Chemistry I – Cy1001
Introductory Quantum Mechanics and Spectroscopy
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Lecture - 03
Schrodinger Equation Particle-in-a-one-dimensional box

Welcome back to the lecture for the introductory chemistry using Schrodinger and quantum mechanical methods for the atomic structure. So, what we will do in this and 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.

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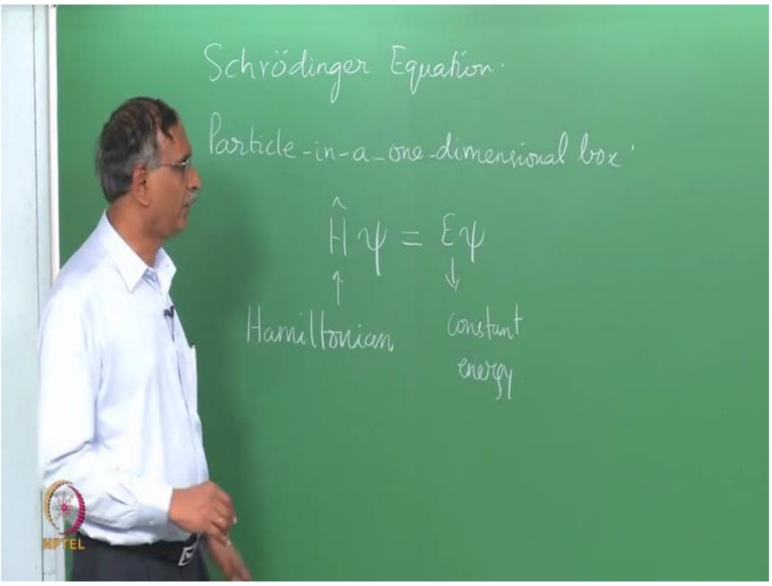

Let us take a quick look at the Schrodinger equation, in the lecture earlier I mentioned that I would be talking about the time independent Schrodinger equation in which this quantity was referred to as the Hamiltonian and this as an constant, but with the dimensions of energy and the function psi is 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.

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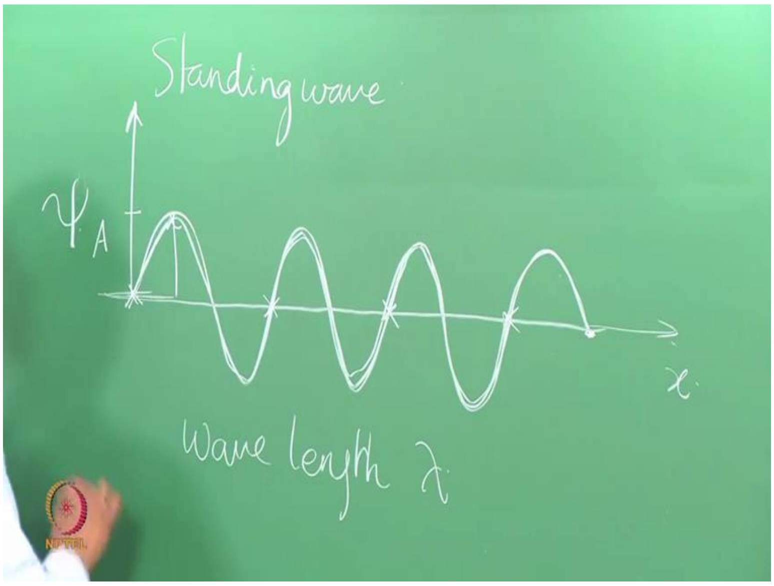

We can do a very simple example of a standing wave and you know that a standing wave is something that happens between fixed points and the wave motion of a particle fixed to the end; something of that kind and let me put it precisely so that the wave, when it reflects it still follows and therefore, the standing wave remains as a wave and the amplitudes do not cancel each other. So, 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 wave length 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 wave length or a full wave length for this to be a standing wave. Now 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 this psi that we talk about, but for that psi; if we have the maximum amplitude as A; this quantity A. Then the wave functions psi of x is written as A sin 2 pi by lambda of x, this is something that you are familiar with for a standing wave.

