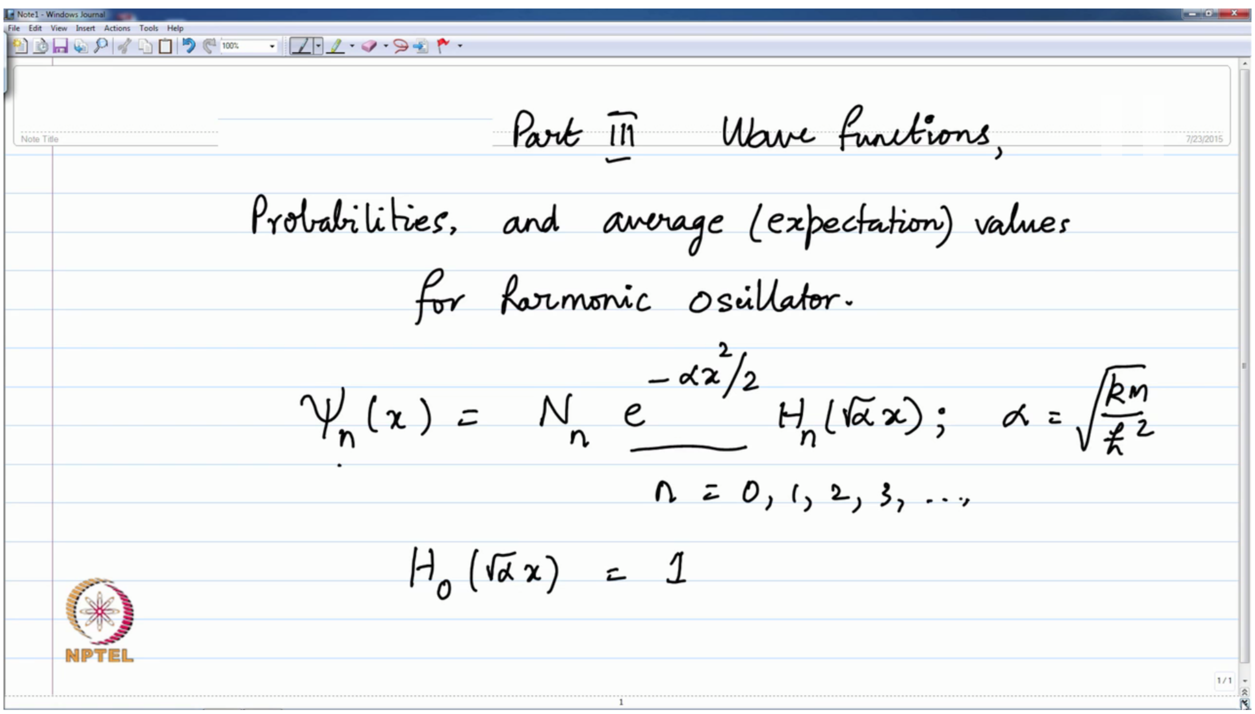
Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 22
Harmonic Oscillator Model – Part III Wave functions, Probabilities and Average (expectation) Values

Prof. Mangala Sunder Krishnan,
Department of Chemistry,
Indian Institute of Technology Madras

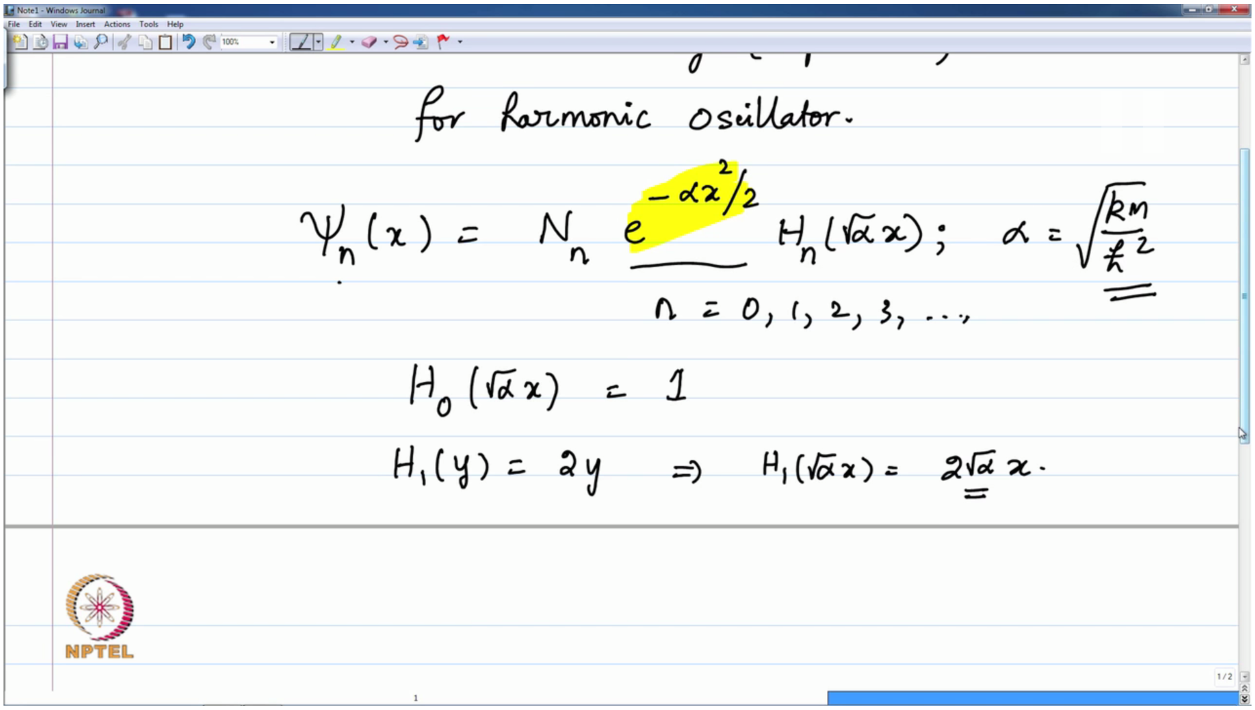
Prof. Mangal Sunder Krishnan: Welcome back to the lectures in chemistry, and this is the continuation of the quantum mechanics and the elementary atomic structure course and this particular lecture continues from where we left off in the harmonic oscillator.



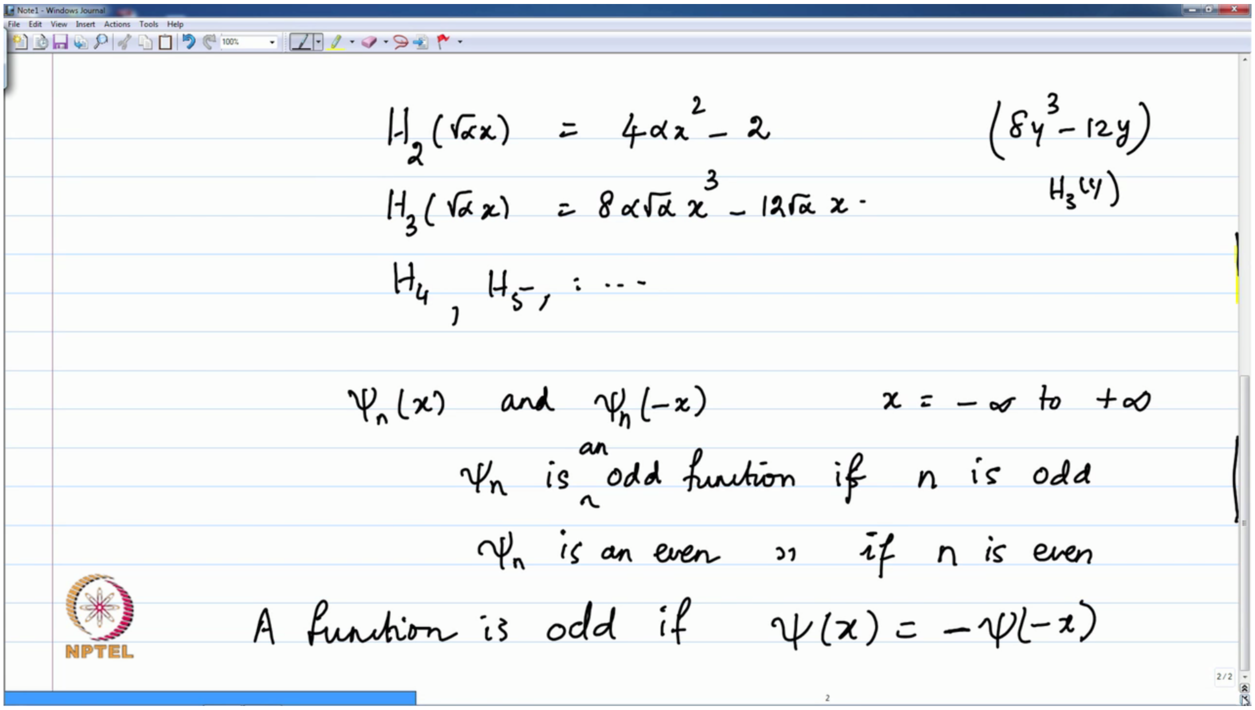
In the last lecture that we recall what we did. I mentioned that the wave functions and the harmonic oscillator Hamiltonian. However, I did not solve the Schrodinger equation but gave you the final solution, which you might recall here in the last line, namely the wave functions $\psi_n(x)$ where n is the quantum number and takes values from 0 all the way up to ∞ assuming that the harmonic oscillator motion continues to be like a harmonic oscillator for very large amplitudes as well.

