Introductory Quantum Mechanics and Spectroscopy
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Lecture - 3
Part I
Schrodinger Equation
Particle-in-a-one-dimensional box

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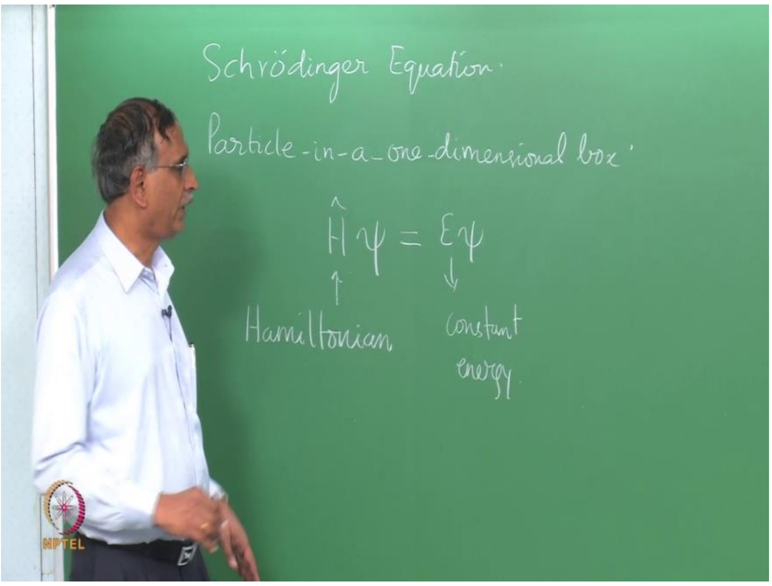

Welcome back to the lecture for the introductory chemistry using Schrodinger and quantum mechanical methods for the atomic structure. So, what we would do in this and in the next segment is introduce the Schrodinger equation and also do a model problem using the particle-in-a-one-dimensional box model. This is one of the simplest models that we have. Let us take a quick look at the Schrodinger equation.

In the lecture earlier, I mentioned, that I would be talking about the time independent Schrodinger equation in which this quantity was referred to as the Hamiltonian and this as a constant, but with dimensions of energy. And the function psi is the function that we wanted to find out by solving an equation of this sort, but we do not know what this is right now. We have to introduce that to understand how this equation comes about or what is its origin. We can do a very simple example of a standing wave.

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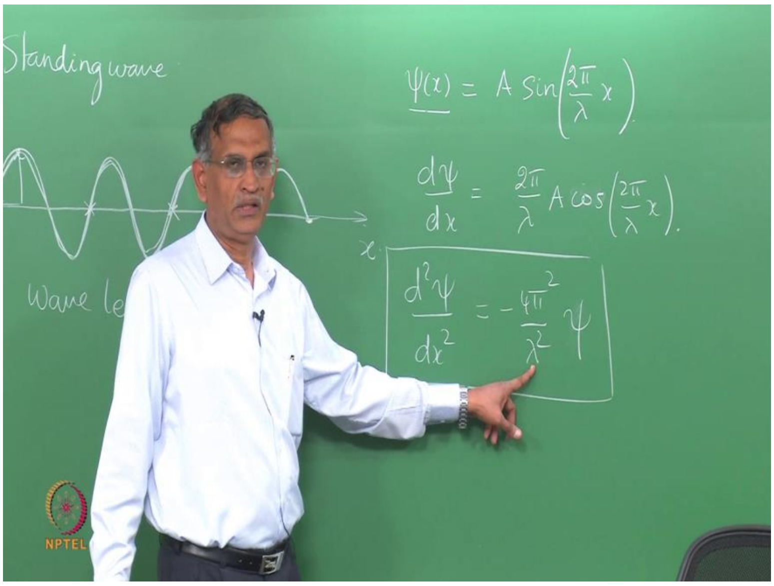

And you know, that a standing wave is something that happens between fixed points and the wave motion of a particle fixed to the end, something of that kind. And let me put it precisely, so that the wave when it reflects, it still follows and therefore, the standing wave remains as a wave and the amplitude do not cancel each other.

So, if you, if you want to look at the axis, this is the coordinate or the x-axis, that you might want to talk about. And this is the axis for the amplitude of the wave at any position x between some fixed points. Obviously, for this wave the length of the repeating unit is, obviously, called the wavelength lambda. And here we have 1, 2, yes, 2, this is 1, and this is 2, and then you have 3, and 3 and a half. It has to be either exactly half wavelength or a full wavelength for this to be a standing wave.