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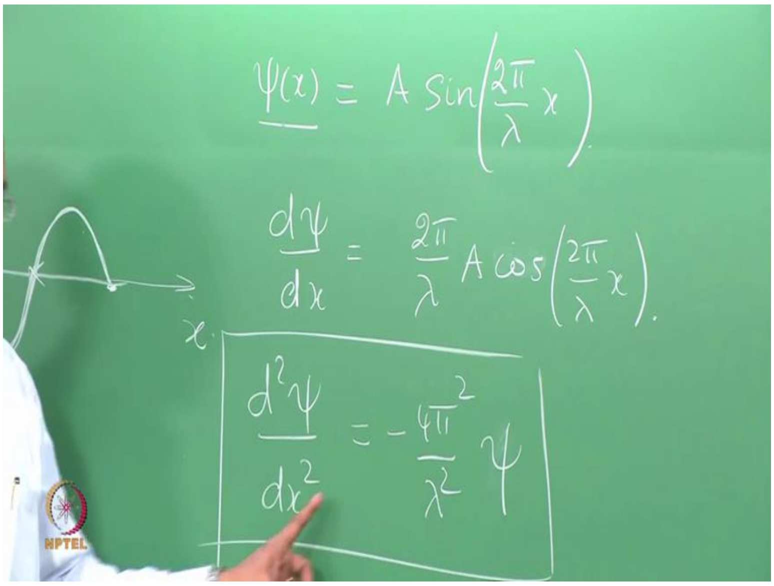

Now, this quantity psi when you differentiate twice, it satisfies the derivative equation. Let us do that for the first derivative d psi by dx as 2 pi by lambda times; A cos 2 pi by lambda x and the second derivative d square psi by dx square is equal to minus 4 pi square by lambda square; psi of x because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

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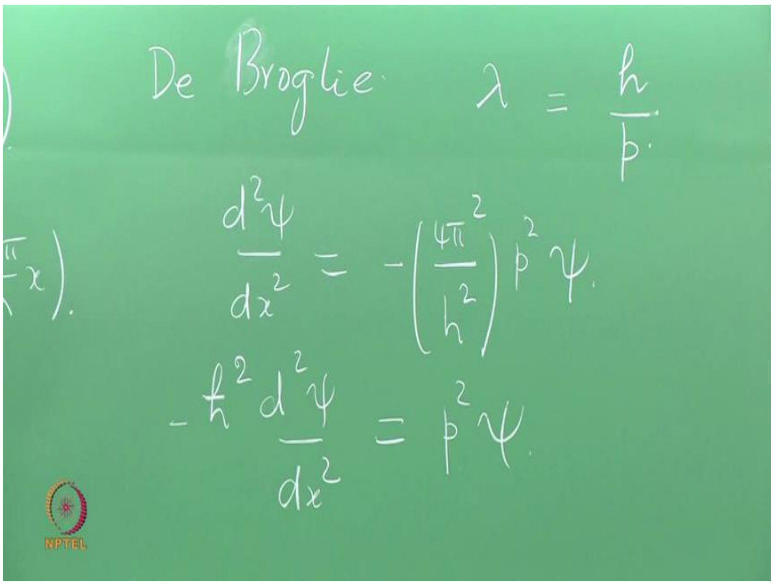

Now, De Broglie if you remember in the lecture earlier gave an expression for the matter waves lambda in terms of the momentum of the particle you have here therefore, if we write the wave equation it is d square psi by dx square which is equal to minus 4 pi square by h square, multiplied by p square psi or minus h bar square, we know that h by 2 pi is h bar. Therefore, we bring that in this minus h bar square, d square psi by dx 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 same thing as the second derivative on the wave function multiplied by minus h bar square.

