in the case of Harmonic Oscillator n = 0 does not give you a trivial solution it still gives you a finite solution. So the energy $E_n$ turns out to be $h\upsilon(n + ½)$ where n is a quantum number.

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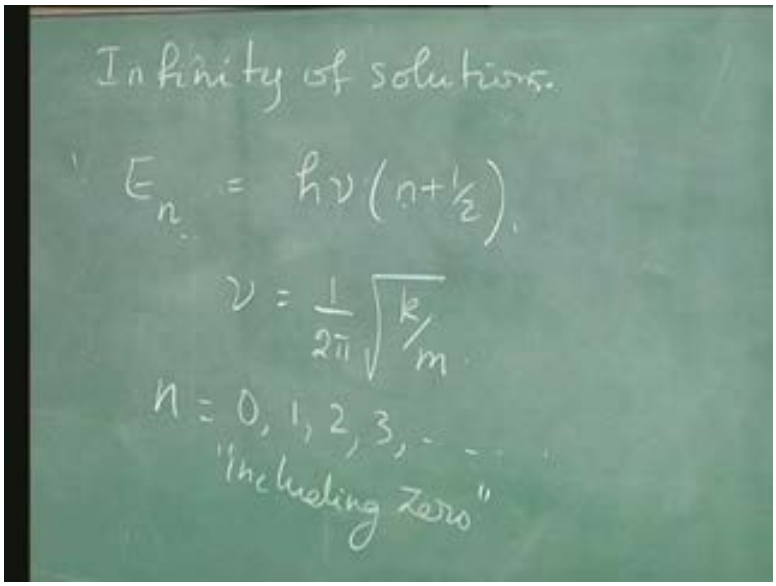


So, if you write the Harmonic Oscillator energies in Quantum Mechanics you have $E_0$ which is ½hυ, $E_1$ which is (1+½)hυ so 3½ hυ, $E_2$ which is (2 +½) hυ so it is a 5½hυ and so on. So it is always half integral number of the corresponding n value. $E_2$ is (2 +½)hυ. Likewise it is any number but there is nothing in between $E_0$ and $E_1$ so there is quantization.

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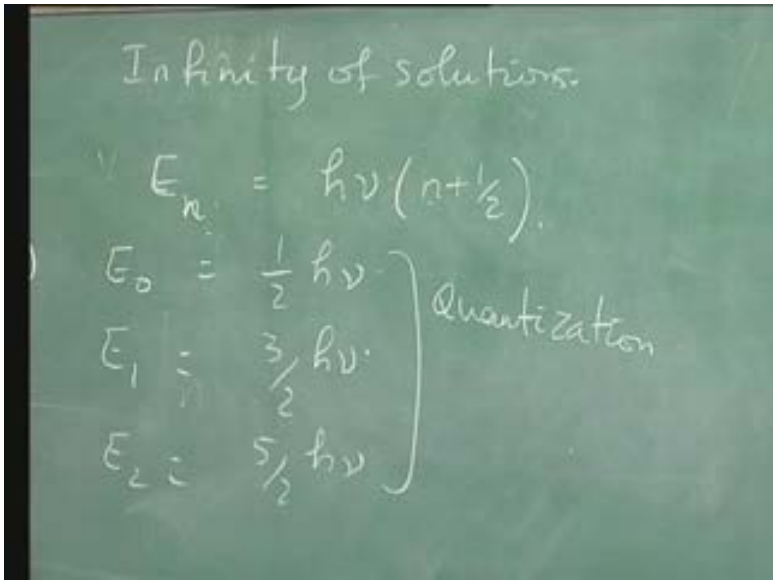


It also means another thing, if you recall the particle in a box $E_2 - E_1$ was $h^2/8mL^2(4-1)$ where n corresponding to 2 is 4 and n corresponding to 1 is 1 so it is $3h^2/8mL^2$ and $E_3 - E_2$, that is the difference between the successive energy levels is $5h^2/8mL^2$ where $E_3$ of $n^2$ is 9 and 2 is 4 so 9 – 4 = 5. And you see that these differences are not the same. Likewise when you go on calculating

the difference between successive energy levels in a particle in a box this energy gap keeps on changing. In the case of Harmonic Oscillator the successive energy levels differ by the same amount $E_1 - E_0$ is $h\upsilon$, $E_2 - E_1$ is again $h\upsilon$, $E_3 - E_2$ is again $h\upsilon$ that is Harmonic Oscillator energies are equidistant. The particle in a box energies are not equidistant.