The equation for the standing wave for the amplitude A, or let us call that amplitude as psi in relation to what we have here. We will see later, that this psi is not necessarily the same as the psi that we talk about, but for that psi if we have the maximum amplitude as A, this quantity as A when the wave function psi of x is written as A sine 2 pi by lambda of x. This is something that you are familiar with for a standing wave.

Now, this quantity psi, when you differentiate twice, it satisfies the derivative equation. Let us do that for the first derivative d psi by dx as 2 pi by lambda times A sine, A cos 2 pi by lambda x. And the second derivative d square psi by d x square is equal to minus 4 pi square by lambda square psi of x, because this will become sine 2 pi by lambda of x, and that is the something as psi of x. Therefore, you see that the standing wave satisfies the differential equation d square psi by d x square, where psi is the amplitude of the wave with lambda the wavelength associated to that.

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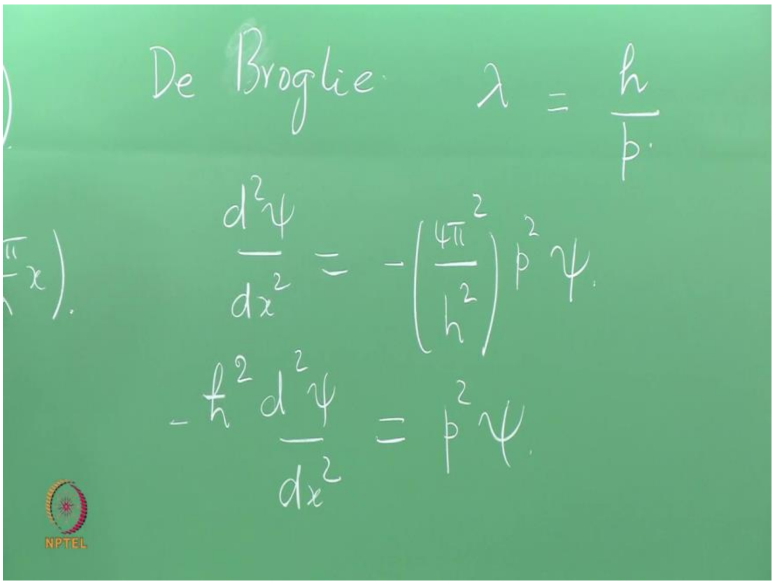

Now, De Broglie, if you remember in the lecture earlier, gave an expression for the matter wave's lambda, in terms of the momentum of the particle, in terms of momentum of the particle you have here. And therefore, if we write the wave equation, it is d square psi by d x square, which is equal to minus 4 pi square by h square multiplied by p square psi or minus h bar square. We know, that h by 2 pi is h bar, therefore if we bring that in, is minus h bar square d square psi by d x square is equal to d square psi.

This is the equation for the standing wave using the De Broglie idea and the quantization idea namely, that the energy quantum for material particles, light, etcetera, given in terms of the Planck's constant. So, the Planck's constant enters naturally here in describing what happens to the momentum square on the wave function is the same thing as the second derivative on the wave function, multiplied by minus h bar square.

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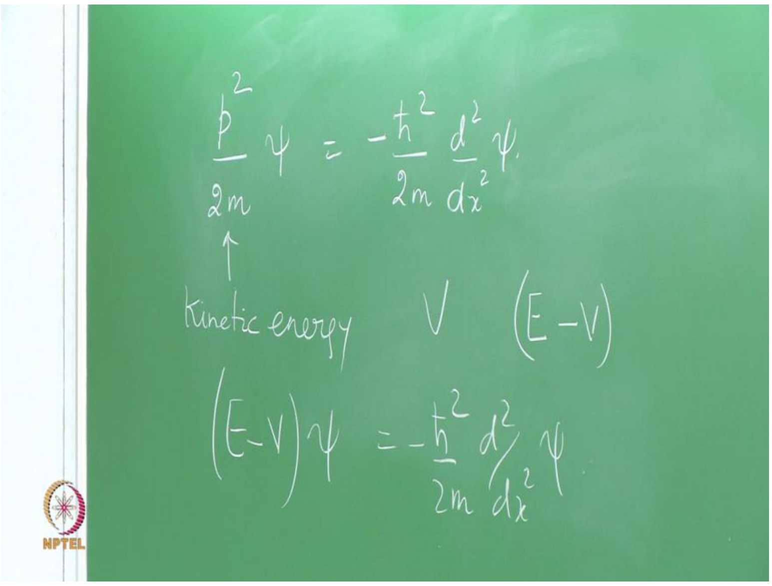