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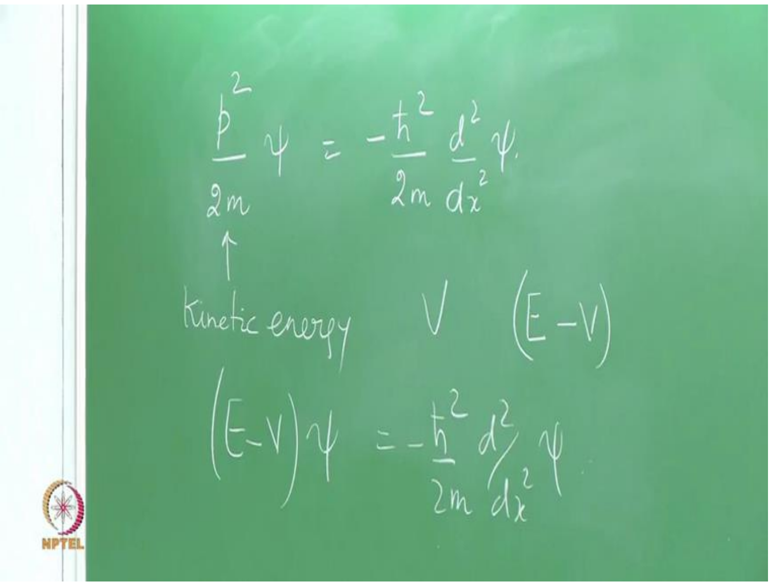

Therefore, if we write the kinetic energy p squared by 2m psi that turns out to be minus h bar square by 2m d square by dx squared psi. This being the kinetic energy, this is the difference between if there is a potential energy V, then it is a difference between the total energy e and the potential energy V, which may be a function of x for whatever, if there is a potential we have to consider that therefore, what happens is p squared by 2m is nothing but e minus V on psi giving you minus h bar square by 2m d square by dx square psi. Now one last step and then you see the equation h psi is equal to e psi making sense to us.

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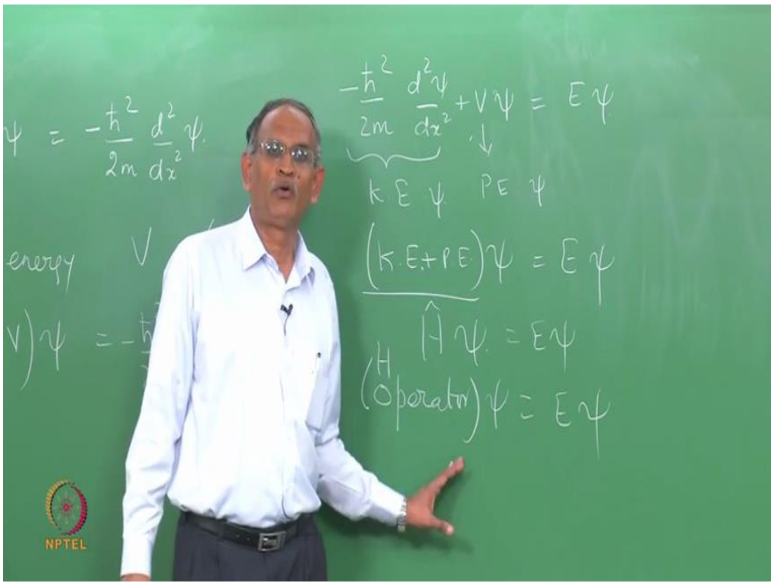

Because now if you bring the V here; just rewrite the equation you have minus h bar square by 2m d square psi by dx square plus V of psi is equal to e of psi. Please remember, we had already written this as the kinetic energy and this is on psi, this is the potential energy on psi and therefore, you see that this is nothing but kinetic energy plus potential energy on psi giving you a constant times e psi and 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 fixture 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 2m that we have; now we have put a derivative here and therefore, the Hamiltonian is a derivative acting on the wave function and the potential which is of course your function of the position of whatever particle of the system that you talk about, the differential generally multiplies the wave function, but the two together is actually an operator acting on sorry; to be 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 equation for whatever quantities that appear here.