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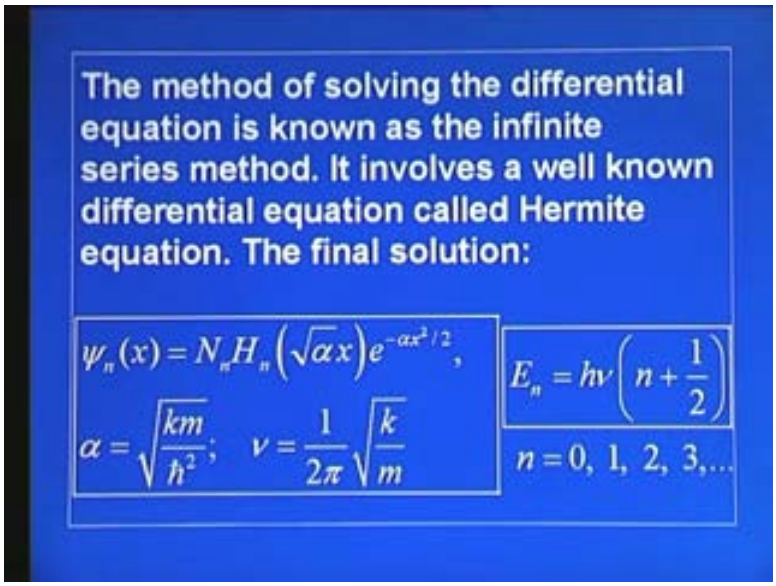


This is as for as the energy is concerned. What about the wave functions? Let us keep the solution $H_n\psi = E_n\psi_n$ at top corresponding to various values of E there are different values of Eigenfunctions. What is $\psi_0(x)$? The solution for $\psi_0(x)$ turns out to be $\exp(-\alpha x^2/2)$. What is the value of α? α is given in terms of the constants and we already know namely $\sqrt{km/\hbar^2}$. Just let us do a simple analysis, $\exp(-\alpha x^2/2)$ what should be the dimension of the whole thing? Exponential should not have any quantity which has dimensions overall. If x has the dimension of the length then $x^2$ has a dimension of $(\text{length})^2$ and α must have the dimension of $1/(\text{length})^2$ so that this whole quantity does not have any dimension. What is the dimension of k being a force constant? You recall that $kx^2$ represents energy and energy is $ML^2T^{-2}$. The force constant has the dimension $MT^{-2}$. And the mass here is $\sqrt{km/\hbar^2}$ so if you do k is that $MT^{-2}$and M for the mass and $\hbar^2$ is $(ML^2T^{-1})^2$. Then,$\sqrt{[MT^{-2}M/(ML^2T^{-2})^2]}$ so what do we get? So $(T^{-1})^2$ goes away and therefore what you have here is square $\sqrt{(1/L^4)}$ or you get $1/L^2$. So dimensionally $\exp(-\alpha x^2/2)$ this particular quantity is dimensionless because $x^2$ is $L^2$ and α is $1/L^2$. So the solution makes sense dimensionally as of now. We do not know how to do this.

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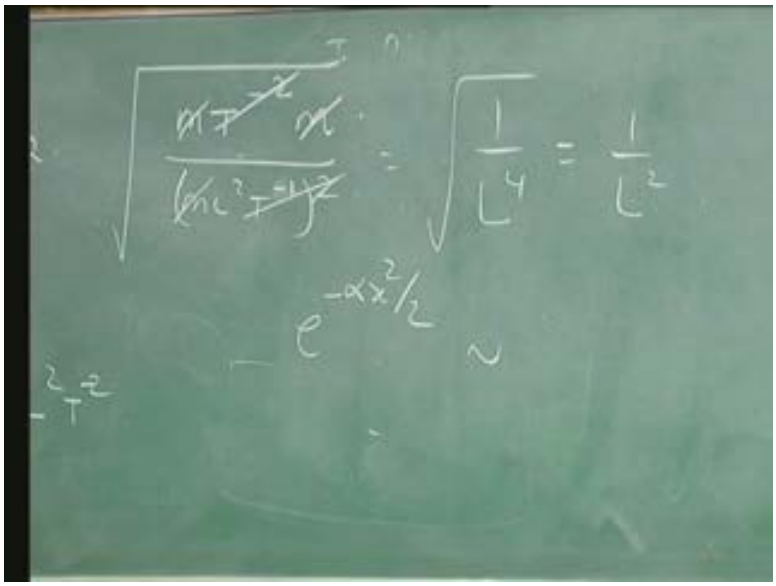