Therefore, if we write the kinetic energy p square by 2 m psi, that turns out to be minus h bar square by 2 m d square by d x square psi. This being the kinetic energy, this is the difference between, if there is a potential energy V, then it is a difference between the total energy E and the potential energy V, which may be a function of x for whatever, if that is a potential we have to consider that. Therefore, what happens is p square by 2 m is nothing but E minus V on psi giving you minus h bar square by 2 m d square by d x square psi.

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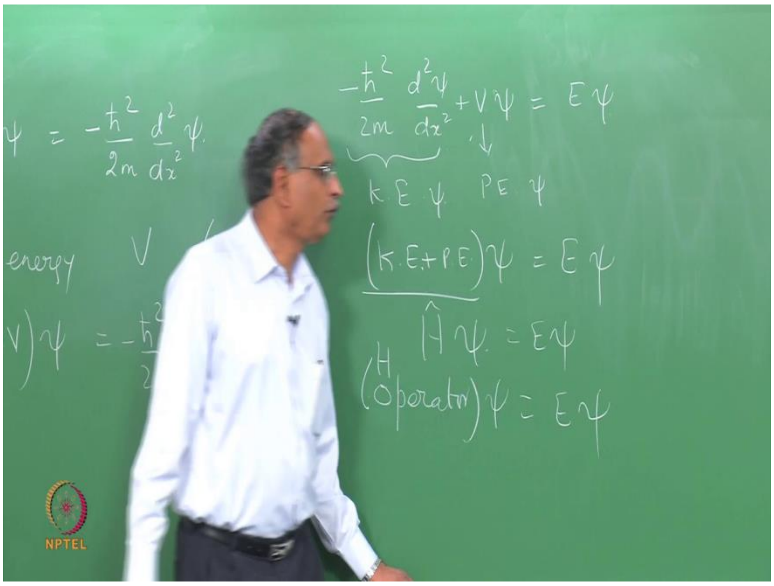

Now, one last step and then you see the equation h psi is equal to E psi making sense to us because now, if you bring the way here just rewrite the equation you have minus h bar square by 2 m d square psi by d x square plus v of psi is equal to E of psi. Please remember, we have already written this as the kinetic energy and this is on psi; this is the potential energy on psi. And therefore, you see, that this is nothing but kinetic energy plus potential energy on psi, on psi, giving you a constant times E psi. So, you see, that this is nothing but the Hamiltonian on psi giving you E psi.

This is a very simple justification. I do not think we can really say that we have derived it from any fundamental principles or whatever, it is a justification to see from a simple standing wave picture, and using the De Broglie principle or the proposition with the Planck's constant. It looks like the particle wave function satisfies the equation Hamiltonian.

But the Hamiltonian looks somewhat odd, it has a derivative instead of the p square by 2 m that we have, now we have put that derivative here. And therefore, the Hamiltonian is a derivative acting on the wave function and the potential, which is, of course, a function of the position of whatever particle or the system that you talk about, the potential generally multiplies the wave function, but the two together is actually an operator acting on psi. The Hamiltonian operator acting on psi giving you a constant times psi.

Schrodinger equation is a very specific equation for the Hamiltonian operator, and such equations in mathematics are known as Eigen value equations for whatever quantities that appear here.

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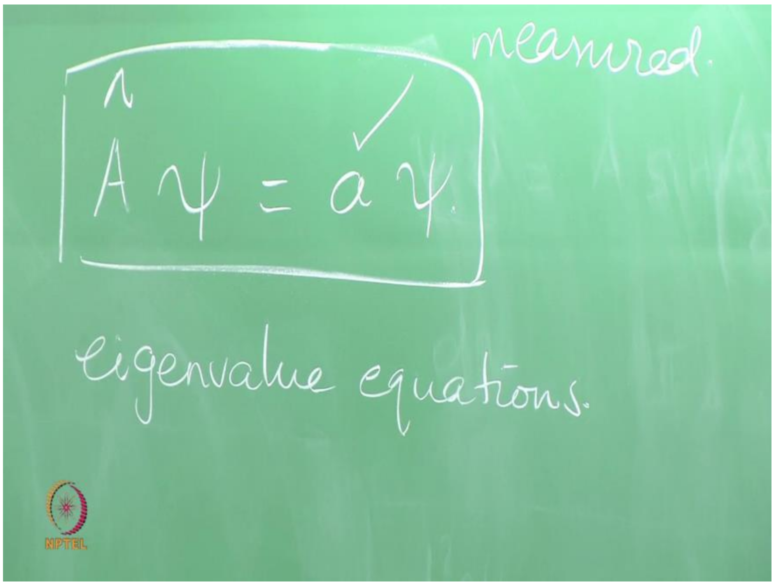