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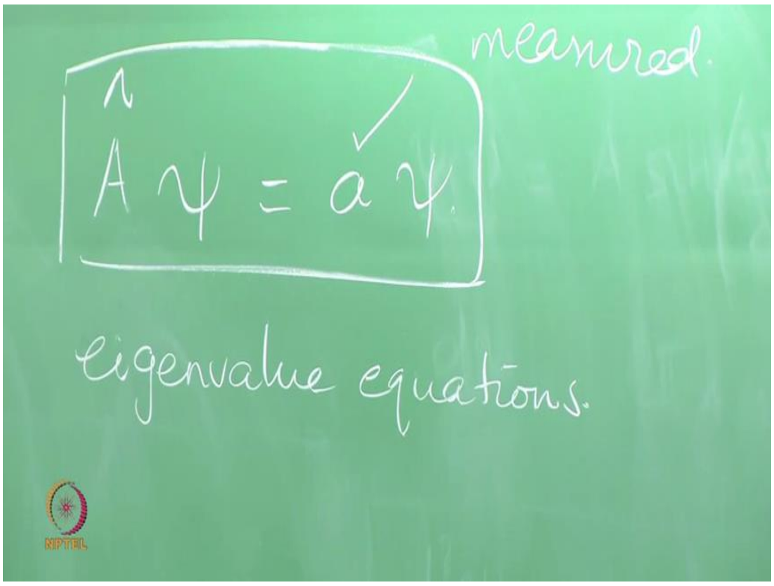

Suppose instead of h, any other operator that we are going to look at; A psi, any operator giving some constant time psi. Please remember this constant has to have the same dimension as the operator A here. In the same way that this constant has the energy dimensions for the Hamiltonian operator which is also energy. Any such equation in which a can be measured experimentally such equations are called Eigen value equations and the Schrodinger equation; the time independent Schrodinger equation is the eigen value equation for the Hamiltonian or the energy operator. Here this is the picture that you 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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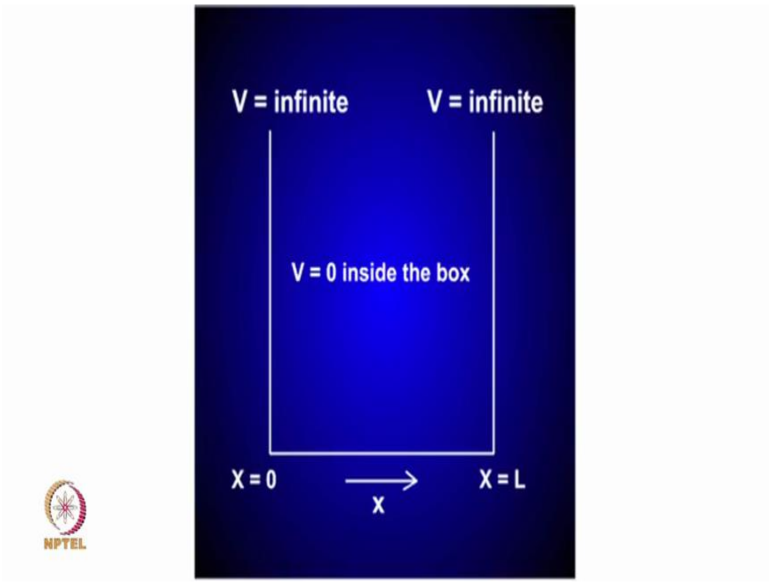

Now what is the model? Let us look at the model now of the particle in one dimensional box. I have a, small drawing here that tells you that we have a particle in a finite region. The potentials are infinite at two points, namely points with X equal to 0 and the point X is equal to L; meaning that the 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 the one dimensional box with infinite barriers and what does this particle give you.

