Introductory Quantum Mechanics and Spectroscopy
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Lecture – 6
Part III
Wave Functions, Probabilities and Average (expectation) Values for Harmonic Oscillator

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 of in the harmonic oscillator.

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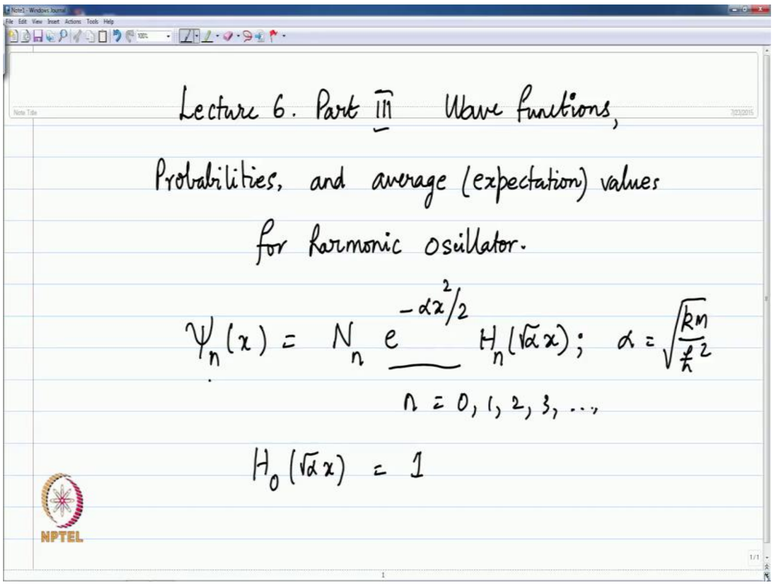

In the last lecture, let me recall what we did; I mentioned that the wave functions and the harmonic oscillator Hamiltonian. However, I did not solve the Schrodinger equation, but gave you the final solution, which you might recall here in the last line namely, the wave functions psi n of x; where n is a quantum number and takes values from 0 all the way up to infinity assuming that the harmonic oscillator motion continues to be like a harmonic oscillator for very large amplitudes as well. The wave function psi n of x – it consists of two parts. An exponential minus alpha x square by 2; where alpha is the parameter – a set for the harmonic oscillator; alpha 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 root. And alpha has the dimensions of 1 over the length square. Therefore, if x represents the displacement; then alpha x square is dimension less.

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 root alpha x, so that the polynomial has quantities, which are dimensionless. And the quantum number n is of course, 0, 1, 2, 3, etcetera. 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 is important in terms of making certain that the wave function is a normalizable wave function.

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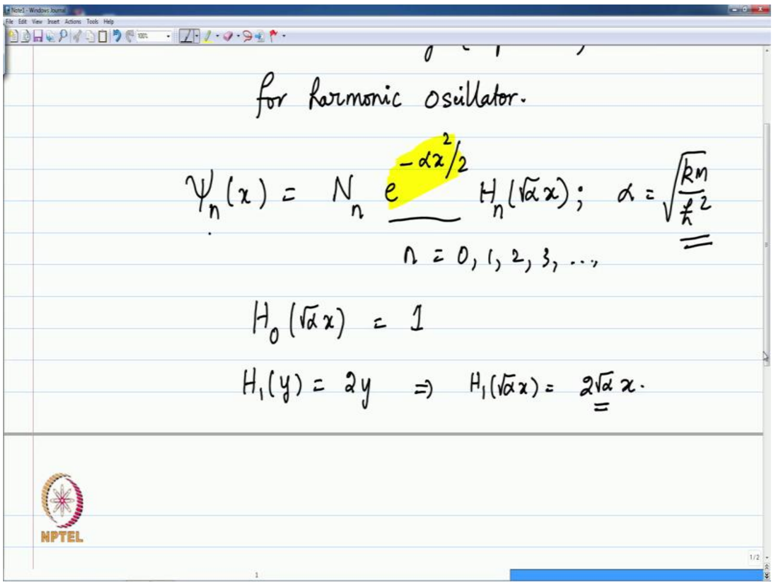

And now, if you go back and look at these formulae; what you have here is the Hermite polynomials. And you might recall that, the Hermite polynomial for the first quantum number H 0 of root alpha x is actually 1; it is independent of the displacement. H 1 – if you recall, I use to write y and I said it was 2y. Therefore, H 1 of root alpha x is 2 root alpha times x. And alpha is specific to the harmonic oscillator that we have in question. Therefore, if the oscillator is a very rigid oscillator; that is, it has a force constant, which is very high; or, if the oscillator is very heavy like its mass is very large; then you see alpha is also very large. And that is very important, because if you see if alpha is large, that has something to do with the exponential minus alpha x square that I have here – that we just… 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 wills them through the exponential as well as through the Hermite polynomial.