The wave functions $\psi_n(x)$, it consists of two parts an exponential $e^{-\alpha x2/2}$ where α is the parameter set for the harmonic oscillator, α is defined here as the force constant times the mass of the harmonic oscillator divided by the square of the Planck's constant and this whole thing is a square √, and α has the dimensions of 1 over the length squared, therefore if x represents the displacement, then αx^2 is dimensionless. And then the other part of the harmonic oscillator wave function is the solution to the Hermite's differential equation, which is given in terms of the Hermite polynomials H_n, again, of $\sqrt{\alpha}x$ so that the polynomial has quantities, which are dimensionless, and the quantum number n is of course 0, 1, ,2 3, et cetera.

So this wave function was not derived for you, but the solutions were given to you as solutions derived from the differential equation as well as the requirement that the harmonic oscillator wave function for very large values of the displacement of the oscillator from equilibrium, the wave function goes to 0, so that asymptotically the wave function dies off and that's important in terms of making certain that the wave function is a normalizable wave function. And now if you go back and look at these formulae what you have here is the Hermite polynomials and you might recall that the Hermite polynomial for the first quantum number $H_0(\sqrt{\alpha}x) = 1$, it's independent of the displacement.

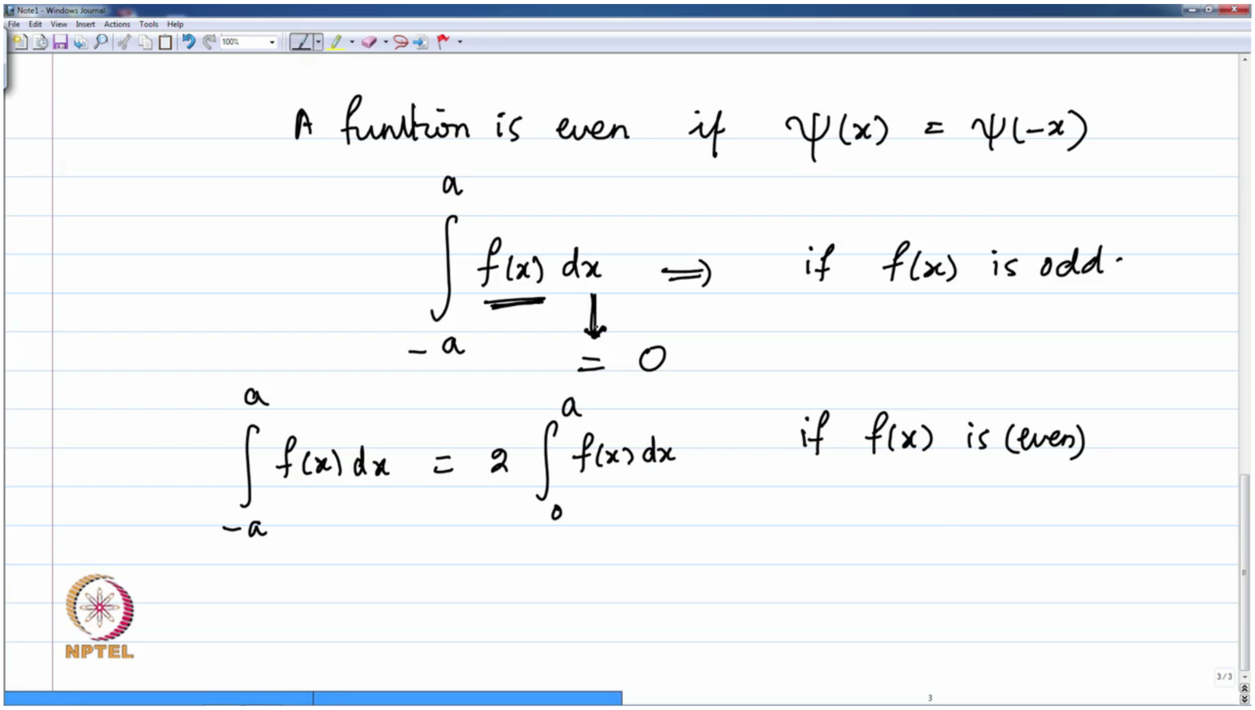


H_1, if you recall, I used to write y and I said it was 2y, therefore, $H_1(\sqrt{\alpha}x) = 2\sqrt{\alpha}\, x$, and α is specific to the harmonic oscillator that we have interest in. Therefore, if the oscillator is a very rigid oscillator, that is it has the force constant which is very high or if the oscillator is very heavy, like its mass is very large, then you see α is also very large, and that's very important because if you see if alpha is very large that has something to do with the exponential $e^{-\alpha x^2}$ that I have here. Let me just -- yeah. It has a bearing on this term because the exponential will become very narrow, and therefore, the properties of the harmonic oscillator are reflected in the wave function, which builds them through the exponential as well as through the Hermite polynomial.



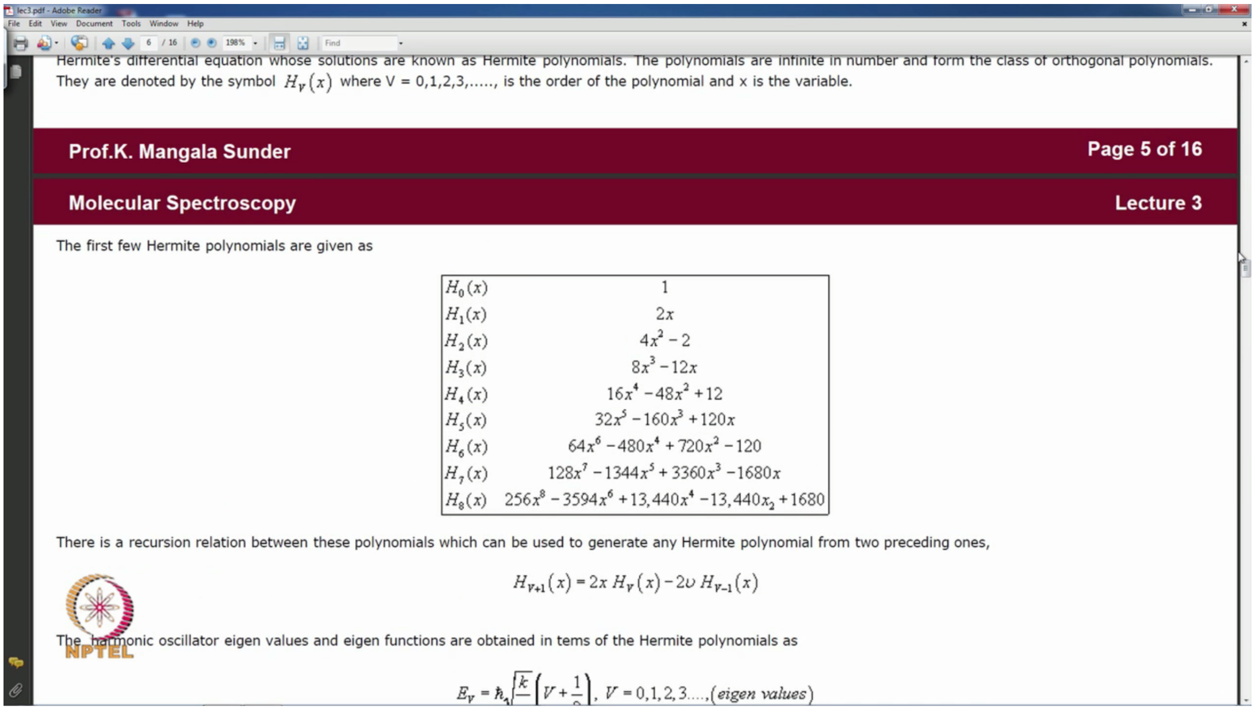
What is the second Hermite polynomial? $H_2(\sqrt{\alpha}x)$, you remember that was $4y^2$-2, therefore, it becomes $4\alpha x^2$-2, and likewise for the third, $H_3(\sqrt{\alpha}x)$, if you recall, it is $(8y^3$-12y) H_3y, and therefore, that becomes -- when you put y = $\sqrt{\alpha}x$, it becomes $8\alpha\sqrt{\alpha}x^3$-12$\sqrt{\alpha}$ x, and likewise for H_4, H_5 and so on, okay. And if you recall, there was a table of the harmonic oscillator functions, which was given to you and you might recall that the wave functions have a specific parity, that is if you look at the wave function ψ_n(x) and ψ_n(-x), if you consider the wave function ψ_n(x) and ψ_n(-x) since you know that x can take values from -∞ to ∞ that is on either side of the oscillator's equilibrium position, then ψ_n(x) and ψ_n(-x) have this property, namely ψ_n is an odd function if n is odd. If ψ_n(x) is an even function if n is even, okay.