And at least I am not going to tell you how to get this solution. So the only thing that you can do immediately is to see whether this solution when you substitute in the differential equation $[-\hbar^2/2m\ d^2/dx^2 + ½\ k\ x^2]\ \psi(x) = E\ \psi(x)$, gives you, when you substitute the $\psi_0(x)$. Therefore if this is the above solution you want to substitute in this equation you must get the values $E_0\psi_0(x)$, where what is $E_0$? $E_0$, we just wrote the expression $(n + h\upsilon)$ with $n = 0$ so E0 is $½h\upsilon$. I will leave this as an exercise for you to verify this differential equation with the solution $\psi_0(x)$ being $-\alpha x^2$ with $\alpha$ being defined as $\sqrt{km}/\hbar^2$ when you substitute that you get everything right with $\upsilon$ also given as $½\pi\sqrt{k/m}$.

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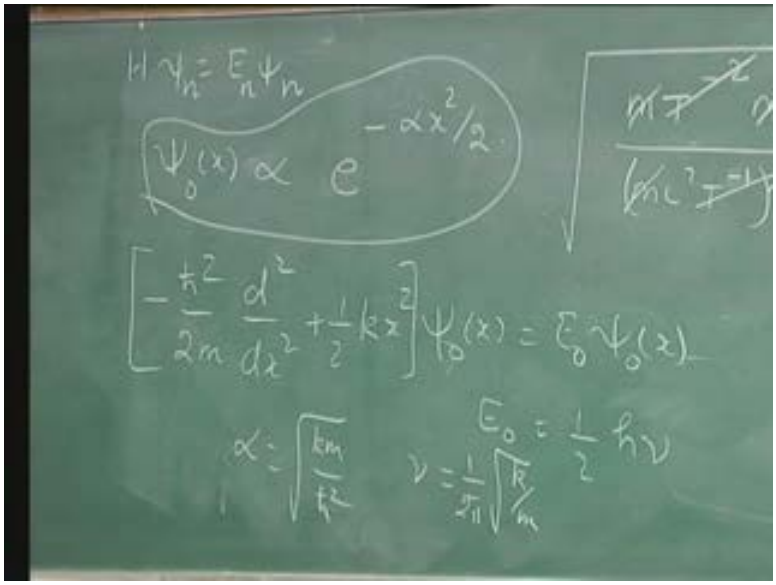

So this is for you to verify. This is only one solution. What are the other series of solutions for the Harmonic Oscillator?

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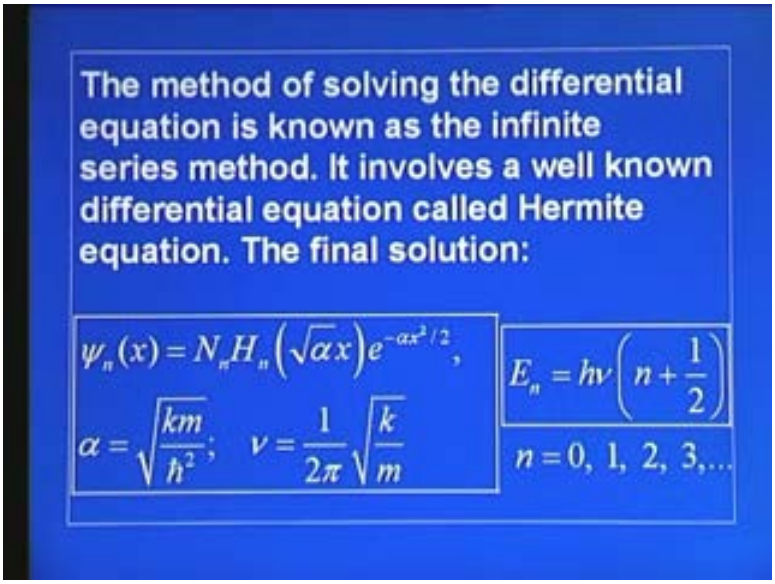