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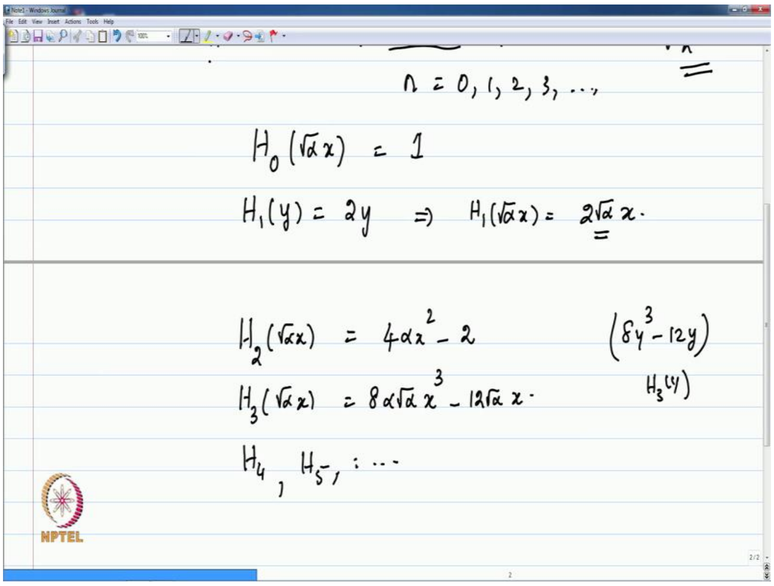

What is the second Hermite polynomial? H 2 of root alpha x. You remember – that was 4y square minus 2. Therefore, it becomes 4 alpha x square minus 2. And likewise, for the third – H 3 root alpha x. If you recall, it is 8y cube minus 12y for H 3 y. And therefore, that becomes when you put y is equal to root of alpha x. It becomes 8 alpha root alpha x cube minus 12 root alpha times x, and likewise for H 4, H 5 and so on. 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.

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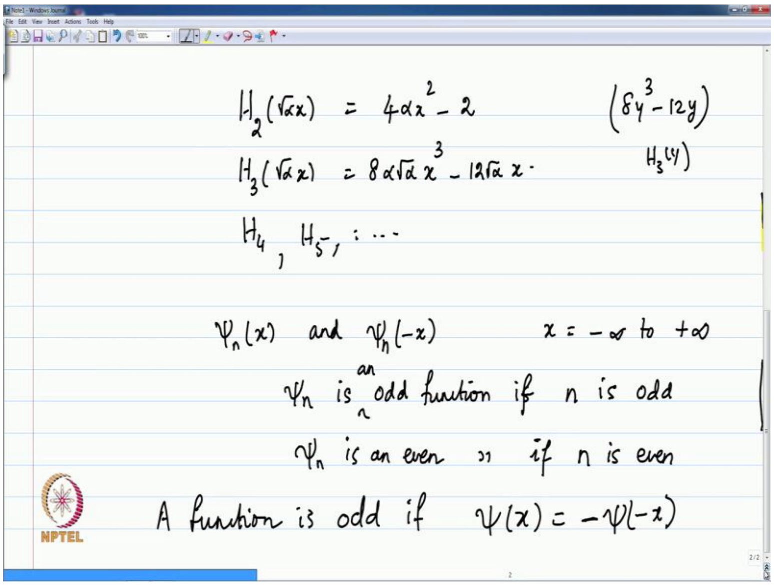

That is, if you look at the wave function psi n of x and psi n of minus x; if you consider the wave function psi n of x and psi n of minus x; since you know that, x can take values from minus infinity to plus infinity, that is, on either side of the oscillators equilibrium position; then psi n of x and psi n of minus x have this property namely, psi n is odd function – is an odd function if n is odd – if n is odd; and psi n of x is an even function if n is even. And this is quite obviously dependent on the properties of the Hermite polynomial that you see here, because you see the exponential of minus alpha x square is always even; whether it is plus x or minus x since you have the square of the 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 of x is independent of x. Therefore, it is independent of the sign of x. H 1 of x is simply x. Therefore, H 1 of root 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 it has this property namely, psi of x is a negative of psi of minus x. Therefore, if the argument is negative, then the function changes sign. This is odd.