This is quite obviously dependent on the properties of the Hermite polynomial that you see here, because you see the exponential of $-\alpha x^2$ is always even, whether it is x or -x since you have the square of x here, this function is independent of the sign of x. However, this function obviously depends on the sign of x as you can see it in some of the examples here, namely H_0(x) is independent of x, therefore, it's independent of the sign of x. H_1(x) is x, therefore, $H_1(\sqrt{\alpha}x)$ is an odd function if x is negative, because the function is also negative. What is the relation between odd and even functions? You might kindly recall, that a function is odd if or if it has this property, namely ψ(x) is a negative of ψ(-x), therefore, if the argument is negative, then the function changes sign, okay.



This is odd. A function is even obviously when this does not happen even if $\psi(x) = \psi(-x)$, and with this definition in mind, you will immediately see that the odd numbered Hermite polynomials, namely H_1, H_3 and if you recall H_5, it contained x^5, x^3 and an x, nothing else. Therefore, the odd numbered, odd indexed Hermite polynomials or all odd functions and likewise, the even quantum number indexed Hermite polynomials like H_0, H_2, H_4, H_6 et cetera are all even. Therefore, this property is very important in terms of determining the average values and the momentum et cetera since integrals have some very specific properties with respect to odd and even function

Remember if you are integrating a function between symmetric limits ∫ -a to a and f(x) dx, you can say something about it if f(x) is odd. The answer is this integral will be 0. If f(x) is even, you can't say immediately what the answer is, but you can write the following, namely the ∫ -a to a f(x) dx for an even function is 2 ∫ 0 to a f(x) dx. So these are properties, which are extremely important and you can see that if the integral is our integrand is or between symmetric limit, that integral is 0. These are mathematical requirements, which are very useful later on when you study more mathematics and more quantum mechanics and other problems in physical chemistry, okay.



Hermite's differential equation whose solutions are known as Hermite polynomials. The polynomials are infinite in number and form the class of orthogonal polynomials. They are denoted by the symbol $H_V(x)$ where V = 0,1,2,3,....., is the order of the polynomial and x is the variable.

The first few Hermite polynomials are given as

$H_0(x)$	1
$H_1(x)$	$2x$
$H_2(x)$	$4x^2-2$
$H_3(x)$	$8x^3-12x$
$H_4(x)$	$16x^4-48x^2+12$
$H_5(x)$	$32x^5-160x^3+120x$
$H_6(x)$	$64x^6-480x^4+720x^2-120$
$H_7(x)$	$128x^7-1344x^5+3360x^3-1680x$
$H_8(x)$	$256x^8-3594x^6+13,440x^4-13,440x_2+1680$

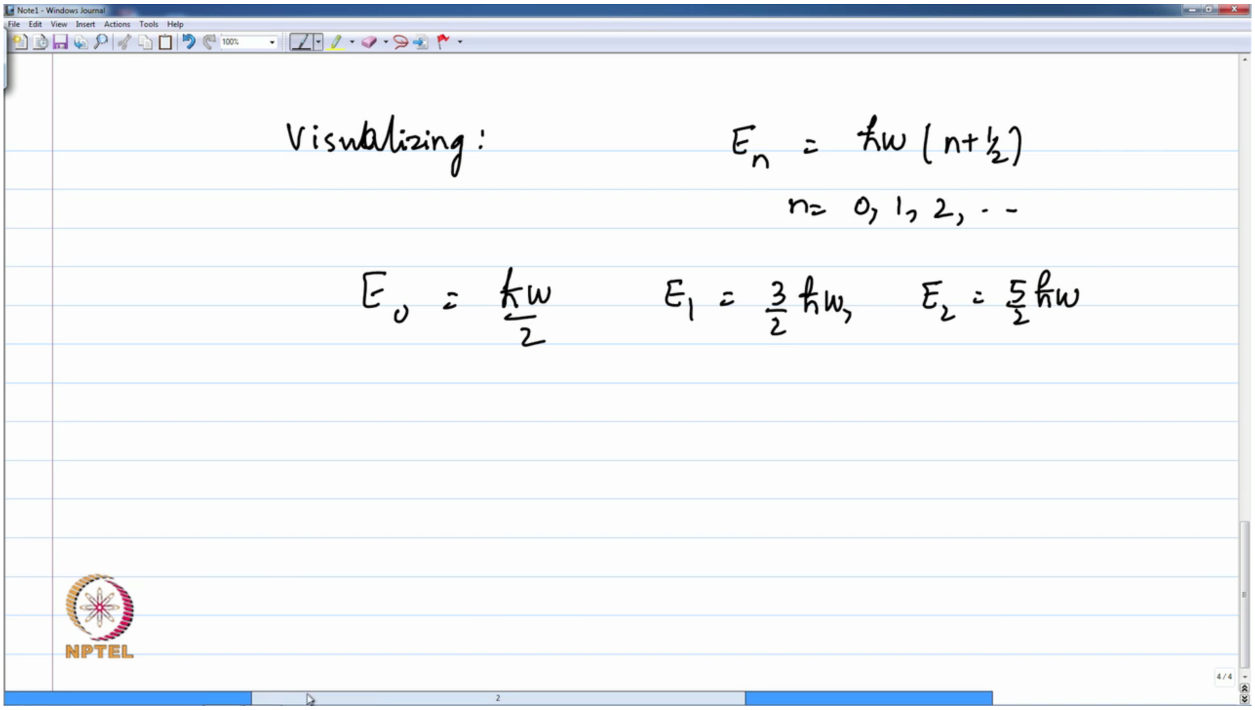
There is a recursion relation between these polynomials which can be used to generate any Hermite polynomial from two preceding ones,

$$H_{V+1}(x) = 2x\,H_V(x) - 2\upsilon\,H_{V-1}(x)$$

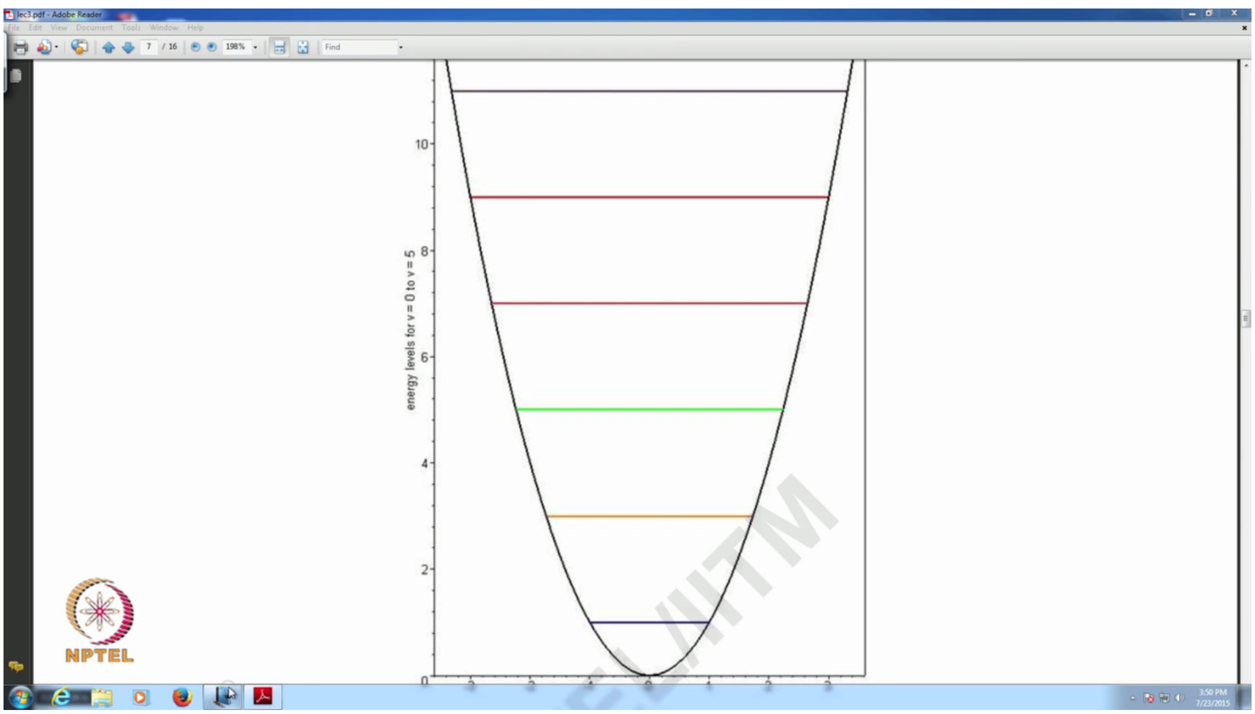
The harmonic oscillator eigen values and eigen functions are obtained in tems of the Hermite polynomials as

$$E_V = \hbar\sqrt{\frac{k}{\mu}}\left(V+\frac{1}{2}\right),\ V = 0,1,2,3....,(eigen\ values)$$

Now what do we have with respect to these functions? Let's get to the possibility of visualizing these functions and visualizing the -- visualizing this and visualizing the squares, okay. I have some pictures here. Yeah this table is extremely important. You might recall that this was probably shown in the last lecture. You can see that H_0, H_2, H_4, H_6, H_8 all have even powers of x and H1, H_3, H_5, H_7 all have odd powers of x, and therefore, the odd Hermite polynomials are odd functions and the even Hermite polynomials are even functions of x.

