Quantum Physics
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Lecture No. #09

Let's go on to the problem of particle in a 1 D box.

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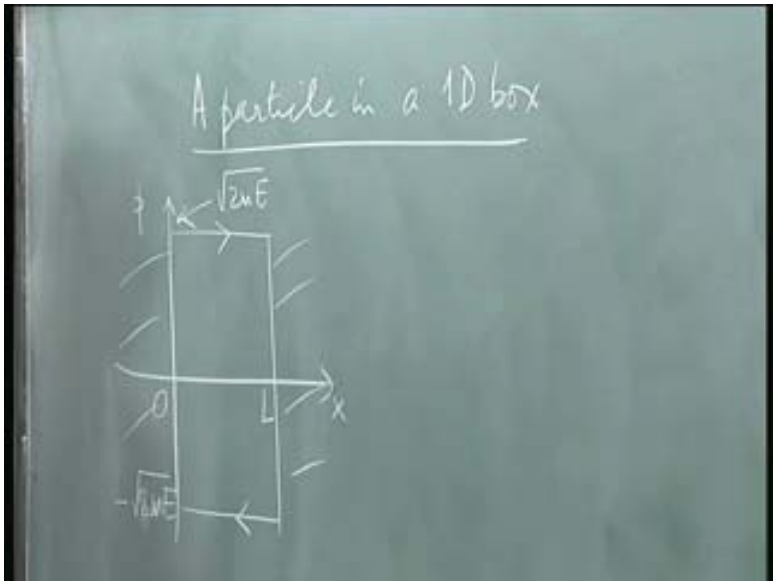

This is a free particle which is moving back and forth in a one dimensional box. And if you recall classically, we plot x versus p the phase trajectories are just little sizes of rectangles. This is – root 2mE (Refer Slide time: 01:46). This is root 2mE. The regions on either sides of the box are forbidden. Let L be the length of the box along the x axis.

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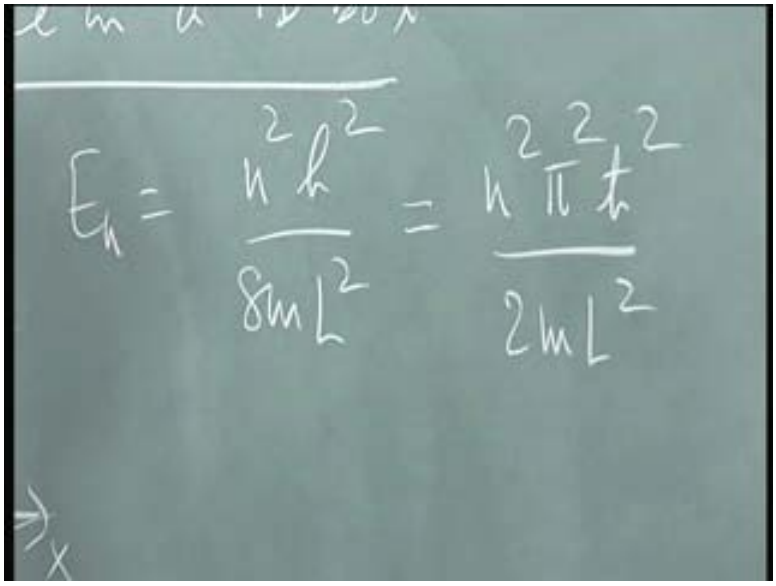

The original Bohr quantization gave us a set of discrete energy levels and these energy levels were given by E_n = n squared h square over 8 m L squared which I prefer to right as n squared pi squared h cross squared over 2mL squared where h cross is h over two pi. So this gave us a set of quantized energy levels. Now let us solve the Schrodinger equation and find out what the actual energy levels are. I would expect the result that we get to merge with result for sufficiently large n when n becomes much greater than 1. But it will turn out that it is actually true for all n (1, 2, 3, etc).