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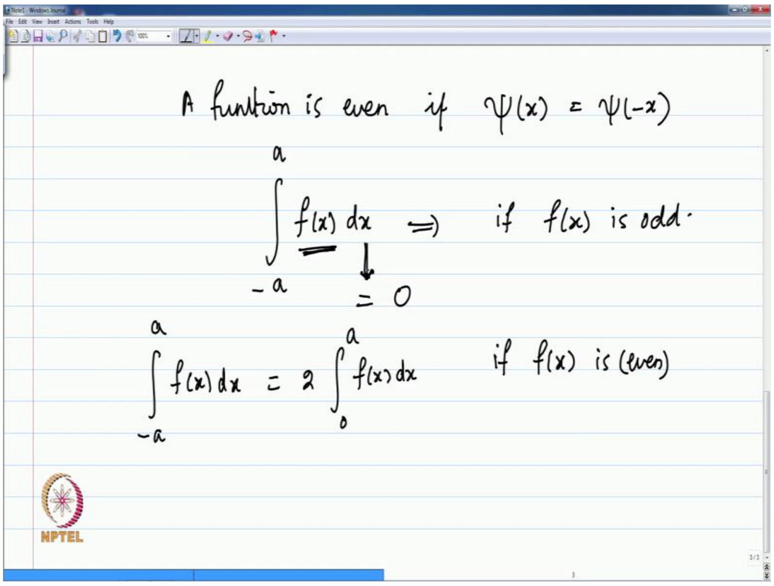

A function is even obviously when this does not happen – even if psi of x is equal to psi of minus x. And with this definition in mind, you will immediately see that, the odd numbered Hermite polynomials namely, H 1, H 3; and if you recall H 5; it contain x raise to 5, x cube and then x; nothing else. Therefore, the odd numbered – odd indexed Hermite polynomials are all odd functions; and likewise, the even quantum number indexed Hermite polynomials like H 0, H 2, H 4, H 6, etcetera are all even. Therefore, this property is very important in terms of determining the average values and the momentum, etcetera since integrals have some very specific properties with respect to odd and even function. Remember – if you are integrating a function between symmetric limits – minus a plus a and f of x dx; you can say something about it if f of x is odd. The answer is this integral will be 0. If f of x is even; you cannot say immediately what the answer is; but you can write the following namely, the integral minus a to plus a f of x dx for an even function is 2 times 0 to a f of x dx. So, these are properties, which are extremely important. And you can see that, if the integral is odd – integrand is odd 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.

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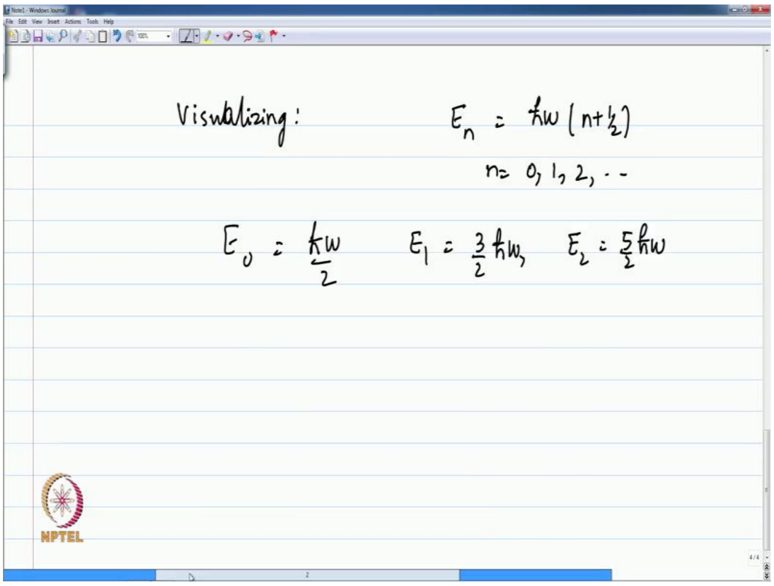

Now, what do we have with respect to these functions? Let us get to the possibility of visualizing these functions and visualizing the – visualizing this and visualizing the squares. I have some pictures here.