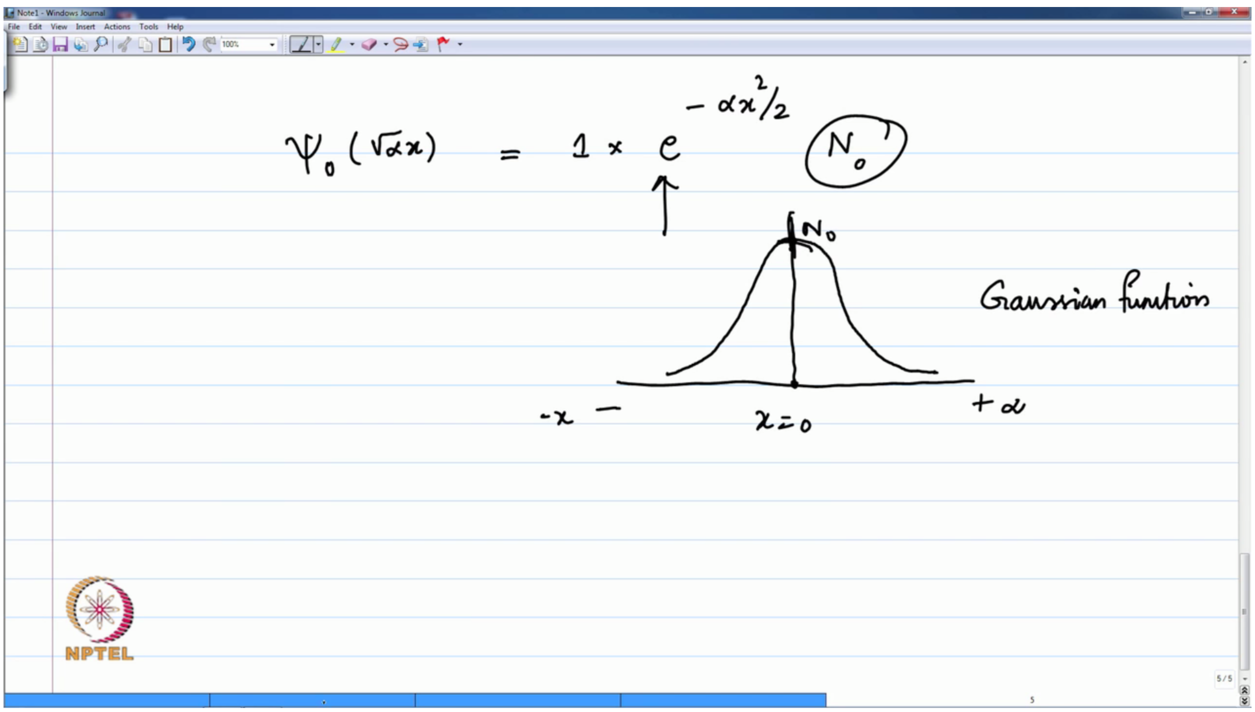


Now how does the wave function look? Okay, you recall the energy levels, the energy levels if you remember have this expression, namely $E_n = \hbar\omega (n+½)$ where n = 0, 1, 2, 3 et cetera. Therefore, you can see that $E_0 = \hbar\omega/2$, E1 = 3/2 ħω, and E2 = 5/2 ħω and so on. So what does that tell you?

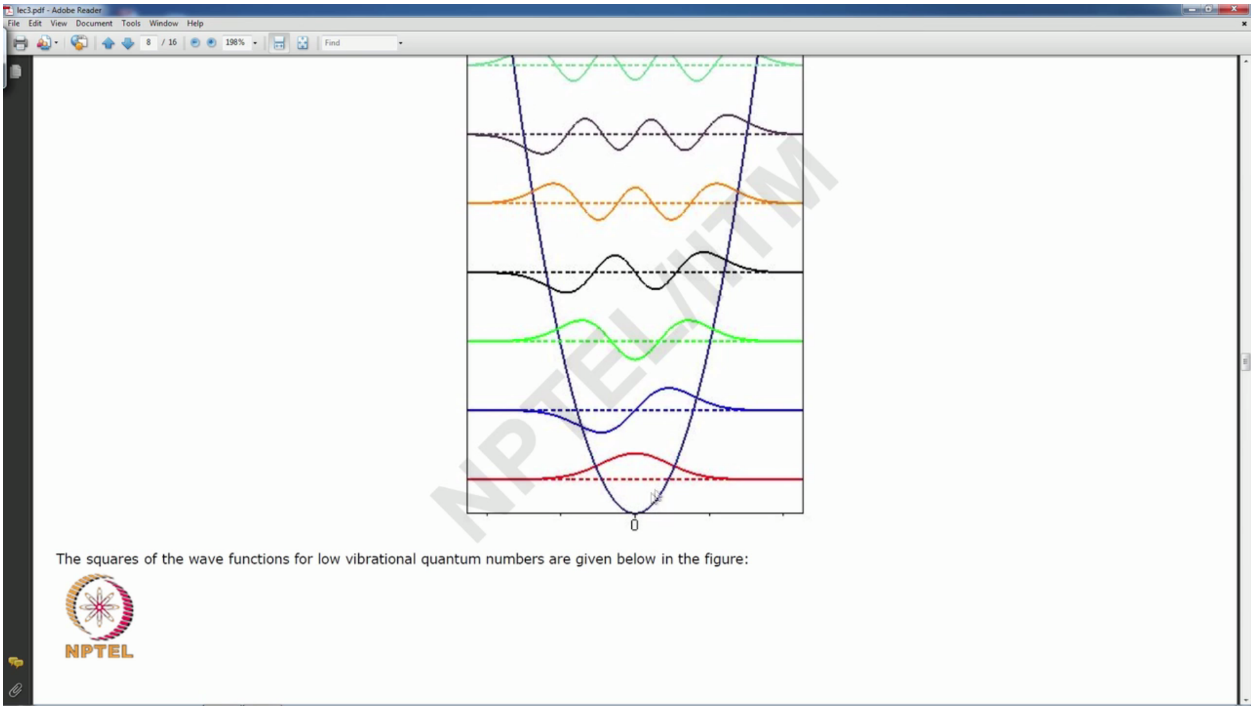


That gives you the picture that the energy levels are equidistant and the gap between any two successive energy levels is exactly ħω. So this is the ½ ħω, this is the 3/2 ħω, this is all in ½ ħω kind of units. So don't worry about these numbers, 2, 4, 6 et cetera. So the base level is ħω/2, 3/2, 5/2, 7/2, 9/2, and so harmonic oscillator is equidistant and it has an interesting consequence in the spectrum of a harmonic oscillator. In fact, the spectrum of a pure harmonic oscillator contains exactly one line, namely the transition between any pair of nearby energy levels and nothing more than that.

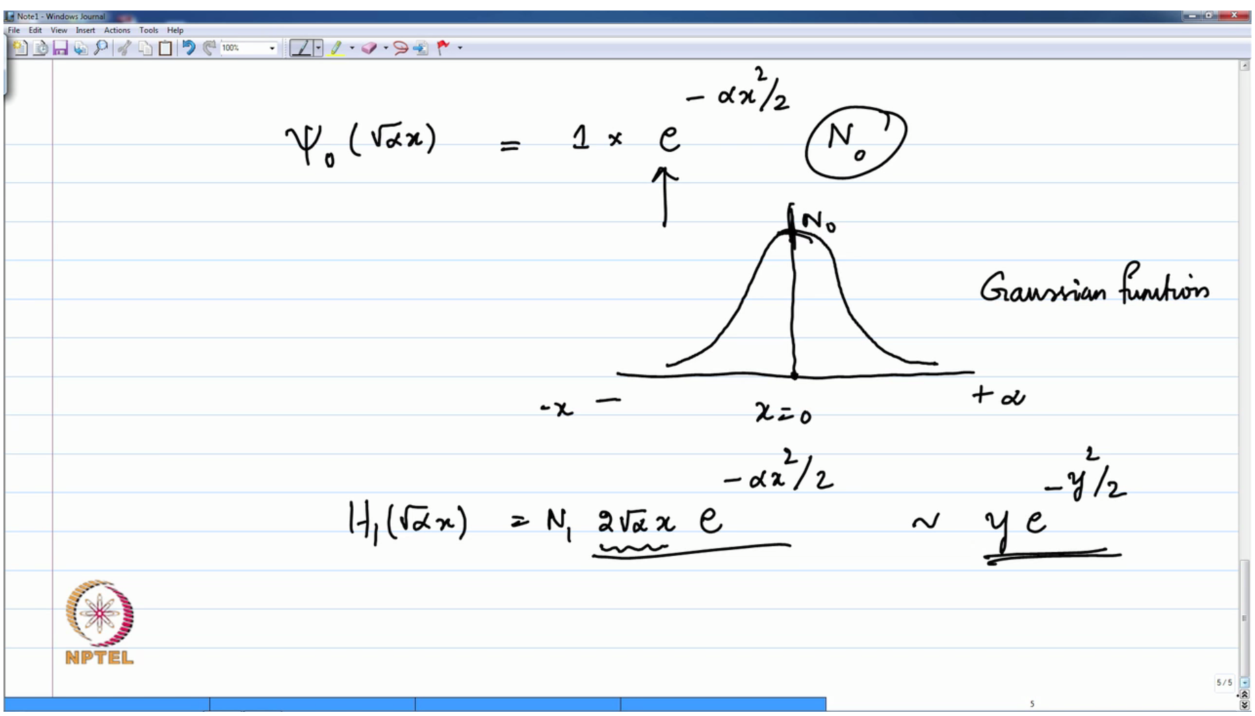
In order to excite energy transitions between say the level 0 to the level 1 or level 2 or level three, you need to have the harmonic oscillator behave as an anharmonic oscillator. These things will become clearer when we talk about the spectroscopy part of it. But now, having looked at the energy a little bit, let us see what the wave functions are, okay.