Suppose, instead of h any other operator, that we are going to look at, A psi, any operator giving some constant times psi. Please remember, this constant has to have the same dimension as the operator A here in the same way, that this constant has the energy dimension for the Hamiltonian operator, which is also energy. Any such equation in which A can be measured experimentally, such equations are called Eigen value equations, Eigen value equations.

And the Schrodinger equation, the time independent Schrodinger equation is the Eigen value equation for the Hamiltonian or the energy operator. This is the picture that you have to have. So, let me give you some small problems associated with whatever we have done right after this, but then we will go to the next part, namely, how do we solve this for the specific case of a simple model?

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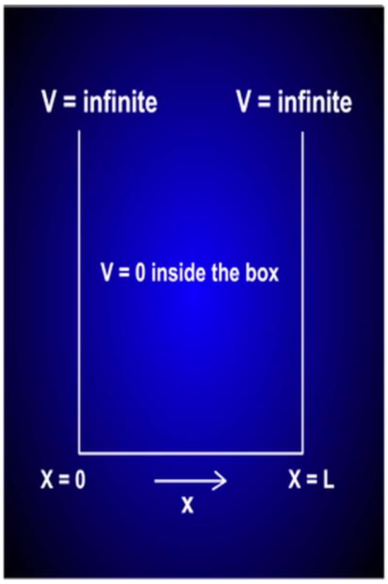

Now, what is the model? Let us look at the model now or the particle-in-a-one-dimensional box. I have a small drawing here that tells you, that we have a particle in a finite region. The potentials are infinite at two points, namely, points with x equal to 0, and the point x is equal to L meaning, that the particle is confined to a region of a box of length L, and the particle motion or the particle coordinate is only one coordinate or one variable, namely x. Let us assume for the time being, that the potential inside the box is 0.

So, this is what we call as the particle-in-a-one-dimensional box with infinite barriers. And what does this particle give you?

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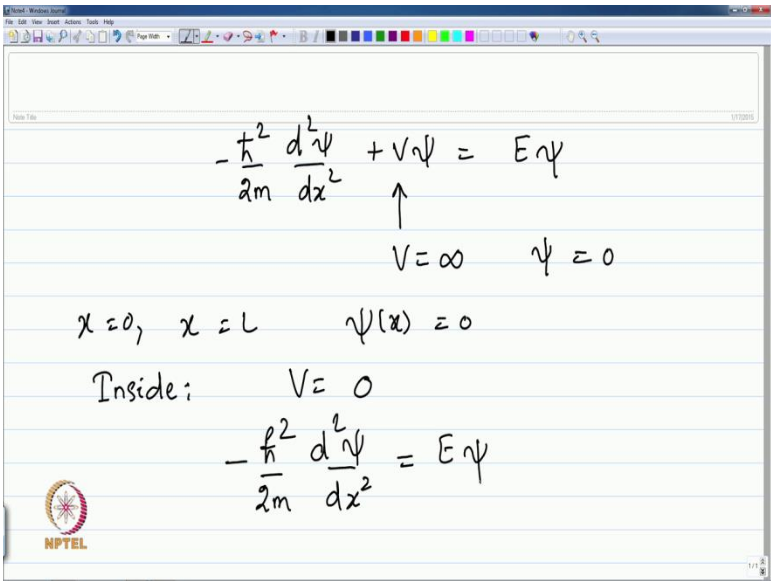

Now, let us look at the equations. We have minus h bar square by 2 m d square psi by d x square plus v of psi is equal to E of psi. If the potential is infinite, then psi has to be 0 in order to satisfy that. Therefore, at the boundaries x is equal to 0, x is equal to L, the wave function psi of x is 0. Inside the box we have V is 0, therefore what we have is minus h bar square by 2 m d square psi by d x square is equal to E psi, the total energy, because there is no potential inside the box.