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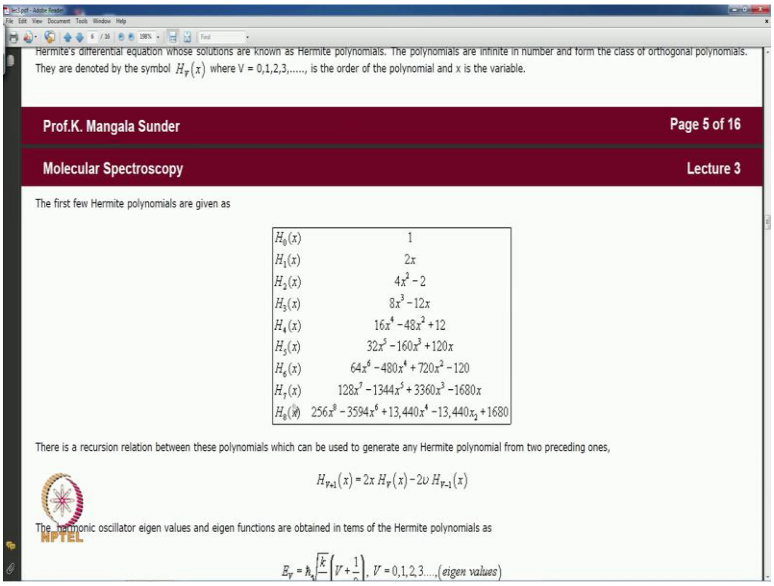

This table is extremely important. You might recall that, this was probably shown in the last lecture; you can see that, H 0, H 2, H 4, H 6, H 8 – all have even powers of x. And H 1, H 3, H 5, H 7 – all have odd powers of x. Therefore, the odd Hermite polynomials are odd functions and the even Hermite polynomials are even functions of x.

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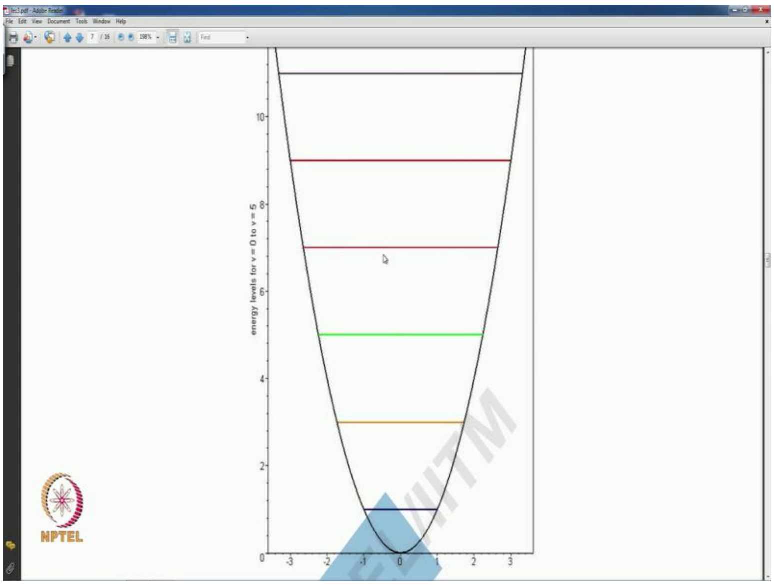

Now, how does the wave function look? You recall the energy levels. The energy levels if you remember have this expression namely, E n is h bar omega times n plus half; where, n is equal to 0, 1, 2, 3, etcetera. Therefore, you can see that, E 0 is h bar omega by 2; E 1 is 3 by 2 h bar omega; and E 2 is 5 by 2 h bar omega 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 h bar omega. So, this is the half h bar omega; this is the 3 by 2 h bar omega; this is all in half h bar omega kind of units. So, do not worry about these numbers: 2, 4, 6, etcetera. So, the base level is h bar omega by 2, 3 by 2, 5 by 2, 7 by 2, 9 by 2. And so harmonic oscillator is equally distant 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 to level 2 or level 3; you need to have the harmonic oscillator behave as an unharmonic oscillator. These things will become clearer when we talk about the spectroscopy part of it.

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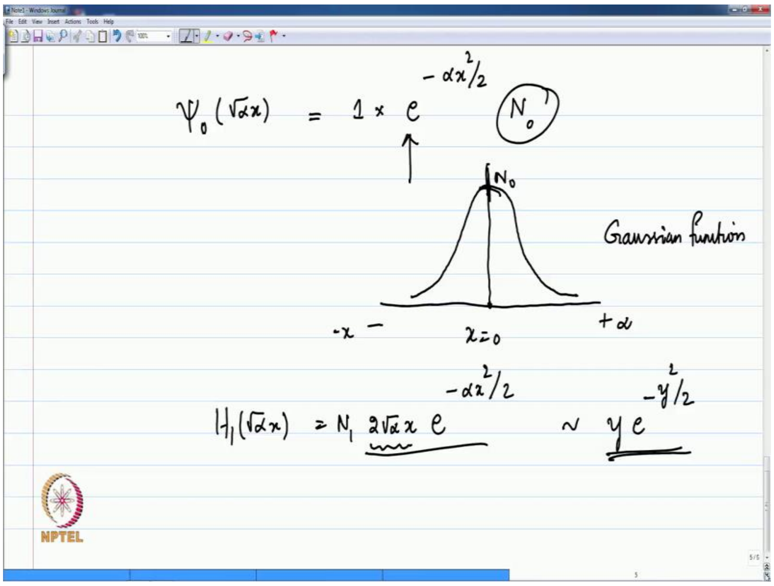