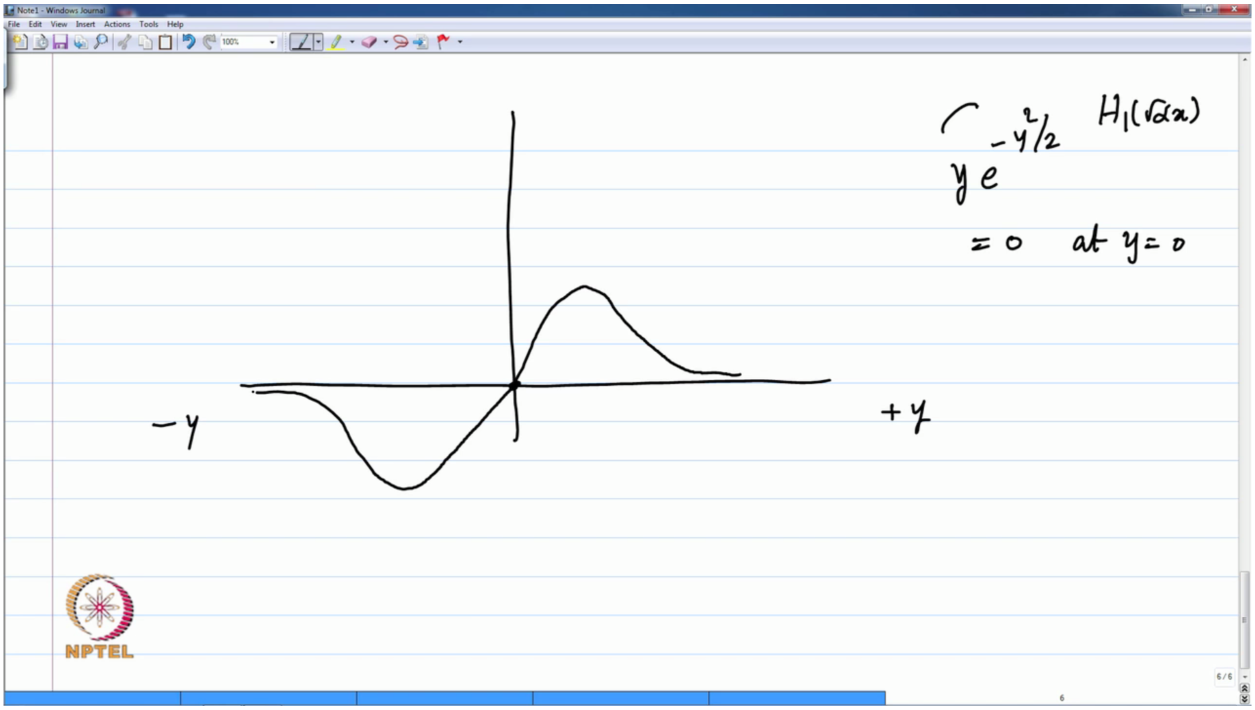
$\Psi_0(\sqrt{\alpha}x) = 1$ x $e^{-\alpha x2/2}$ x N_0 (normalization constant). Let's not worry about that, we will only concern ourselves with this, and this when you plot it as a function of -x, and this is -x and this is x. if you do that, this is an even function and this is the familiar bell shaped curve, which is the Gaussian function, centered at 0, at x=0 and this height is obviously N_0, okay. That's the value, because the exponential goes to 1, then x is 0, but for larger values of x, the exponential function decreases, the Gaussian function decreases in value, and therefore, the system bell shaped curve you have here.



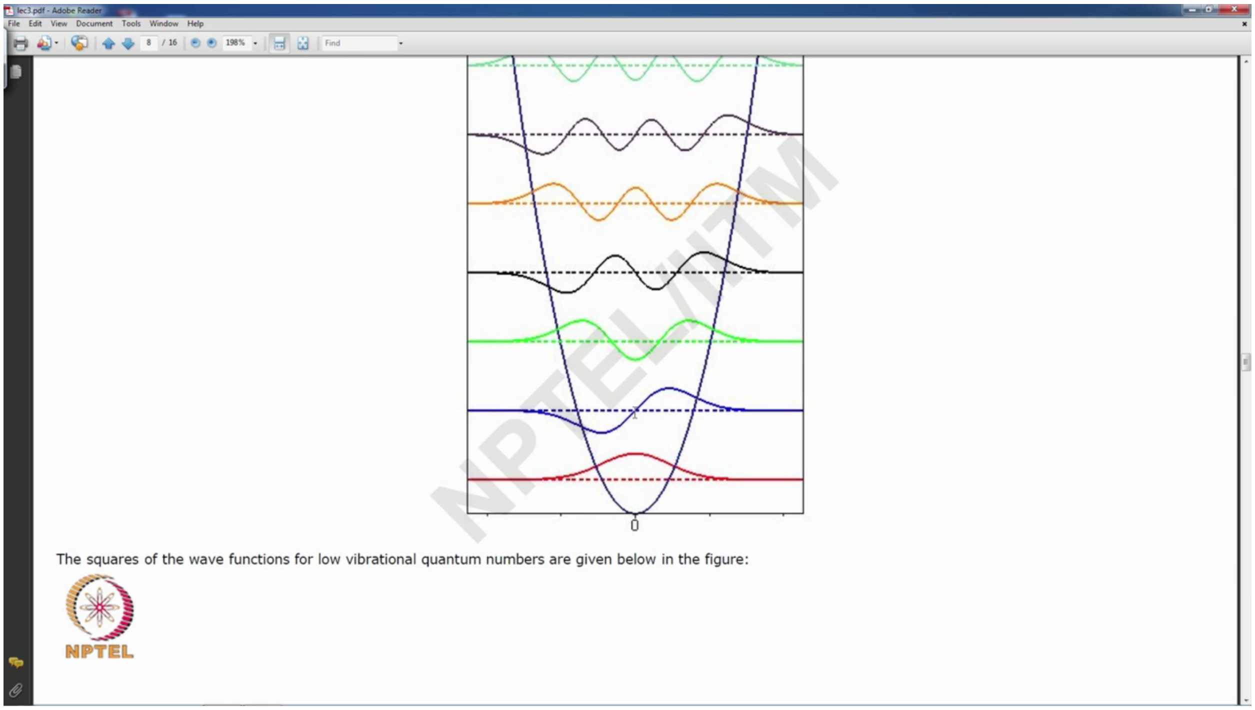
And in a sense, that's what you see in this picture. That's the bell -shaped Gaussian function that you see here and I have put in the parabola, the ½ kx^2, which is the potential energy parabola to sort of indicate something in the next few minutes. Let's look at the next function namely $H_1(\sqrt{\alpha}x)$, okay.



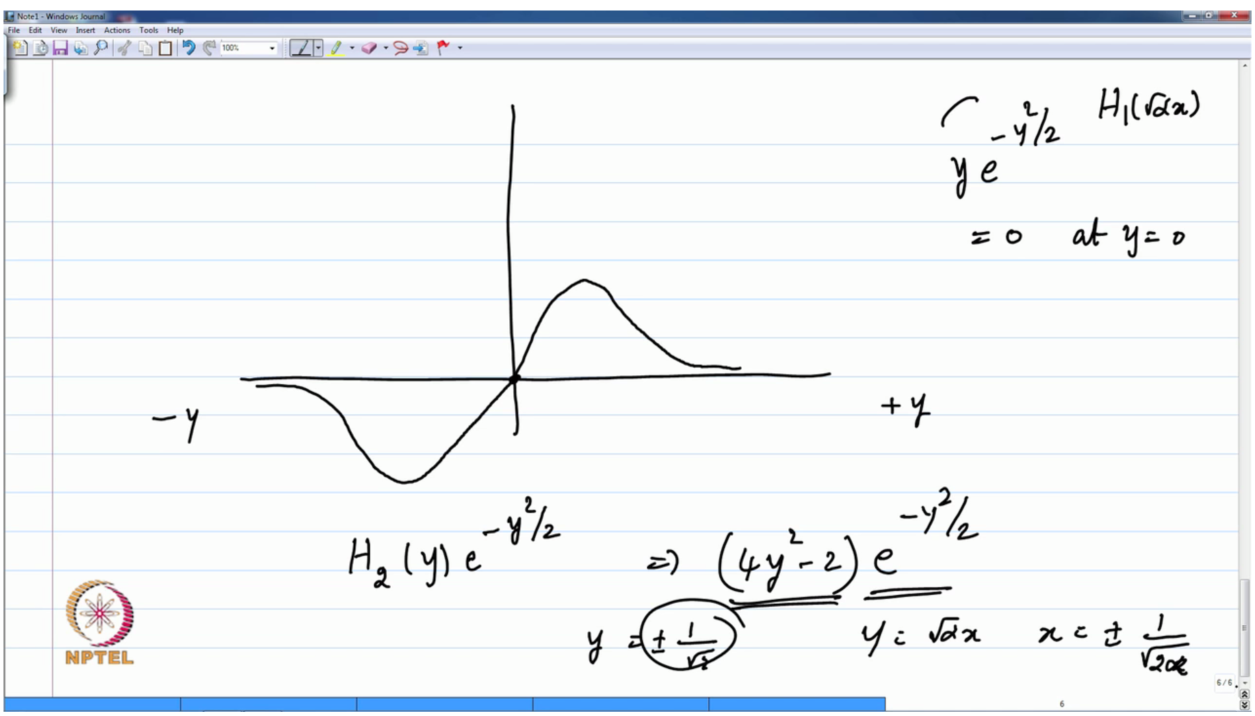
$H_1(\sqrt{\alpha}x) = N_1$ (normalization constant) $2\sqrt{\alpha}x$, if you remember, this is the H_1 $e^{-\alpha x2/2}$. So if we have to look at it simply, we will plot it as y $e^{-y2/2}$, if you want the picture, this is the same as the picture that you have where I have put in $y = \sqrt{\alpha}x$.