The next one is $\psi_1(x)$, by doing one and two solutions and then we can generalize as to what the solutions should be. The $\psi_1(x)$ turns out to be proportional to $2x \exp(-\alpha x^2/2)$. The $\psi_0$, earlier was $\psi_0(x)$ proportional to $\exp(-\alpha x^2/2)$. In fact the whole infinity of solutions $\psi_n(x)$, all of them have some function of x or f(x) or a polynomial of x to some order multiplied by $\exp(-\alpha x^2/2)$. That turns out to be the Harmonic Oscillator solution. Here we are always using a proportionality sign but not using the exact form, implies that there is a constant which you need to put in here. All these solutions have the $\exp(-\alpha x^2/2)$. Now, what is the value of this as x goes to very large values? The $\exp(-\alpha x^2/2)$ goes to 0 very quickly as x increases either as a positive x or as a negative x because it is $x^2/2$.

Therefore this function goes to 0 very quickly for large values of x. No matter what the value of this function is this always goes to 0. And this exponential goes to 0 much more quickly than any function for sufficiently large values of x. Therefore this function actually dies down extremely quickly for large values of x. So the solution makes sense that the likelihood of finding the particle at very large values of x is actually very small because when you take the square of this function in a small region that is what is called the probability of finding the oscillator in that region and if this function is small, the square of this function is small therefore this function goes to 0 very quickly. The probability of finding the oscillator at very large values of x away from its equilibrium that possibility or that probability goes to 0 very quickly. It is not 0 but it is very small. So, the solution makes sense in terms of the boundary condition.

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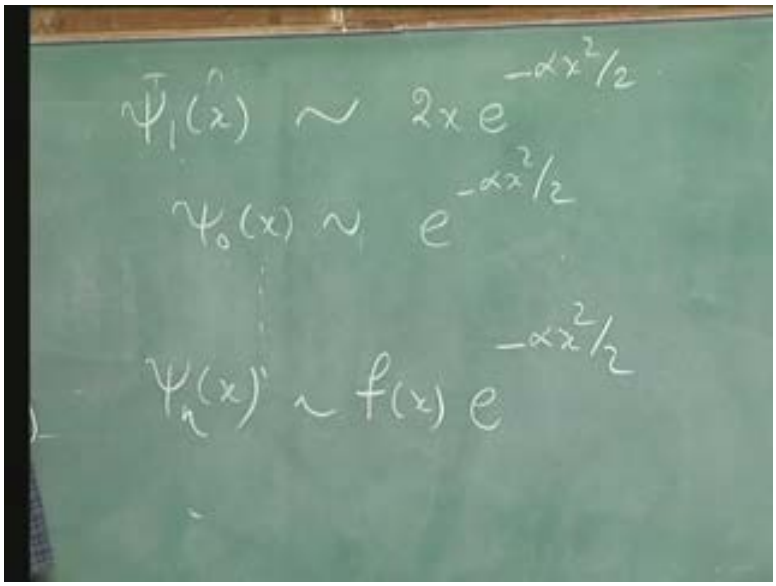


The second part here, what is the polynomial? How does it change for different values of n? Let me write down the general solution as you have here:

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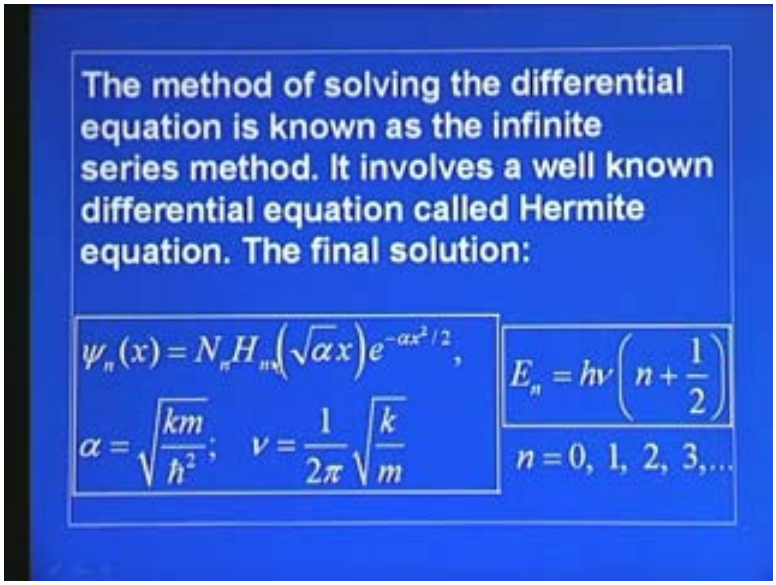