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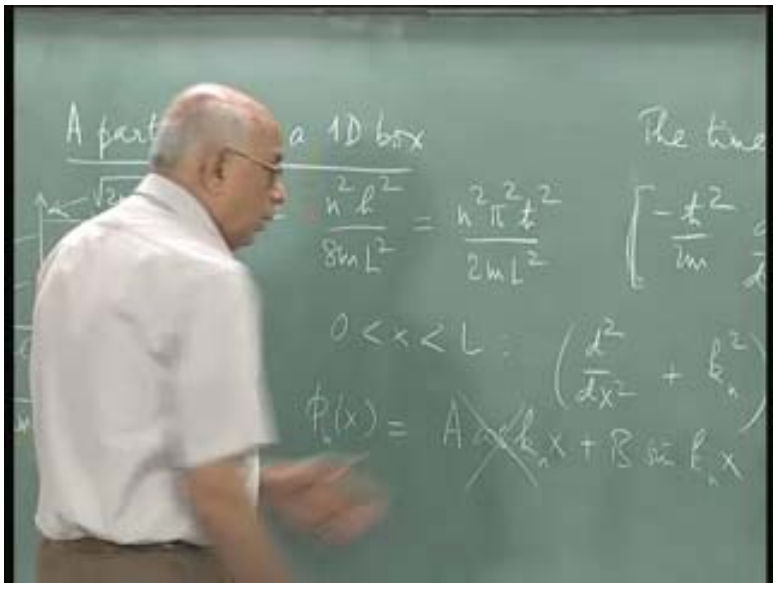

The time independent Schrodinger equation is - h cross squared over 2 m, since we talking about one dimension, it is just d 2 over dx 2 + V of x the whole thing acting on phi $_n$ of x = E_n phi $_n$ of x. t V of x is 0 inside the box its infinite outside the box. So let's look at what happens inside the box; 0 > x > l. we have d 2 over dx 2 + kn squared phi $_n$ of x = 0 where kn squared is 2 m E_n over h cross squared. The solutions to this are trivial. This is just the simple harmonic equation and therefore phi n of x is of the form Acos k_nx + B sin k_nx. Notice that we should write down the general solution. So it's a superposition of all possible linearly independent solutions.

Now we have to impose boundary conditions at 0 and l. It should be continuous but that's not sufficient. It should be 0 at the boundaries because it's an infinite barrier. The probability of finding the particle outside the box is 0. So at the boundaries, the condition we will impose are phi n of 0 = 0 = phi n of L. this is going to determine the spectrum. Had we changed some of the boundary conditions, you get another spectrum. And of course you put at x = 0, we get A=0 and we are left with B sin k_nx.

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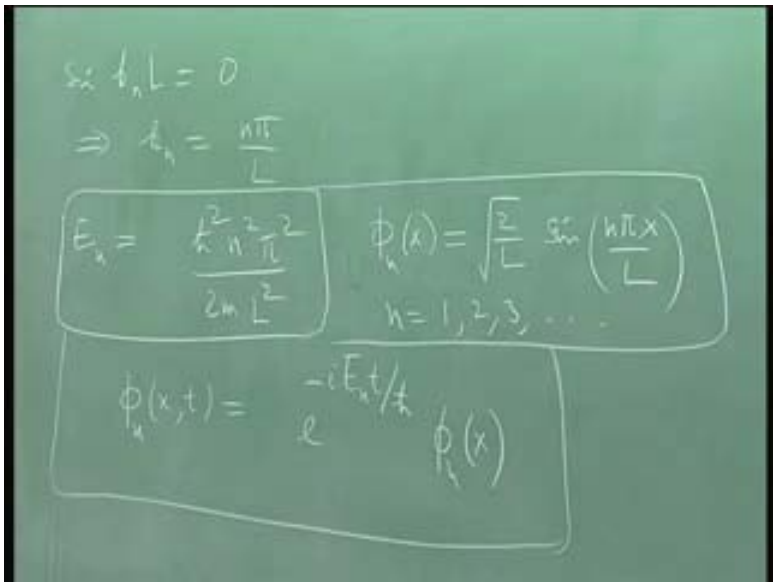

Imposing the other boundary condition says that sin k_n L = 0, unless B is also identically 0. But if B is 0, then you can't normalize the solution. Because we would also like to have the normalization condition 0 to L dx B squared sin square k_n x to be equal to 1 since you want the total probability of finding the particle inside the box to be equal to unity at all times.

So that says that sin k_n L = 0 which implies that k_n equal to n pi over L. therefore if you put this in, you immediately get the E_n = h cross squared times n squared pi squared over 2 m L squared. So these are the exact energy levels which were also got by the Bohr quantization rule. Now in this particular problem, the problem is so simple that the Bohr rule actually gives the exact answers because there is no potential inside and it's infinite outside. So it's not quite an accident. There are reasons why this should be so. But we

will see this later on why in this particular instance, the Bohr quantization rule actually gave the exact Eigen values. Corresponding to this, you have phi n of x = B times sin n phi x over L. but this B should be normalized by the rule. Please notice that this wave function is arbitrary up to a phase factor because the normalization only fixes modulus phi n squared of x up to a constant.