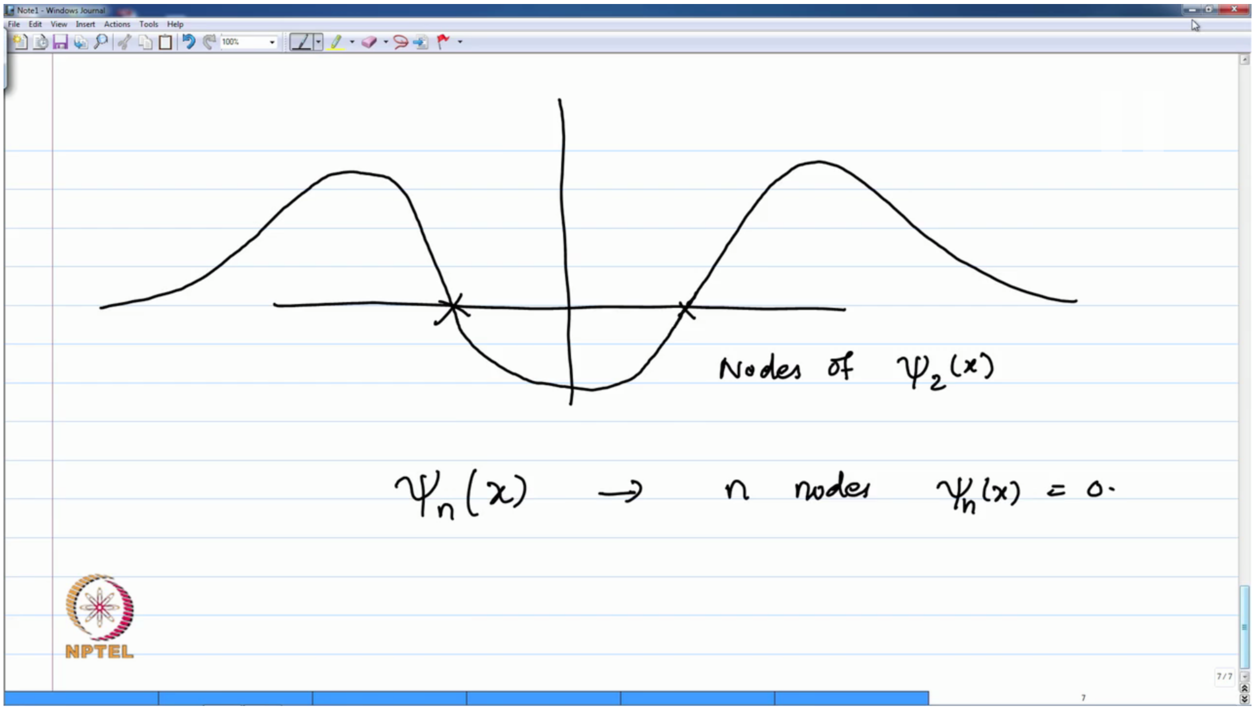
What does the graph look like? so if you plot this graph, +y and -y if you do that, then since it is y $e^{-y2/2}$, this is 0 at y=0. Therefore, the function is like this and this is also -- please remember from H1(√αx), because y = √αx. Therefore, you see that this is an odd function depending on the value of y abilities, plus or minus, the function will have plus or minus value. As y increases from 0, the plot sort of goes up with the e^{-y2} very small until it reaches a point that $e^{-y2/2}$ starts dominating the function and then this whole thing goes back to 0. And since it is an odd function, for -y, it’s exactly the same except that it is on negative side. So it's not exactly symmetric.



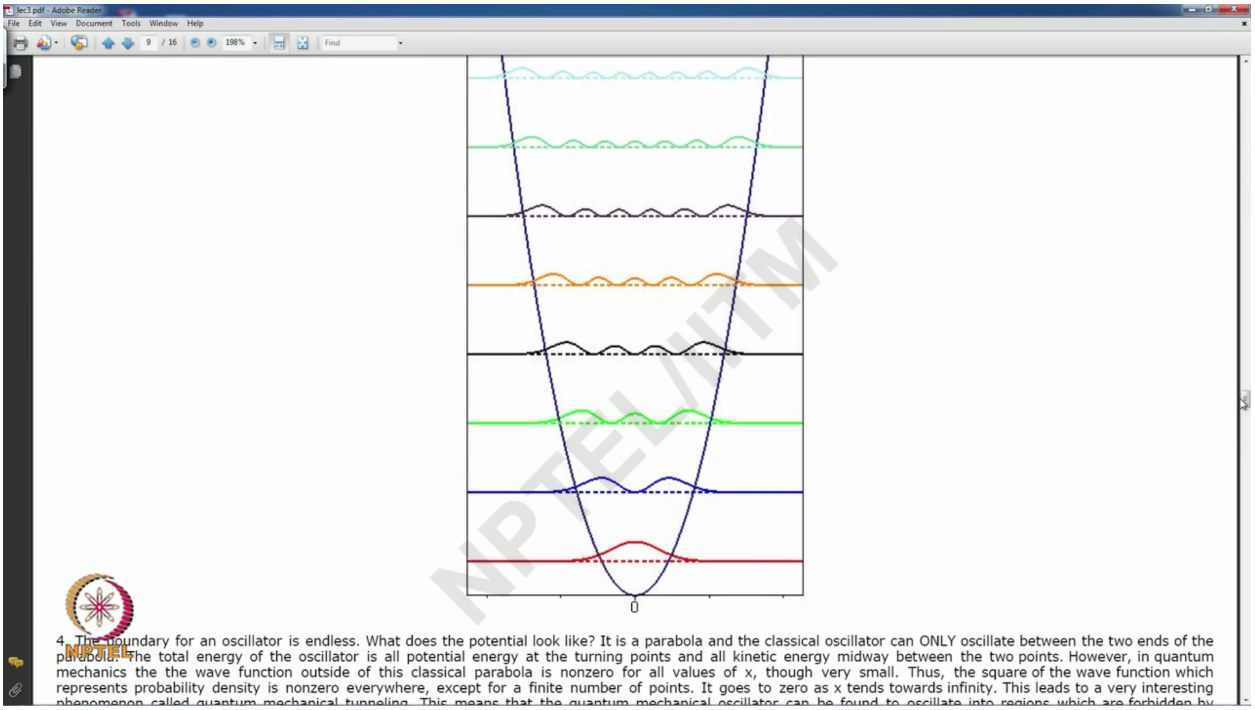
But if you look at this picture, you see that the function is 0 in the middle where y is 0, increases and decreases. Therefore, this is the odd function. These are wave functions, and likewise, the next function, which is $4y^2-2$ x $e^{-y^2/2}$ gives you this shape, namely it is negative in the middle.



And then there are two points where the function goes to 0, and those two points are essentially the points where the function for y^2-2, $H_2(y)e^{-y2/2} = (4y^2-2)\ e^{-y2/2}$. The exponential never goes to 0 except when y is very infinitely large, positive or negative. Therefore, this goes to 0 at values $y = \pm 1/\sqrt{2}$. There are two values. And remember $y = \sqrt{\alpha}x$, therefore, $x = \pm\ 1/\sqrt{2\alpha}$.



So there are two points at which the function goes to 0. So to plot that here, you have -- this is the negative side for the initial value and then you have the positive side, which goes back to 0, and also this even function where it goes back to 0 and you can see these are the two nodes of the function, $\psi_2(x)$, and for any wave function that the quantum number $\psi_n(x)$, which is the harmonic oscillator eigenfunction, there are n nodes at which the $\psi_n(x)$ goes to 0. There are n points, but the n is finite, therefore, the number of nodes is finite. The nodes are not a serious problem. What is important is around the nodes, when you worry about the probabilities, which is the square of the wave function, what you do is that you see that the negative parts are all canceled out, everything is positive, but near the nodes, the probabilities will be very small.