The value for any n we talked about n = 0, n = 1. The value of any n the function as a particular form namely as the constant N but that constant depends on the quantum number that we choose multiplied by a polynomial function $H_n$ with the functional argument being ($\sqrt{\alpha}$ x) and the $\exp(-\alpha x^2/2)$, $\alpha$ have already written down as $\sqrt{km/h^2}$ and $\upsilon$ is given as $\frac{1}{2}\pi\sqrt{k/m}$.

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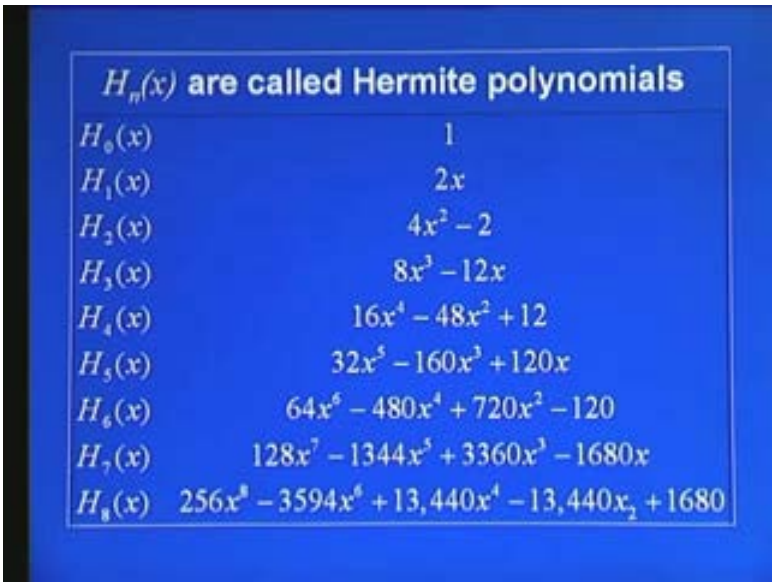


What are these polynomials? You see that for n = 0, the polynomial is $H_0(\sqrt{\alpha}\, x)$ as in the above slide here $H_0(x)$ is a constant 1 and it does not depend on $\sqrt{\alpha}$ or x but simply 1. What you have in that slide is $H_1(x)$ as 2x. Therefore the Harmonic Oscillator solution $H_1(\sqrt{\alpha}\, x)$ is $2\sqrt{\alpha}\, x$.

What you have here are $H_n(x)$ and these are called Hermite polynomials. The Hermite polynomials turn out to be part of the solutions of the Harmonic Oscillator. The solutions of Hermite polynomials are obtained by solving what is called the Hermite differential equation where the Harmonic Oscillator Schrödinger equation will be reduced to when you do the Mathematics right.

We are giving the final solutions the Hermite polynomials are in principle it is an infinite number of polynomials and they are increasing powers of x as you have them here. For example, Hermite polynomial of order 0 is a polynomial of degree 0, Hermite polynomial of order 1 is a polynomial in x of degree 1, it is just a function of simply x, order 2 is a quadratic function, order 3 is a cubic polynomial and so on. So there is a direct relation whatever is the order that is the highest power of this polynomial and there is way of generating this polynomial through what is called recurrence relations between these Hermite polynomials $H_n$, $H_{n-1}$, $H_{n+1}$. Therefore one can generate the above table for n = 20 in no time.