But, now, having looked at the energy a little bit, let us see what the wave functions are. Psi 0 of root alpha x is 1 – times exponential minus alpha x square by 2 – times the normalization constant N 0; let us not worry about that. We will only concern ourselves with this. And this, when you plot it as a function of x – negative x and this is minus x and this is positive x. If you do that, this is an even function and this is the familiar well-shaped curve, which is the Gaussian function centered at 0 – at x is equal to 0. And this height is obviously N 0; that is the value, because the exponential goes to 1 when x is 0. But, for larger values of x, the exponential function decreases – a Gaussian function decreases in value. And therefore, this is the well-shaped curve you have here.

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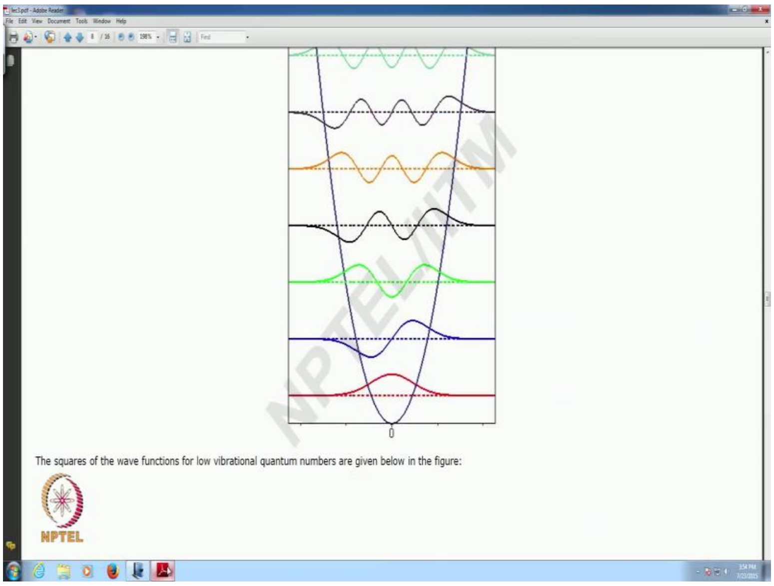

And in a sense, that is what you see in this picture. That is the well-shaped Gaussian function that you see here. And I have put in the parabola – the half k x square, which is the potential energy parabola to sort of indicate something in the next few minutes. Let us look at the next function namely, H 1 of root alpha x. H 1 of root alpha x is the normalization constant N times 2 root alpha x. If you remember, this is the H 1 times exponential minus alpha x square by 2. So, if we have to look at it simply, we will plot it as y times e to the minus y square by 2; if you want the picture, this is the same as the picture that you have; where I have put in y is equal to root alpha x. What does the graph look like?

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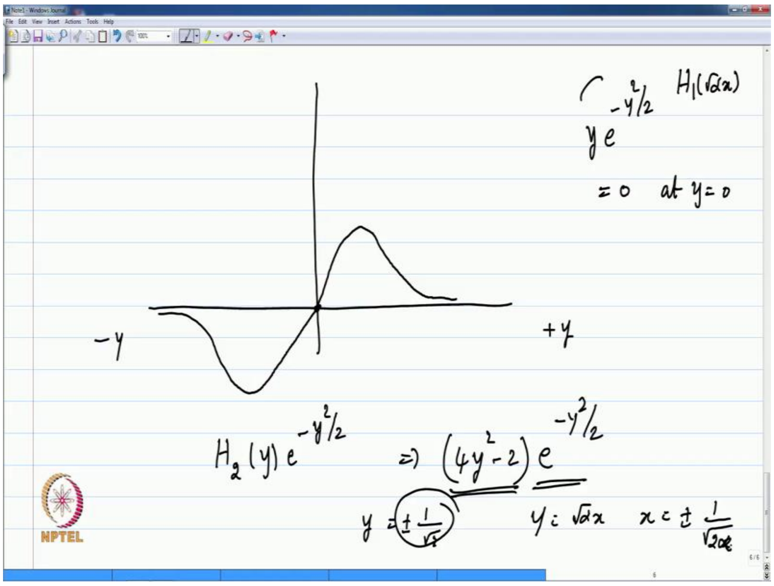

So, if you plot this graph – plus y and minus y; if you do that; then since it is y times e to the minus y square by 2; this is 0 at y is equal to 0. Therefore, the function is like this. And this is also… Please remember from H 1 of root alpha x; this y is root alpha x. Therefore, you see that this is an odd function depending on the value of y whether it is plus or minus; the function will have plus or minus value. And as y increases from 0, the plot sort of goes up with the exponential minus y square very small until it reaches a point that exponential minus y square by 2 starts dominating the function; and then this whole thing goes back to 0.