So now let us look at that part in this rough. Let's take the square of the wave function and when you plot the square of the wave function this is what you get, namely the first one is simply e^{-y^2} and therefore it has the same shape, except that it's narrower than the wave function, but what is important is that the probability of finding the harmonic oscillator outside of the classical potential region that you have here, okay, that's non-0. This happens only with harmonic oscillator and for any other system in which the potential is finite in any given region.

Remember the particle in a one-dimensional box that we looked at, we ensured that the particle stays inside the boundary by making certain that the wave, the potential energy is infinitely positive and repulsive at the boundaries, which meant that there was no leaking of this probabilities of the system outside of the forbidden -- outside of the allowed region.

So the harmonic oscillator if you look at that, there is this part which is non-0 outside the classical potential energy region. The classical potential energy region is only an indicator to tell you that if the harmonic oscillator were to obey classical mechanics, then it's impossible for the harmonic oscillator to be found outside of these two turning points. These are the turning points or essentially that point where the harmonic oscillator turns in the other direction, okay. That means that's the point where its kinetic energy is 0, its potential energy is maximum, and that's equal to the total energy of the harmonic oscillator. This is classical system.

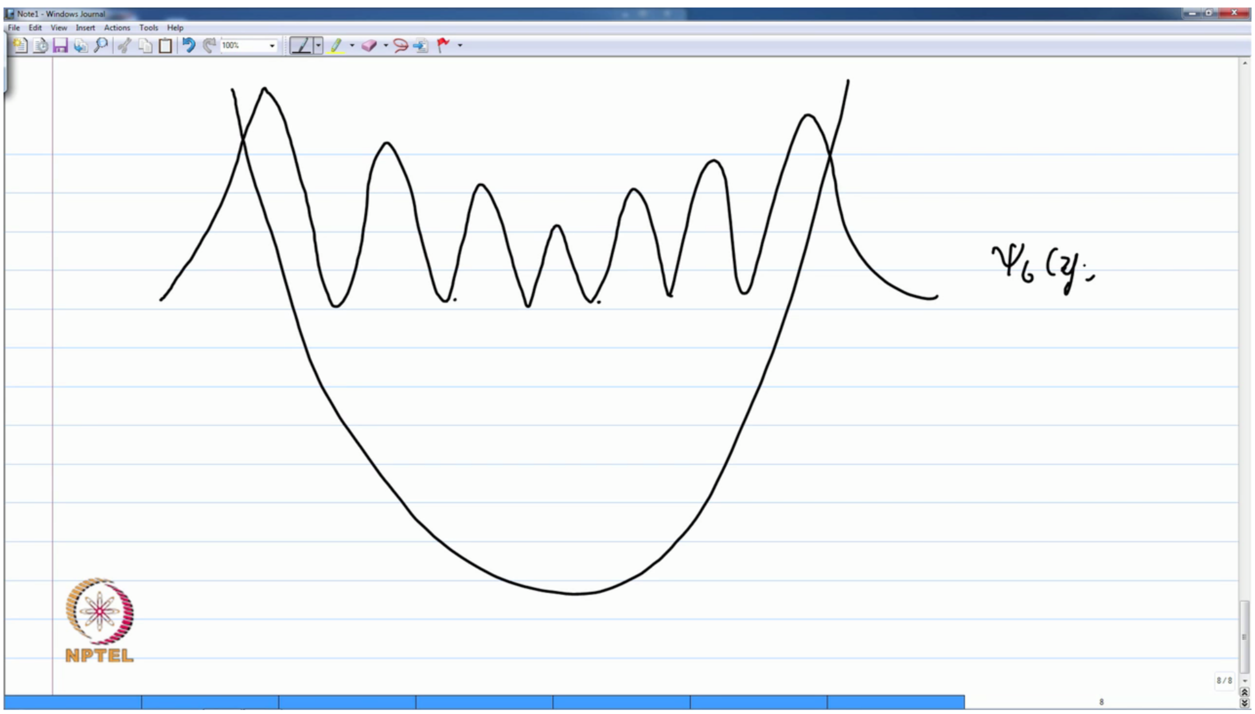
Therefore, for a classical harmonic oscillator, there is nothing called finding the harmonic oscillator outside of the potential barrier. Unfortunately, in quantum mechanics, the whole this is more difficult to imagine, but that's what happens that the square of the wave function being non-0, except at finite number of points here, these are the nodes that you see here, okay. So the nodes here, for example, this is with the quantum number 2 and this is with the quantum number 3. This is with the quantum number 4 and so on, you see the number of nodes. Around the nodes, the probability of finding the harmonic oscillator is small, but never 0, because we never talk about the probability of finding the harmonic oscillator at a given point when the variable for the harmonic oscillator motion is continuous, it's always a small interval that you have to variable and in no finite interval how small that maybe, the harmonic oscillator probability is ever 0.

Therefore, you see that the probably of finding the harmonic oscillator is always finite in all regions, however, something more subtle. The second subtle point -- the first point is the probability of finding the oscillator outside the forbidden -- I mean outside and in the forbidden region, region which is classically not allowed. That probability is finite, it's never 0. This is called tunneling. This is a phenomena, which is introduced for the first time. When you have finite potential barriers, one-dimensional barriers, the phenomenon of tunneling is something that we find, namely it’s a region in which the system probably will have in a classical sense negative kinetic energy, but that's difficult to visualize. It's possible for the system to be found in regions which are classically forbidden. That's a quantum mechanical statement, okay.

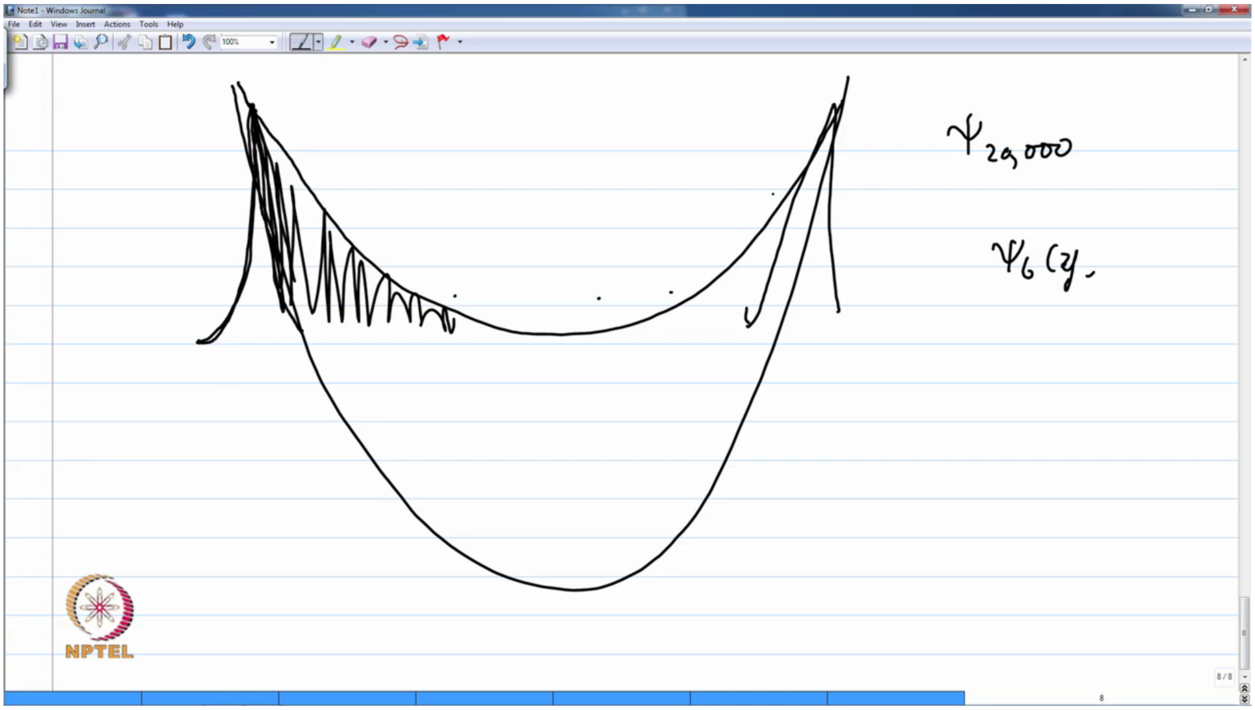
Now the second important point is that if you take this wave function, which is the ground state harmonic oscillator wave function with the quantum number n=0, you see that the probability of finding the harmonic oscillator is very large in the middle, that is very near the equilibrium versus the probability of finding the oscillator at the edges where it is extremely small now visualize this from the classical mechanical sense, the harmonic oscillator is very fast when it moves away from the equilibrium, because it’s kinetic energy is maximum and at equilibrium the potential energy is 0, but as it goes towards the extreme, it slows down and it virtually stops there for a moment and then comes back to equilibrium and then goes to the other direction, but the time it spends on either edges that is on either side of the potential barrier is definitely much, much more than the time it spends in the middle that is right where the potential is 0.