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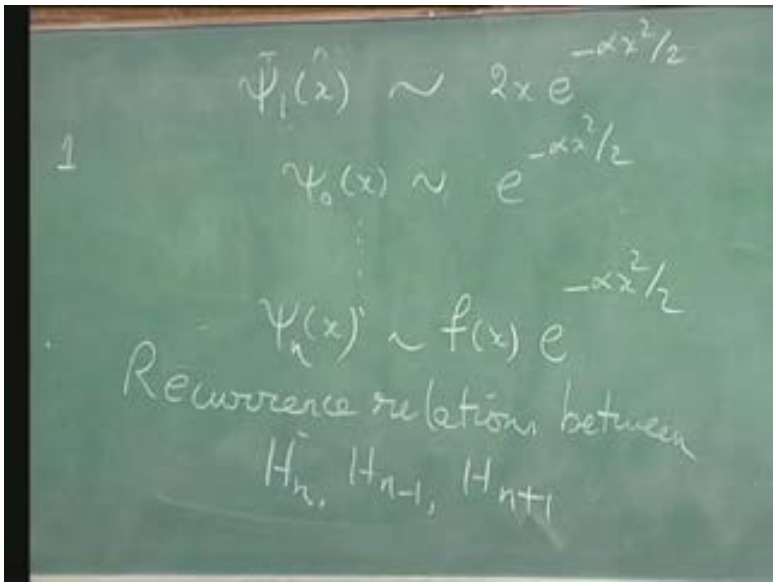


Again that is not of interest, what is of interest is the nature of this polynomial. If you see the first polynomial $H_1(x)$ is 2x which is a function of x but when x becomes – x, the function becomes negative. The next one is $H_2(x)$ as 2x is $(4x^2 – 2)$ which for both positive and negative values of x as the same value $(4x^2 – 2)$ so whether x is +x or –x the function is the same. Likewise $H_3$ is $(8x^3 –12x)$, again this function becomes the negative of the function for negative values of x.

So you see that the series alternate between the functions which do not change signs and functions which change sign as change in x from – to + x and such alternating sets are called odd and even sets. The function $H_0$ is known as the even function of x and function $H_2$ is known as even function of x, $H_4$ is known as an even function of x whereas all the odd functions $H_1$, $H_3$ etc are all called odd functions. So the relation here is if this $H_n(x)$ is $(–1)^nH_n(−x)$ meaning that when n is odd the function becomes the negative when x becomes −x so all these numbers can be easily generated. You must remember the highest power of the polynomial by the order as well as the fact that the order is odd or even depending on whether the quantum number is odd or even.

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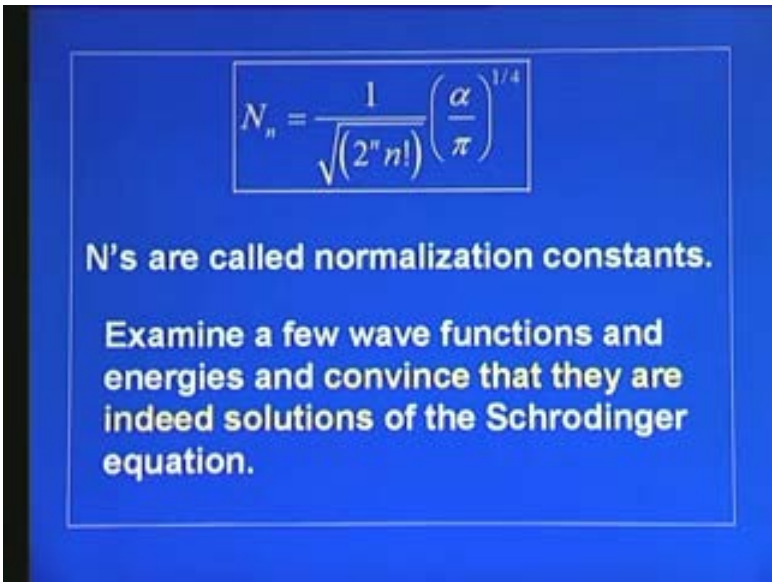


The constants n which where associated with the wave functions are called the normalization constants and they are obtained in the same way that we did the normalization constants for the particle in the box. What we did was $\int \psi_n(x)\psi_n(x)dx$, For the particle in a box the systems space was 0 to L and for the Harmonic Oscillator the system space is x is $+\infty$ to $-\infty$ then the equation becomes $\int \psi_n(x)\psi_n(x)dx = 1$. And when you obtain this condition that the probability of finding the Harmonic Oscillator anywhere along the regions that it can access, if you had all those probabilities that should be 1 is what is expressed by the normalization condition. And it is as an exercise you can obtain $N_n$ when you write $N_n$ as the expression of $1/(\sqrt{2^n}n!)(\alpha/\pi)^{¼}$ and you can do this for n = 0 and n =1 as a simple example. When $N_0$ for the wave function $\psi(0)$ is of course 2 raised to 0 and 0! So these are all equal to 1 so what you have is $(\alpha/\pi)^{¼}$.