So its mod B squared and B could be a complex number with a phase factor and that's not showing up in this wave function at all. It's actually irrelevant because as we will see for all physical quantities, the phase factor multiplying the normalization is irrelevant. Choosing that to be real, this phi n of x turns out to be 2 over L sin (n pi x over L). The allowed values of l is 1, 2, 3 etc. why i chose only the positive integers is because it doesn't matter. Since sin n phi x over L is - sin - n pi x over L. so if n were negative, you would get the same way function over again with just a multiplicative factor

So it's not linearly independent. Notice the energies are actually proportional to n squared. So it really doesn't matter whether n is positive or negative which is the reflection of the fact that sin pi and - sin pi are linearly dependent on each other, just multiplying by a constant. We don't include 0 because then, the wave function would vanish everywhere and if it vanishes everywhere, it can't be normalized to unity. Therefore the allowed values are just n = 1, 2, 3 etc till infinity. Now what is the time dependent state, phi n of (x, t)? It's just e power - iE_n t over h cross phi $_n$ x. it just has this phase factor multiplying it. So this specifies completely the state of an energy eigenstate or the Hamiltonian eigenstate for this particle in a box problem. Now I have several questions to ask.

Are the energy levels degenerate or non-degenerate? Is there a unique state associated with each energy level or is there more than one state associated with it? It's unique and there is no degeneracy in this problem. This is a typical of one dimensional problem and there is no degeneracy in. the reason is rather deep. Degeneracy is a reflection of symmetry in the problem in general continuous symmetry. There is no continuous symmetry in this problem at all.

Later when we look at three dimensional problems, then you would have rotational symmetry. It's a continuous symmetry and associated with it, you would have degeneracy because system would be invariant under rotations of the coordinates axes. In one dimension, there is no question of any rotation at all. The second question is why doesn't Planck's constant appear anywhere in this (Refer Time Slide: 12:04) wave function. After all it's a quantum problem.

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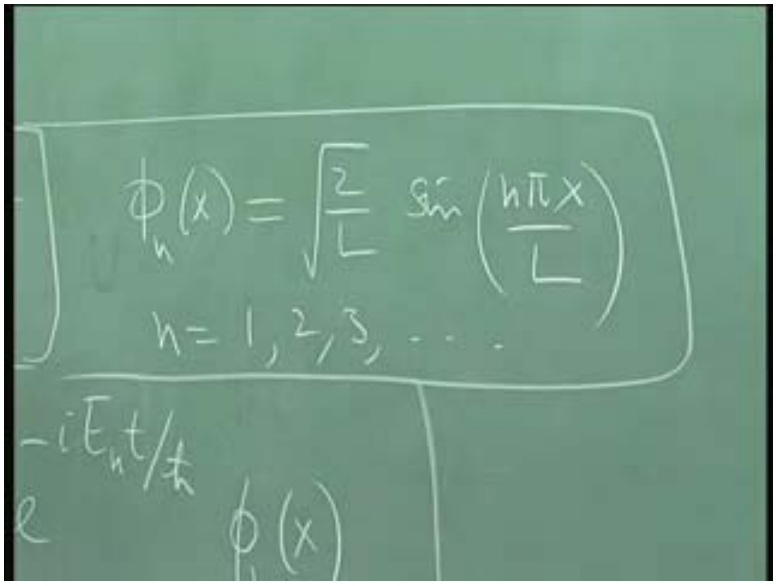

It's purely for dimensional reasons. What are the physical parameters and constants in this problem? The energy is not a constant since it changes. L and m are parameters. Since there is no relativity, c is absent. There is no gravity so G is absent and since you are working at T = 0, the Boltzmann constant k is absent. The only constant that can appear here is the Planck's constant. The wave function outside the box is 0.