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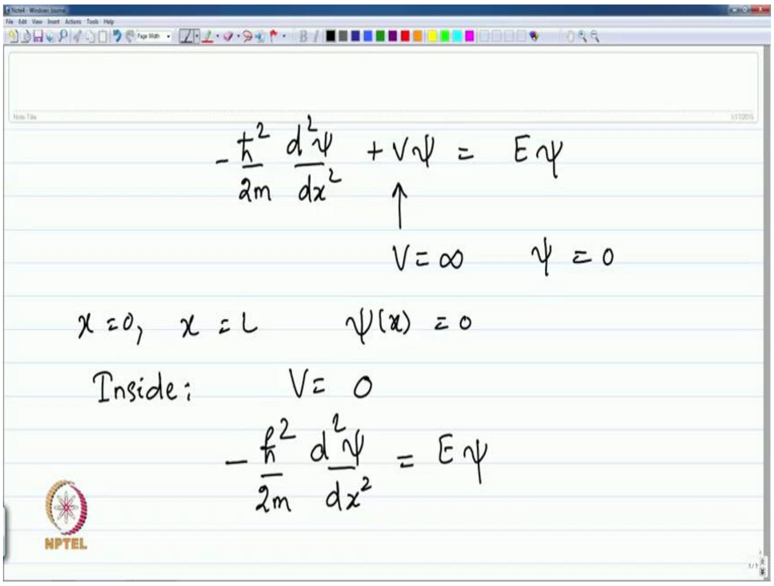

Now let us look at to the equations, we have minus h bar square by 2m; d square psi by dx square plus V of psi is equal to E of psi, if the potential is infinite then psi has to be 0 in order to satisfy that. Therefore, at the boundaries; x is equal to 0, x is equal to L; the wave function psi of x is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

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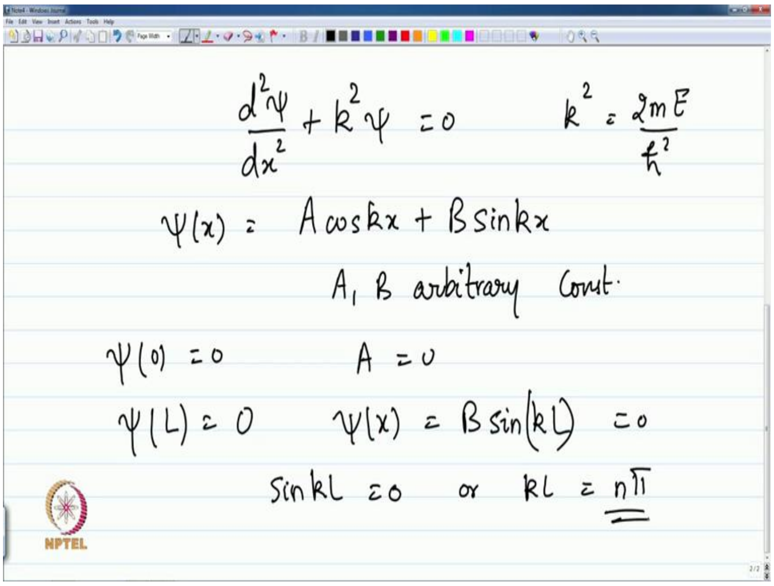

We shall solve this in a very quick manner; namely d square psi by dx square plus a positive constant k squared psi is equal to 0 where k squared is 2m E by h bar square, this is the k square is positive; obviously, and therefore what you have here is a simple derivative equation for second order and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

Let us use the trigonometric function namely A sin; let us write that to be consistent, we have A cos k x plus B sin k x; where A and B are arbitrary constants. Now if you look at that solution with the boundary conditions that you have; namely psi of 0 is 0, immediately you have A is equal to 0 because cos k x is 1 and sin 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 sin k L and that is equal to 0. You do not want B to be 0 because if A and B are 0 that is anyway that is a solution for any such differential equation does not give you anything of interest; I mean there is no meaning, there is no interpretation. Therefore, we are going to consider the case; obviously, a nontrivial solution with B naught equal to 0, which means sin k L has to be 0 or k L has to be an integer times pi; n is an integer; 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.