$N_1$ can be written easily when n =1, $1/\sqrt{2^n}$ is $1/\sqrt{2}$ and n is 1 so what you have is $N_1$ is $1/\sqrt{2}$ $(\alpha/\pi)^{¼}$ and so on. By substituting the corresponding values of n you can generate all the normalization constants and therefore the solution $\psi_n$.

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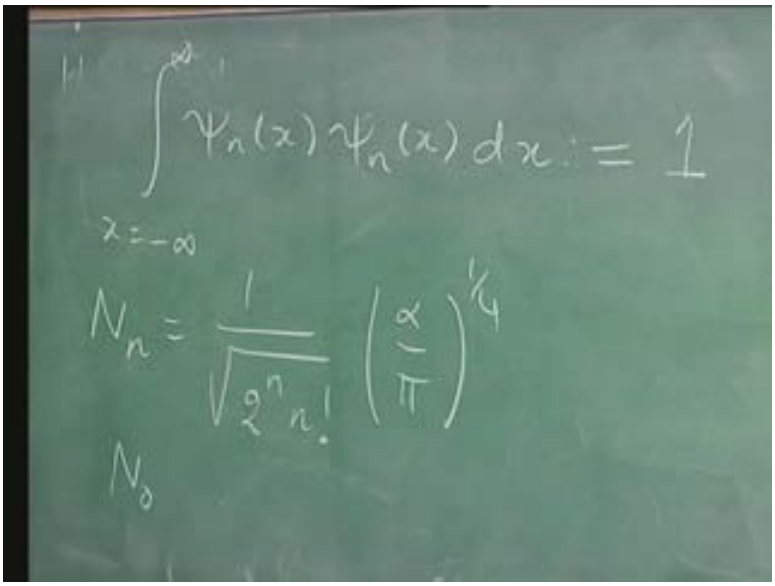


The solution for $\hat{H}\psi_n(x)=E_n\psi_n(x)$ for the Harmonic Oscillator is $\psi_n = N_n H_n (\sqrt{\alpha}\, x) \exp(-\alpha x^2/2)$ as the wave function $\psi_n$ being the normalization constant $N_n$ and the Hermite polynomial $H_{n,} (\sqrt{\alpha}\, x) \exp(-\alpha x^2/2)$ as the eigenfunctions and the eigenvalues $E_n$ as $h\upsilon(n + ½)$ where n is 0, 1, 2, 3, etc. Therefore the energies are quantized and are equidistant.

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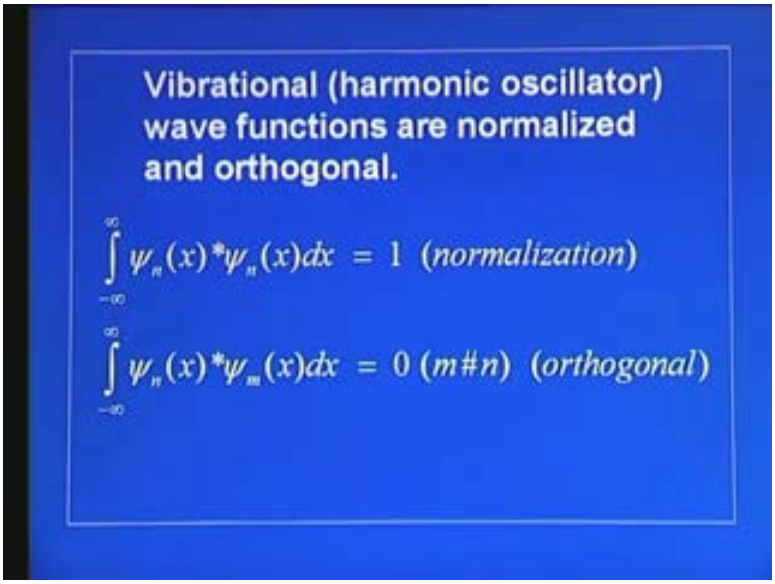