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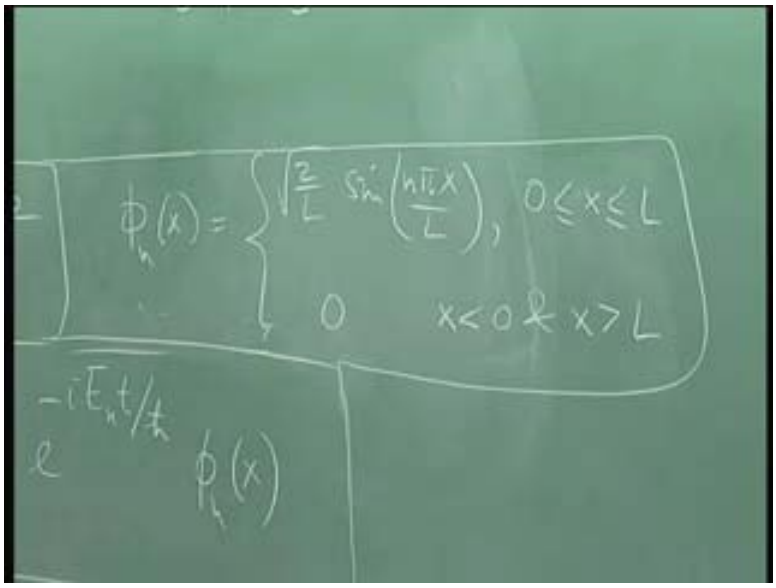

Phi n = root 2 over L sin (n pi x over L); 0 less than equal to x less than equal to L. It is 0 in the region x less than 0 and x greater than L. that's the exact solution

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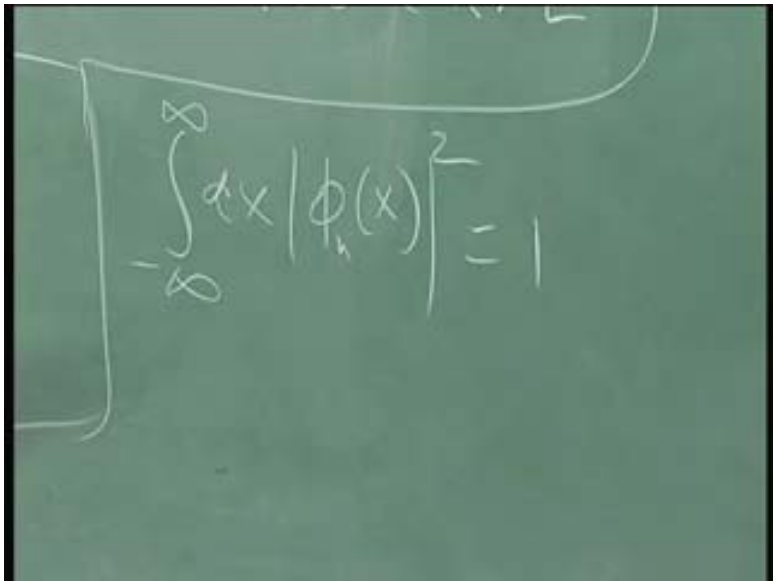

Now the normalization constant of course says - infinity to infinity, dx phi n of x the whole squared = 1. And of course the integral is only from 0 to L because phi n of x is identically 0 outside the box. So what does this imply for the physical dimensions of phi n of x?

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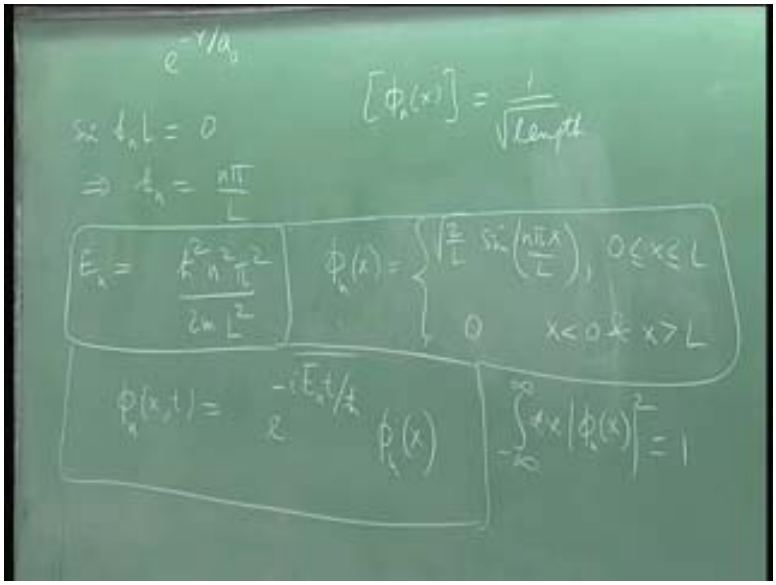

So this must be one over square root of length because when you square it this must be equal to probability which is one. Why doesn't Planck's constant appear anywhere inside here (Refer Slide Time: 16:12)? The argument of the time cannot have dimensions because the sin is a power series that goes all the way to infinity. Therefore sine of

anything cannot be dimensional. So you have an x and that must be compensated for by an L. If you have any Planck's constant appearing, there is a time that appears in the problem and there is no other parameter of time or with dimensions of time involved in it to cancel that.