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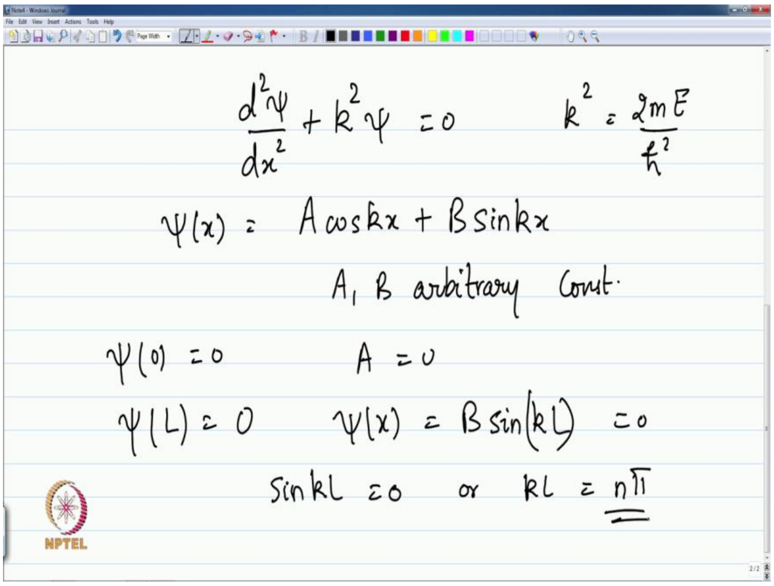

We shall solve this in very quick manner, namely d square psi by d x square plus a constant, a positive constant, k square psi is equal to 0, where k square is 2 m E by h bar square. This is, the k square is positive, obviously. And therefore, what you have here is a simple derivative equation for second order. And you know, such functions can be obtained, the solutions can be obtained from either trigonometric function or the exponential with imaginary argument.

Let us use the trigonometric function, namely A sine plus, write to that, to be consistent, we have A cos k x plus B sine k x, where A and B are arbitrary constants; arbitrary constants. Now, if you look at that solution with the boundary condition, that you have, namely psi of 0 is 0, immediately you have A is equal to 0 because cos k x is 1 and sine k x goes to 0, therefore A is equal to 0. If you have psi at L, which is the other extreme of the box, please remember this model at x is equal to L at this point, therefore we have psi of L is 0, which implies, that since A is already 0, psi of x is B sine k L and that is equal to 0.

We do not want B to be 0 because if A and B are 0, that is, anyway it is a trivial solution for any such differential equation, does not give you any, anything of interest, I mean, there is no meaning, there is no interpretation. Therefore, we are going to consider the case, obviously a non trivial solution with B not equal to 0, which means, sine k L has to be 0 or k L has to be an integer times pi, n is an integer.

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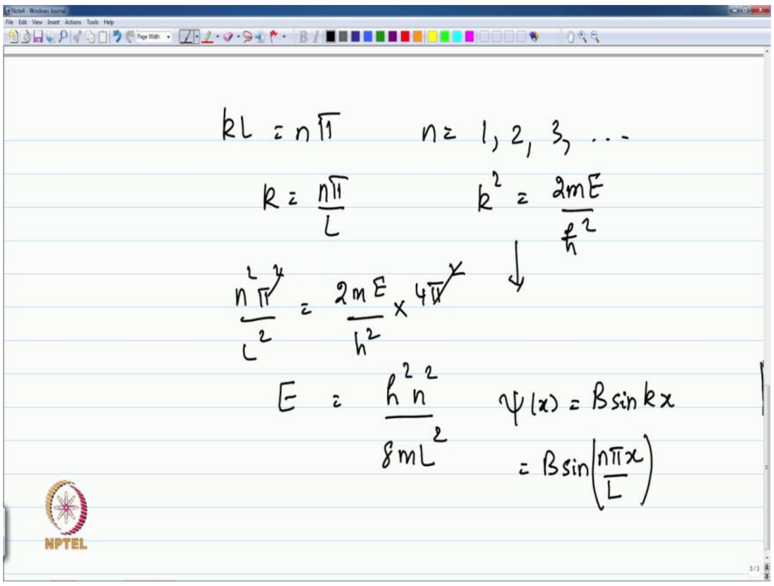

k L is equal to n pi and n has to be, obviously we do not want n equal to 0, which is also the case of triviality. And so, what we have is n equal to 1, 2, 3, etcetera, integers or please remember, k is equal to n pi by L. Look at this k square, if you recall, is 2 m E by h bar square. Therefore, this gives you immediately, that m square pi square by L square is equal to 2 m E by h square times the 4 pi square, that we have cancelled things of, and you immediately get the solution, namely E is equal to h square n square by 8 m L square.