And since it is an odd function, for negative y, it is exactly the same, except to that it is on negative side. So, it is 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 4x square or 4y square minus 2 times exponential minus y square by 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 4y square minus 2 – H 2 of y exponential minus y square by 2 is 4y square minus 2 times exponential minus y square by 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 is equal to 1 by root 2 – plus or minus; there are two values. And remember – y is root alpha x. Therefore, x is equal to – you have plus or minus 1 by root 2 alpha – root 2 alpha. So, there are two points at which the function goes to 0.

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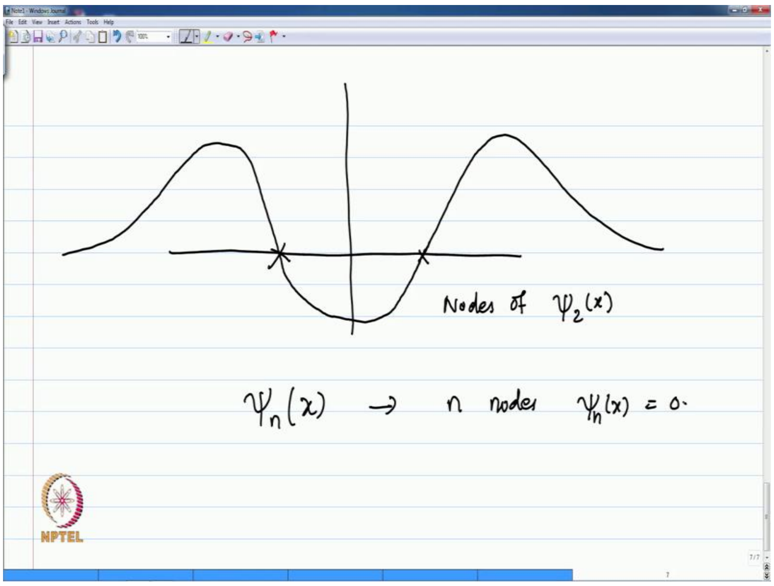

So, to plot that here; you have… This is the negative side for the initial value and then you have the positive side, which goes back to 0. And also this is the even functions when it goes back to 0. And you can see these wrote are two nodes of the function of psi 2 of x. And for any wave function with a quantum number psi n of x, which is the harmonic oscillator Eigen function. There are n nodes at which the psi n of 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 loads of the probabilities will be very small.

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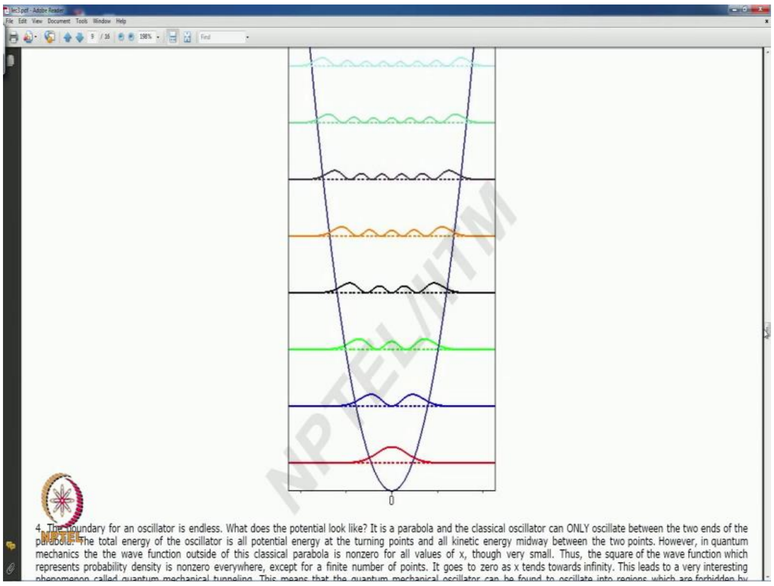

So, now, let us look at that part in this graph. Let us take the square of the wave function. And when you plot the square of the wave function, this is what you get namely, the first one is simply exponential minus alpha y or exponential minus y square. And therefore, it is has the same shape, except that it is 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; that is nonzero. 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; they ensure that the particle stays inside the boundary by making certain that 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 allowed region.