This is the reason why Planck's constant doesn't appear in the wave function. If you look at the hydrogen atom problem, then Planck's constant would appear even in the wave function. Now what does the ground state of the hydrogen atom look like? The wave function is spherically symmetrical. So it goes like e to the - r but it can't go precisely like e to the – r. there must be something else which compensates it or divided by some length. It's a_0 and it's the Bohr radius. So a quantity of dimension length is formed automatically but the hydrogen atom is not inside the box. It's the average distance and so a_0 must come from some fundamental constants. It can't come from r. so it must come from the parameters in the problem. What are the analogs of L m and h? The charge of the electron, e, the mass and Planck's constant would play a role.

The speed of light in vacuum is the fundamental thing. Even though it's non-relativistic, as soon as the electricity and magnetism comes in, the speed of light is going to play a role. So the time in the Planck's constant can be cancelled by the time in the speed of light, c. in fact it appears always as a c h cross because the t inverse in c is cancelled by the t sitting in the Planck's constant always. We don't have Boltzmann constant because we work at t = 0. The gravitational constant also doesn't appear. So, from these quantities you can form a quantity of dimensions length and that will play a role. That's not a_0.

Therefore Planck's constant does appear in the wave function. It generally does but in this particular problem, the particle in a one dimensional box, there isn't another dimension parameter with time involved in it and that's the reason why it can't appear in the wave function. Now that we have the wave function in place, we can write down what a general solution is going to be. It will be a super position of all these quantities. So that's become a trivial matter first of all, is this a momentum eigenstate? If it were a momentum eigenstate then it must obey the following rule. Momentum operator acting on the wave function must give you number times wave function.

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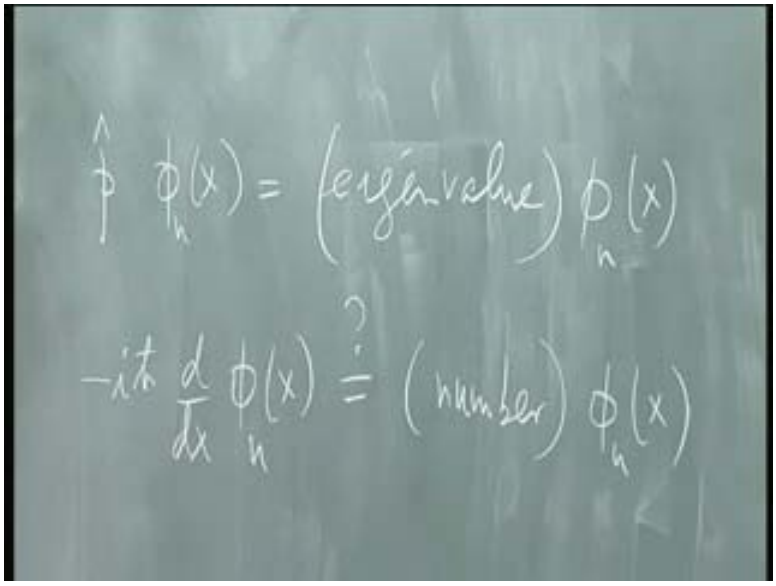

It means the momentum operator p acting on phi n of x must give you the eigen value corresponding to the momentum. Now what's momentum operator represented by? It is represented by - i h cross d over dx phi n of x and the question is, is this equal to number times phi n of x is? The phi n of x sitting there is a sine function. It's definitely not an eigenstate.

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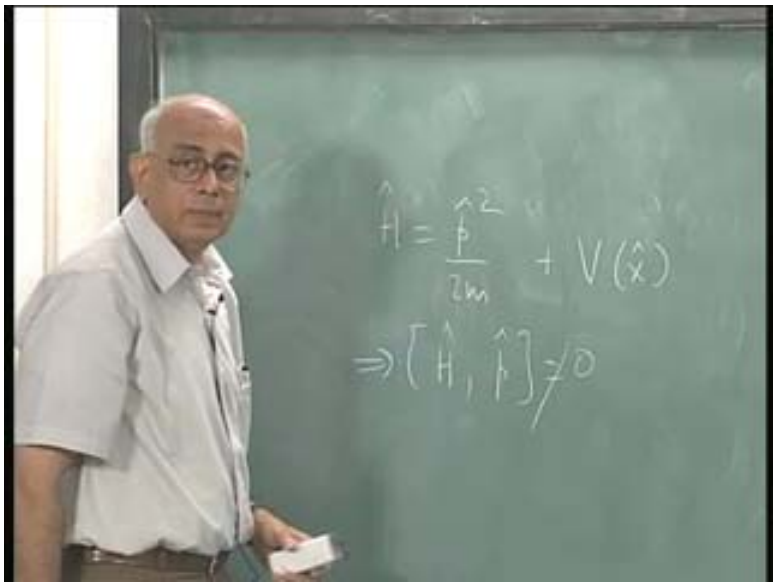