And what is the solution for the wave function? Psi of x is B sine k x, which is B sine n pi x by L because k is n pi by L. So, this is the simplest solution, but two important results. One is, that the energy for the particle in the box, which is subject to boundary conditions that the wave function vanishes at some boundaries, subject to that the particle energy appears to be quantized, is not arbitrary.

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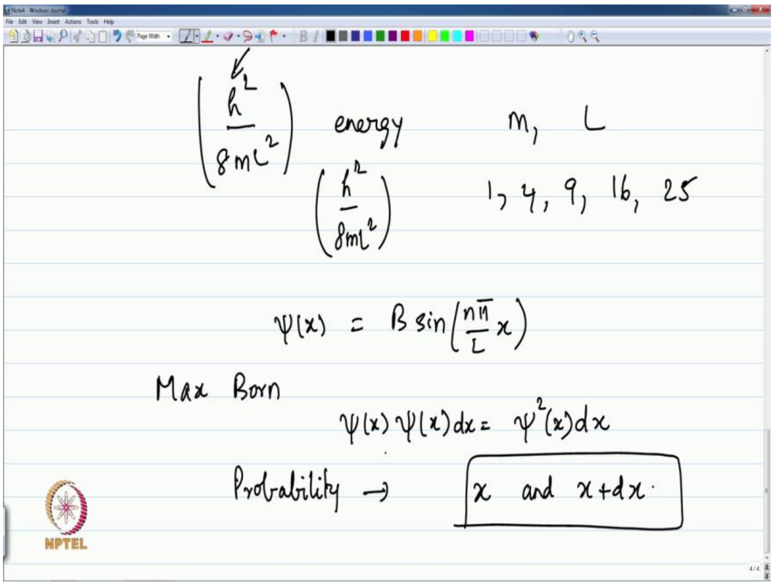

You recall, the dimension, the quantity h square by m square h square by 8 m L square the quantity has the dimension of the energy, and it has the only two inputs, which is, which are the inputs for this problem, namely the mass of the particle m and the length of the box L. And the other constant is, of course, Planck's constant.

So, now the energy seems to be quantized in terms of the two physical parameters, that we introduced, which particle, a larger, a heavier particle or a lighter particle in a smaller box or in the larger box, but with all the other conditions being the same, namely potentials being 0 inside, the potentials being infinite. Given that you see that the energy is discretized and the energy is in the units of h square by 8 m L square, this is the fundamental unit for this box, and then it is 1, 4, 9, 16, 25 as the value of n becomes 1, 2, 3, 4, etcetera. Now, for particle, particle energies are discretized.

The second part is the other, namely, the wave function is given in terms of B sine n pi x by L. Now, what is this wave function? From the beginning of this lecture you might think, that this wave function is essentially a function telling you how the particle is oscillating. That is not true, that picture was a starting point for us to get an idea that a Schrodinger equation is like this. The wave function that we have here is not a function representing how the particle is moving, it is just a function associated with that particle. What is the meaning of it? Max Born gave the interpretation namely, that wave function by itself does not have any meaning, but psi of x square psi star psi. In this case, psi is real, therefore psi of x, psi of x or psi squared of x.

In a small interval dx gives the probability of the particle being in the position between x and x plus dx. The probability of locating the particle between x and x plus dx, that is the number given by the product of the wave function, that itself in this case because it is real that Max Born suggested, that psi square x dx gives the probability, that the system be found in the interval x and x plus dx; that is all they are used to it.