So, the harmonic oscillator if you look at that; there is this part, which is nonzero 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 is impossible for the harmonic oscillator to be found outside of these two turning points. These are the turning points or essentially the points where the harmonic oscillator turns in the other direction; that means that is the point where it is kinetic energy is 0; its potential energy is maximum; and that is 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 thing is more difficult to imagine; but that is what happens that, the square of the wave function being nonzero, except at finite number of points here; these are the nodes that you see here. 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 is always a small interval that you have to worry about. And in no finite interval, however small that may be, the harmonic oscillator probability is ever 0. Therefore, you see that, the probability of finding the harmonic oscillator is always finite in all regions; however, something more subtle.

The second subtle point; the first one is the probability of finding the oscillator outside and in the forbidden region – region, which is classically not allowed – that probability is finite; it is 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 in the phenomena of tunneling is something that we find; namely, it is a region in which the system probably will have in a classical sense negative kinetic energy; but that is difficult to visualize. It is possible for the system to be found in regions, which are classically forbidden. That is the quantum mechanical statement.

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 equal to 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 its 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 starts 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 just space past the equilibrium point in no time; its kinetic energy is maximum. Therefore, the probability of locating the harmonic oscillator at the center – classical mechanical – mechanics tells you it is very small; and the probability of locating the harmonic oscillator at the edges is quite large if one were 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 is not intuitive; you cannot explain these things except that, such things if they can be measured experimentally can be verify our conclusions. It has been done of course; that is a separate lecture. A spectroscopy tells you all the time. 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 is almost is 0; it is very, very small. Looks like it is something close to the classical mechanics; just not true, because then you see in the middle again it has all these functions. So, there is this weird behavior of harmonic oscillator with respect to classical expectations continues until you reach very, very large quantum numbers.

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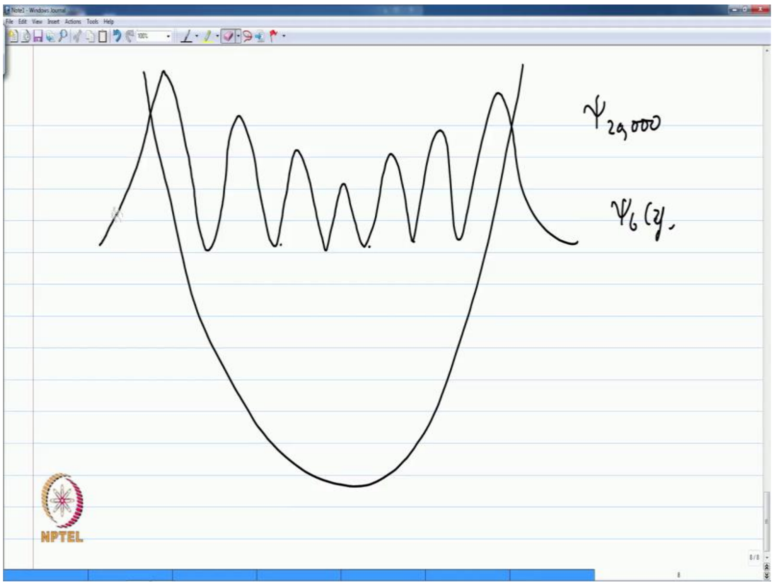

And now, if you reach very large quantum numbers, what does it do? If you try to plot the wave function for very large if the barrier is something like that. And you plot the wave function; you will see that, the wave function square is something like that. And if you plot it for… This is for say 1, 2, 3, 4, 5, 6 nodes that you have. So, this is psi 6 of y. So, if you were to plot this for say psi 20,000; which I cannot do here.

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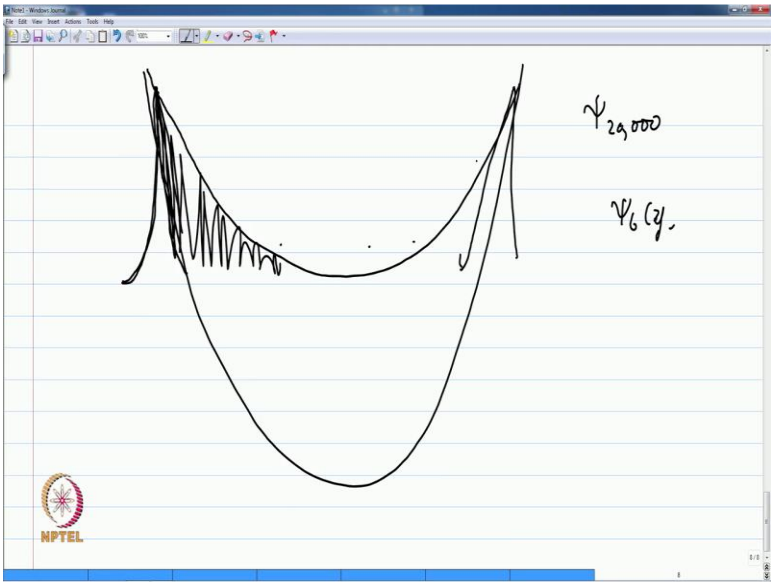