Therefore, classically, one would expect the harmonic oscillator to just swift past the equilibrium point in no time, its kinetic energy is maximum, but for the probability of locating the harmonic oscillator at the center classical mechanical mechanics tells you, it’s very small, and the probability of locating the harmonic oscillator at the edges is quite large if one way to picture the harmonic oscillator. The quantum mechanics at the low energy level gives you the exact opposite of what one would expect, therefore, it's not intuitive, okay. You cannot explain these things except that such things if they can be measured experimentally, can verify our conclusions. It has been done. Of course, that's a separate lecture, spectroscopy tells you all the time, okay.

Therefore, you see that the probability of finding the oscillator for its ground state is very large in the middle, but surprisingly, you go to the next energy, you see that the probability of finding the harmonic oscillator in the middle is virtually 0. I mean it's almost 0, it's very, very small. It looks like it is something close to the classical mechanics. That's not true, because then you see in the middle again it has all these function. So there is this weird behavior of harmonic oscillator with respect to classical expectations continues until you reach very, very large quantum numbers, okay.

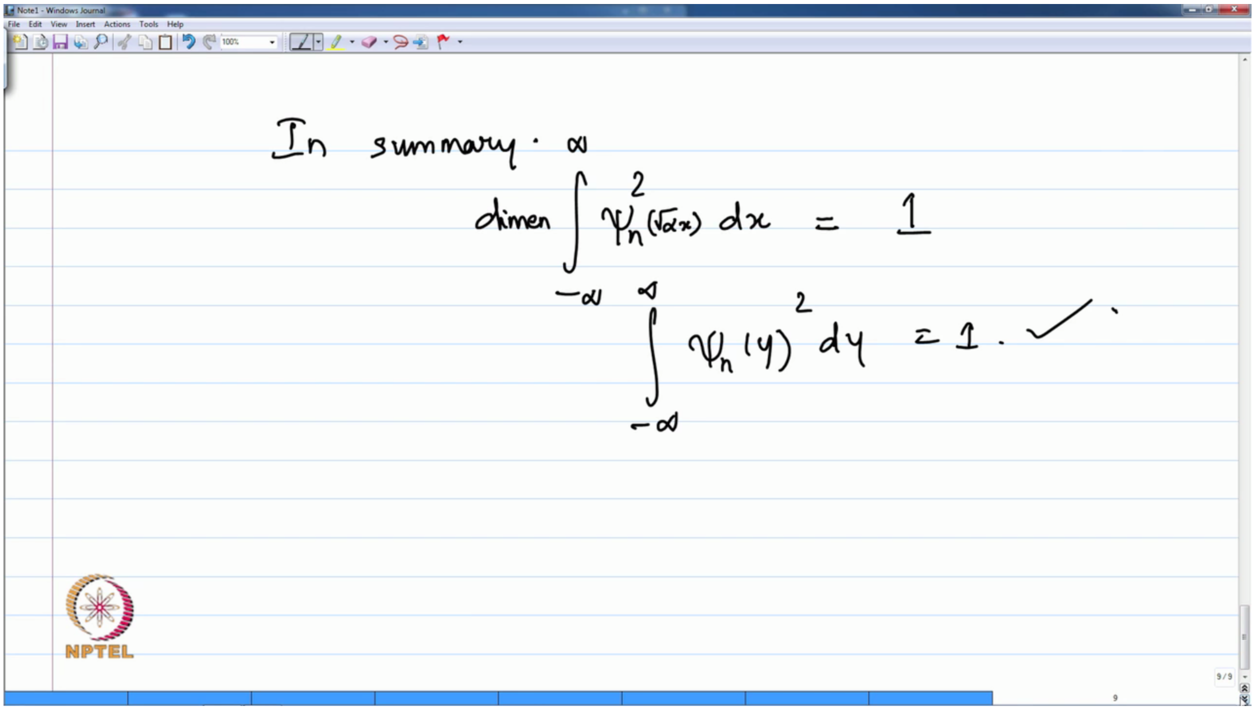


Now if you reach very large quantum numbers, what does it do? If you try to plot the wave function for very large, if the barrier is something like that, okay, and you plot the wave function, you will see that the wave function square is something like that, and if you plot it for -- this is for say 1, 2, 3, 4, 5, 6 nodes that you have. So this is $\psi_6(y)$, okay.

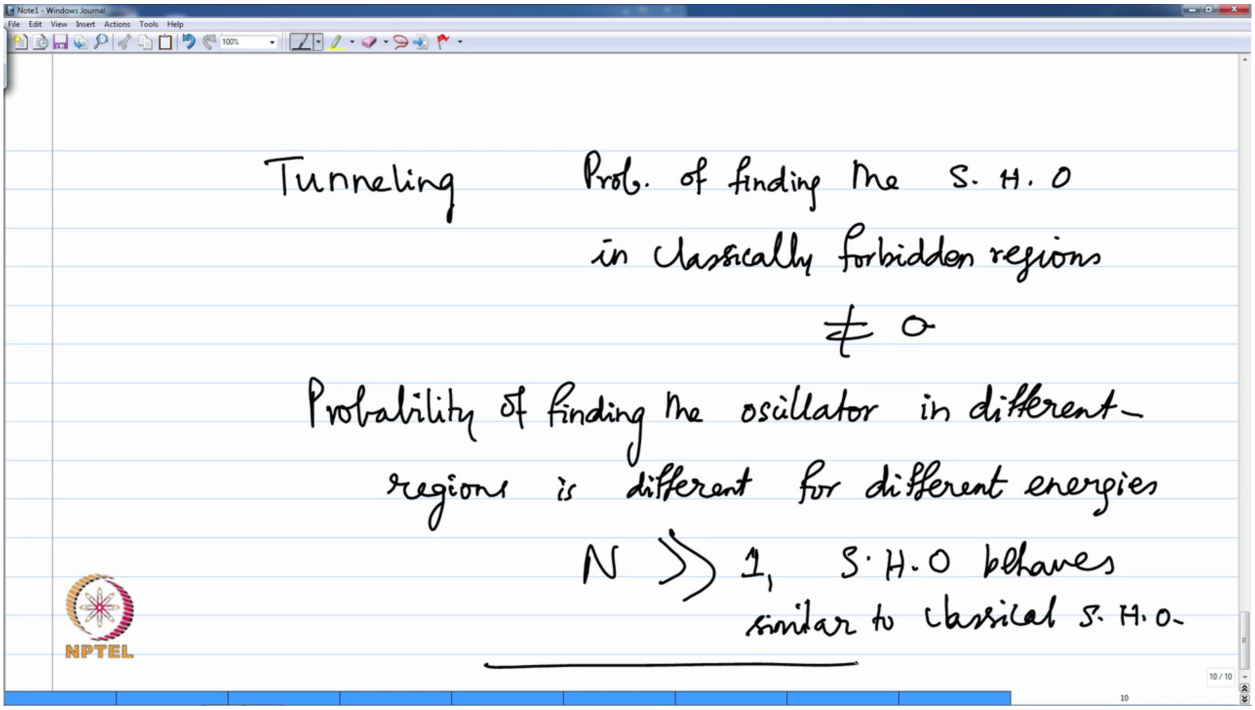


So if you were to plot this for, say, ψ_{20000}, okay, which I cannot do here, but let me remove this graph and tell you what it looks like. It will look exactly like the maximum probability here, and then, I cannot draw those squiggles, so let me just connect to the height of the squiggle, harmonic oscillator will look exactly like that, okay. Imagine there are 20,000 squiggles here, okay, but the probability is very large at the extreme and it's also very large at the extreme and then the squiggles are such that, you can actually plot an amplitude, the height connecting to that.

It almost simulates the potential energy graph, and therefore, the behavior of the harmonic oscillator that it spends most of its time towards the edges and much less, almost no time in the middle, which is what you would expect. Classically, it’s what you see when the quantum number is very large, that is when the energy of the system is very large. So these are important points. Let me summarize.



We will do the probabilities calculations in the next part of the lecture. So in summary, $\int \psi_n(x)^2\,dx$ between $-\infty$ to ∞ is I would say $\sqrt{\alpha}\,x$, so it doesn't matter, but yeah. Let me just write that, okay, $\sqrt{\alpha}x$, and then there has to be some dimension factor here to ensure that you are integrating. This is equal to -- $\psi_n 2 = 1$, best would be to write this as $\int \psi_n(y)^2\,dy$ between $-\infty$ to ∞ is 1, okay. This is the normalization, which means essentially, it's the area under the square of the wave function graph, okay.



Second, tunneling, probability of finding the oscillator, a simple harmonic oscillator, in classically forbidden regions, non-0, okay. Third, probability of finding the oscillator in different regions is different for different energies, different regions is different for different energies. Therefore, there is no uniformity except that when n is extremely large, simple harmonic oscillator behaves similar to classical simple harmonic oscillator, classical simple harmonic oscillator. So these are the things that need to be kept in mind.

What we will do in the next lecture is to study the probability and also calculate some of the expectation values like the average value for the harmonic oscillator position and the momentum, et cetera. Until then, thank you very much.