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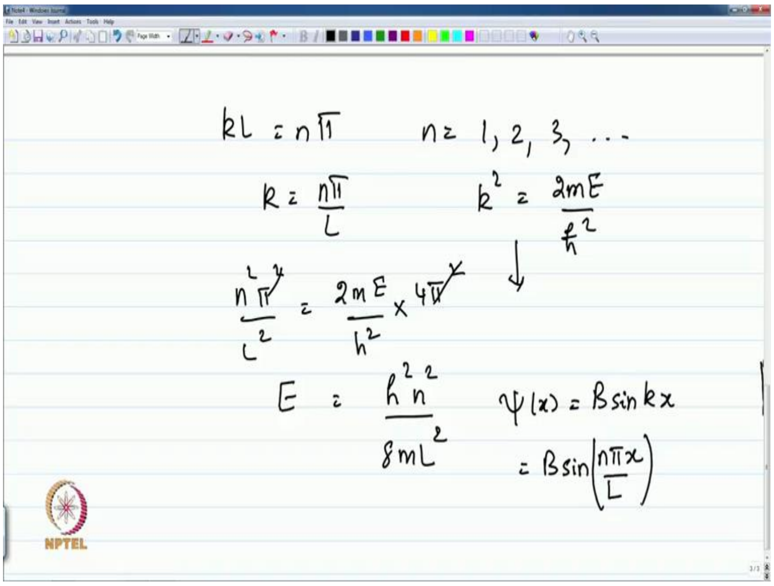

Or please remember k is equal to n pi by L; look at this k square if you recall is 2mE by h bar square. Therefore, this gives you immediately that n square pi square by L square is equal to 2mE by h square times the 4 pi square that we have cancel things off and you immediately get the solution namely E is equal to h square n square by 8mL square and what is the solution for the wave function? Psi of x is b sin k x which is B sin n pi x by L beacuse 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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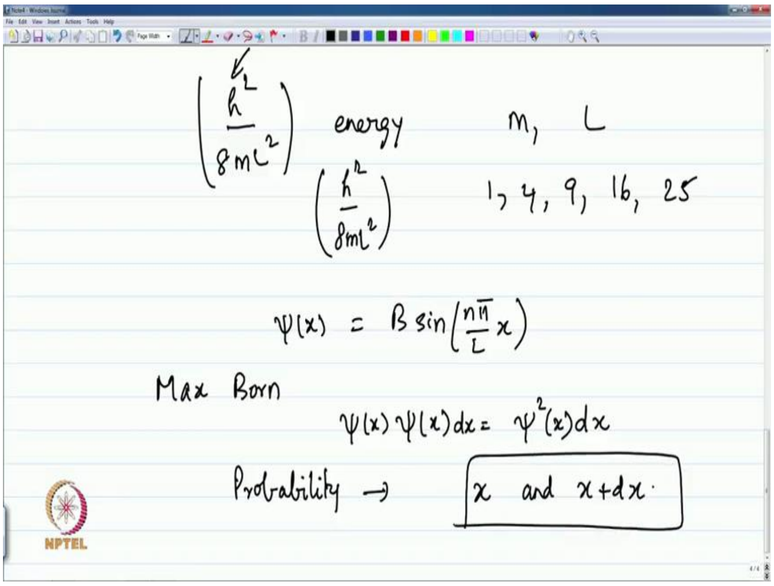

You recall the dimension the quantity h square by n square, h square by 8mL square the quantity has the dimension of the energy and it has the only two inputs which are the inputs for this problem; namely the mass of the particle M and the length of the box L and the other constant is of course, Planck's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

So, now the energy seems to be quantized in terms of the two physical parameters that we introduced which particle a larger particle, 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 energy is in the units of h square by 8mL 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, therefore the particle energies are discretized.

The second part is the other namely the wave function is given in terms of B sin 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 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 sized or 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 with itself in this case because it is real that Max Born suggested that psi squared x; dx gives the probability that the system be found in the interval x and x plus dx. That is all, there is to it.