But, let me remove this graph and tell you what it looks like. It will look exactly like the maximum probability here. And then I cannot draw the squiggles. So, let me just connect to the height of the squiggle. Harmonic oscillator will look exactly like that. That will be… You imagine there are 20,000 squiggles here. But the probability is very large at the extreme and is 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 a potential energy graph. And therefore, the behavior of the harmonic oscillator – that it is spends most of its time towards the edges and much less – almost no time in the middle; which is what you would expect classically, is 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.

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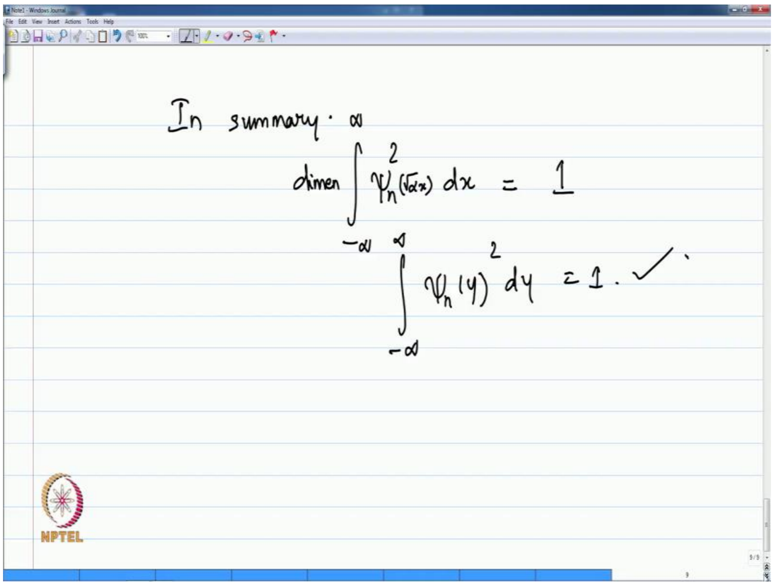

So, in summary, psi n of x square dx between minus infinity to plus infinity is I would say root alpha x. So, it does not matter; but let me just write that – root alpha x; and then that has to be some dimension factor here to ensure that, you are integrating. This is equal to psi n square is equal to 1. Best would be to write this as psi n y square dy between minus infinity to plus infinity is 1. This is the normalization; which means essentially, ((Refer Time: 29:41)) area under the square of the wave function graph.

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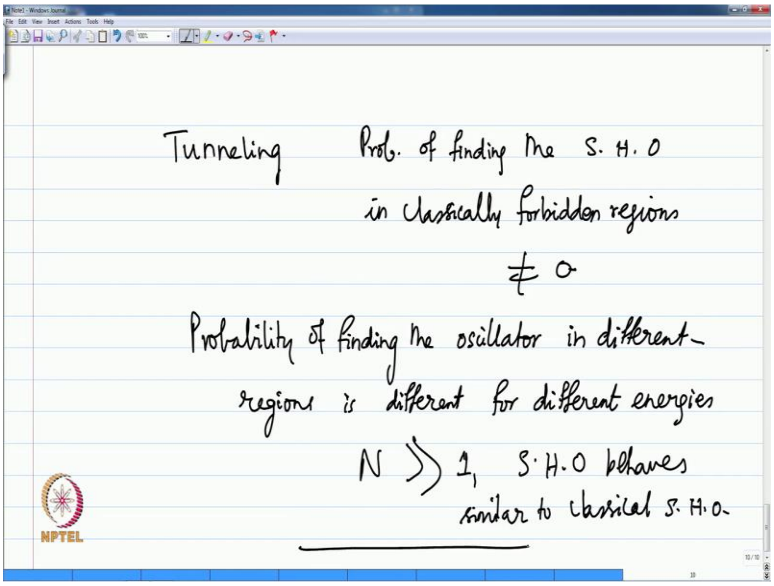

Second: tunneling – probability of finding the oscillator – a simple harmonic oscillator in classically forbidden regions – nonzero. Third – probability of finding the oscillator in different regions is different for different energies, different regions, is different for different energies. Therefore, there is no uniformity except to 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, etcetera.

Until then thank you very much.