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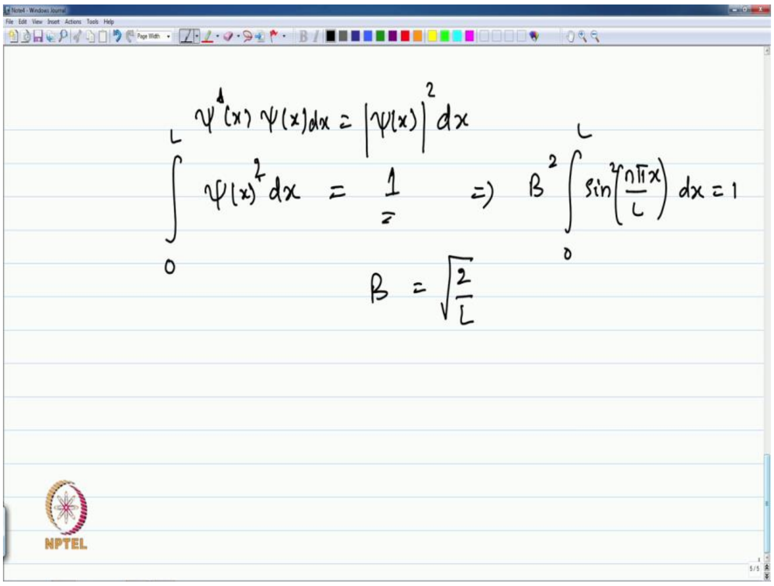

Therefore, let me conclude immediately what B should be because if psi star x psi x, which is the same as psi of x square with a dx is a probability. Then, if you add all the probabilities from 0 to L, because the particle can have any position between the n point, but not on the n point, from anywhere as close to the n point as possible, but as close to the other n point.

Therefore, if you integrate to the total probabilities, this being a continuous function, you have 0 to L psi x square dx. That probability has to add to one, because we have made sure that the potentials are infinite in our model, therefore the particle cannot be found outside of that region. Therefore, the probability that the particle stays inside the box is one. This gives you immediately a value for B, because you have B square sine square n pi x by L dx between 0 and L and that is equal to 1, which gives you a value B is equal to root 2 by L.

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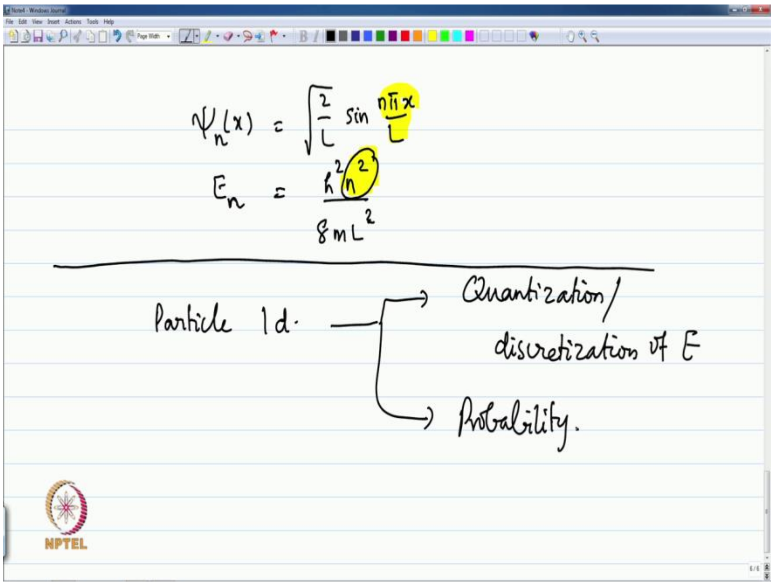

Therefore, you have got two results for the particle in the box, namely the wave function is root 2 by L sine n pi x by L, and E, the particle's energy is given by h square n square by 8 m L square. Now, because the energy is given by the quantum number n, let me use our highlighter here, because it is given by n, and n can take any number of values and for that n the corresponding wave function is sine n pi x by L.

We see that there are many solutions to the wave function and many solutions to the energy. This will also turn out to be a general property when we solve the Hamiltonian equation, the Schrodinger equation for the systems in, on the other models, that in one step you will get all these different types of all the possible energies and all the possible wave functions. And the best way to, I mean a convenient way, I would not call it a best way, a convenient way is to label the wave function with the quantum number psi n of x n E n for a given quantum number n.

So, let me summarize and then stop for this lecture, namely the particle-in-a-1-d-box, has two results: a quantization of energy or discretization due to boundary conditions and of energy E, and a probability statement for determining the position of the particle in the box at various locations.

Let us continue this in the next part and complete the remaining, that we needed to do in terms of, what are called, measurables and then how do we interpret this probability and so on, for various values. We will do that in the second part, until then, thank you.