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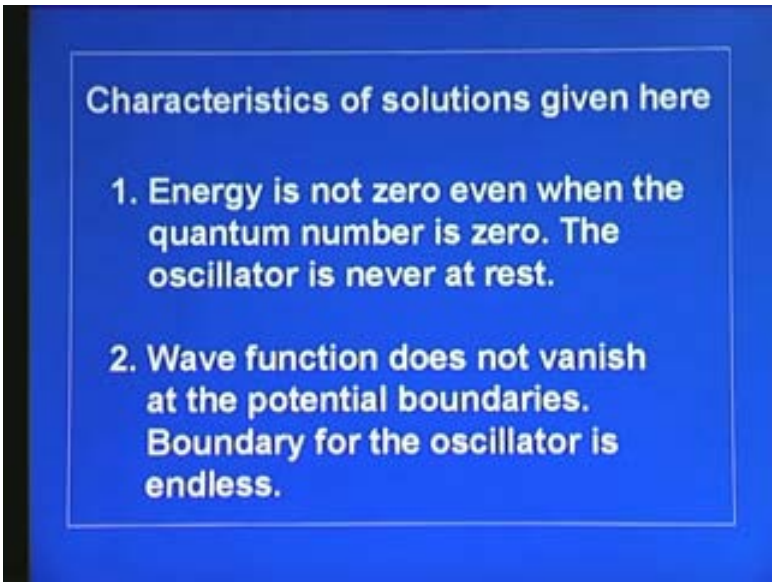


The most important point is that the solution that we have obtained for the energies and the wave functions. The solutions exist even when the quantum number is 0 that is even when we associate with the Harmonic Oscillator is in no motion or of no energy due to motion. There is an energy which is not 0 even when the quantum number is 0 that means the oscillator is never at rest, it keeps oscillating.

The position and momentum of the oscillator no matter what its energy is cannot be determined simultaneously. If the oscillator is at rest, we know its exact position and we know that the momentum p associated with the oscillator is also 0. Therefore we seem to have knowledge which is forbidden in Quantum Mechanics according to Heisenberg's uncertainty principle. So the fact that the Harmonic Oscillator energies are non zero even when the oscillator has a quantum number equal to zero means the oscillator is never at rest and we are quiet happy now that it is consistent with the Heisenberg's uncertainty principle.

The second important thing is you recall that the potential energy was a parabolic function limiting what is called the maximum possible value of energy for any particular motion. The wave function on the other hand for the Harmonic Oscillator does not vanish anywhere in between except at finite points. The boundary for the oscillator is essentially infinity because $\exp(-\alpha x^2)$ is never 0 except x is $+\infty$ to $-\infty$. So this function may have some roots but the product apart from those roots, the product or the wave function is never zero throughout the boundary that is even outside the potential boundary. It appears that the wave function can be or the particle can be obtained the position can be located even outside the region of what is called the classical potential boundary.

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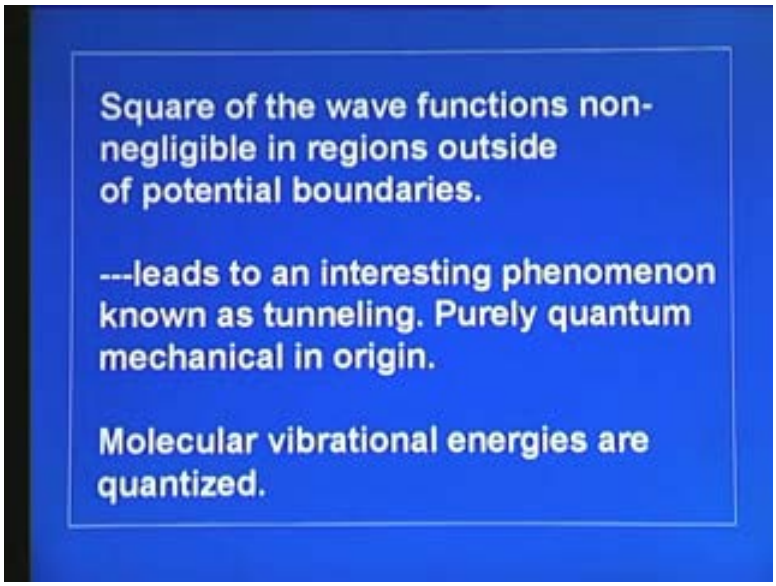


That means the squares of the wave function are non negligible in regions outside the potential boundaries. It leads to an interesting phenomenon called the tunneling. Again we will not do tunneling here. Tunneling itself is a phenomenon that one has to study carefully. We will later on come to know what tunneling is. Obviously when you associate this with molecular vibrations the vibrational energies of the molecules are quantized in the harmonic limit.