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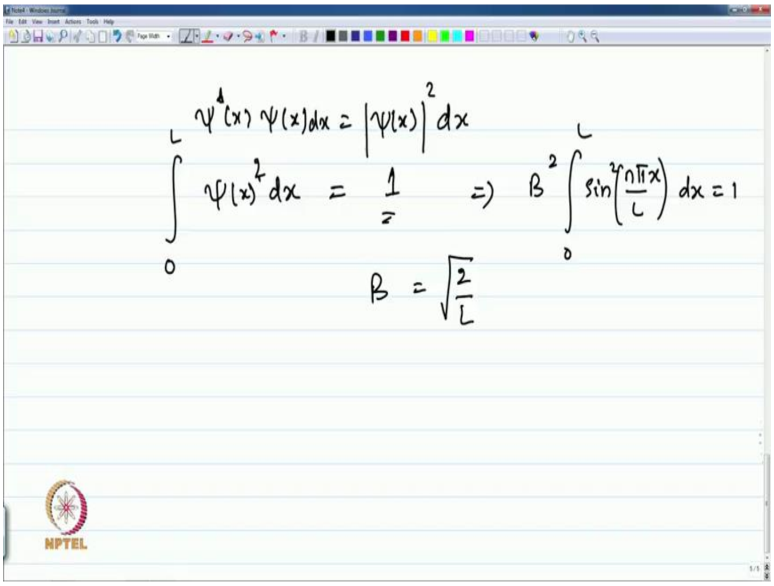

Therefore, let me conclude immediately what B should be because if psi star x, psi x which is the same as psi of x square with a dx is a probability then if you add all the probabilities from 0 to L because the particle can have any position between the end point, but not at the end point from anywhere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

Therefore, if you integrate to the total probability, this is being a continuous function; you have 0 to L psi x square dx, that probability has to add to 1 because we have make sure that the potentials are infinite in our model, therefore the particle cannot be found outside of the region. Therefore, the probability that the particle stays inside the box is 1. This gives you immediately your value for B because you have B square sin 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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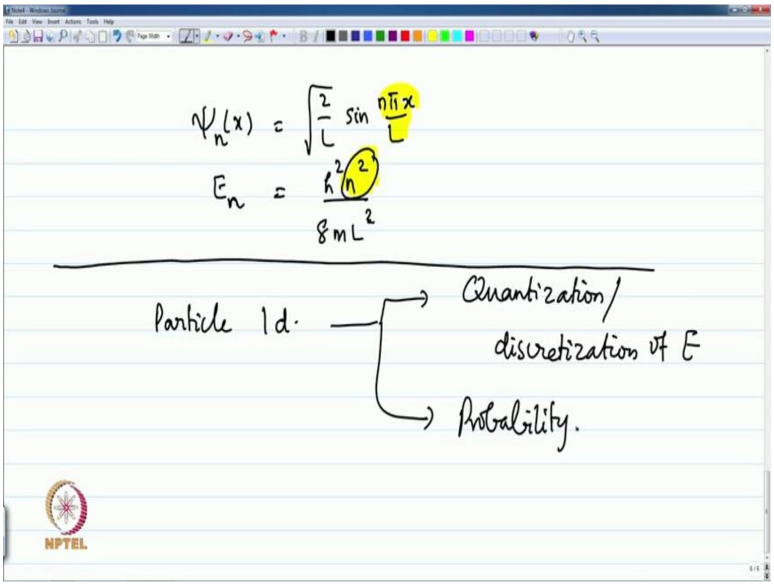

Therefore you have got two results for the particle in the box; namely the wave function is root 2 by L sin n pi x by L; and E, the particles energy is given by h square, n square by 8mL square. Now, because the energy is given by the quantum number m, let me use a highlighter here because it is given by n and n can take any number of values and for that n, the corresponding wave function is sin 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, Schrodinger equation for the systems in all the other models that in one step, you will get all the possible energies and all the possible wave functions and the best way to; I mean a convenient way, I will 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 1d 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 need to do in terms of what are called the 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.