This is a free particle and there is no potential. So the Hamiltonian is just p squared over 2 m which would imply that the Hamiltonian commutes with p. but we just found out that the energy eigen states are not momentum eigen states. What's the resolution to the

paradox? p commutes with p squared. So this this is this is one definitely 0 the h is equal to this is definitely true but we just discovered that those states are not momentum eigen states.

So the paradox is the following. It appears as if the Hamiltonian in this problem is just kinetic energy so it's a free particle. It commutes with the momentum operator because p commutes with p squared and yet the energy eigenstates of the Hamiltonian are not momentum eigenstates. So it's not completely free. It's not true because this has a V of x sitting here (Refer Slide Time: 23:24).

It's so happens that V of x is 0 inside and infinite outside. It's not free. It's sitting inside the box. And then of course this is not true because this does not commute with that. So energy eigenstates are not momentum eigenstates unless the Hamiltonian is truly a function only of the momentum. It says V of x is definitely 0 for x between 0 and L and infinite for all other values of x. so it is not a constant. On the other hand on the other hand what would momentum eigen states actually look like. so let's say p on some state chi of x = eigen function times chi of x, so number p times chi of x. this would imply - ih cross d chi over dx = p chi. So chi of x is proportional to e to the ipx over h cross. sin theta can be written as e to the i theta + e to the - i theta.

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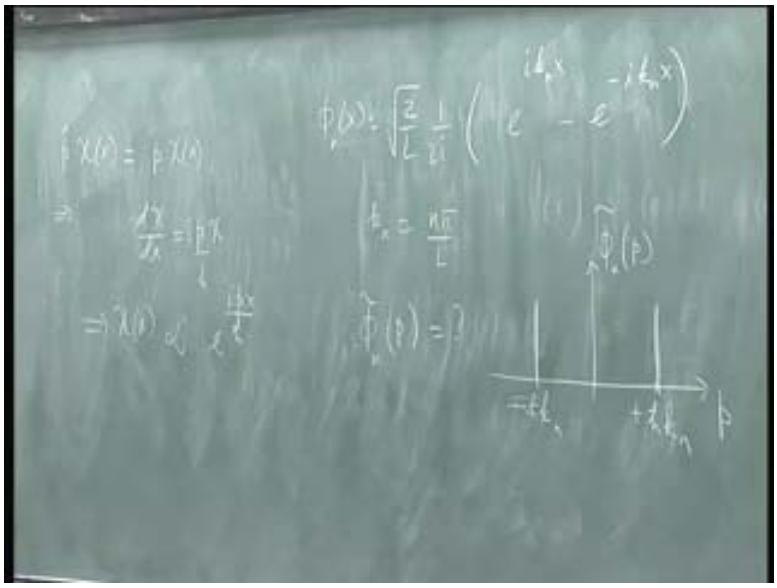

So I can certainly write the phi n of x as root 2 over L, 1 over 2 i times e to the power $k_n x$ - e to the - i $k_n x$ where k_n = n pi over L. so h cross k_n gives you the momentum eigen values. One of goes forward and the other goes backwards. Remember the particle is bouncing back and forth. So classically its momentum would have two values every times its moving forward, it has a value square root of 2 mE and when it's moving backwards, it has a value - square root of 2 mE. Quantum mechanically, the eigen functions of the Hamiltonian are indeed a super position of two apparently momentum eigenstates, one corresponding to the forward motion and the other corresponding to the

backward motion. So what does the momentum space wave function look like? What would phi n tilde of p look like? It would be a super position of two momentum eigen states, one of which has a momentum h cross k_n and the other - h cross k_n. so the distribution will look like two sharp values.

So here is - h cross k_n and here's + h cross kn (Refer Slide Time: 28:43) and it's not a momentum eigenstate. If it were an eigenstate, it would just be a delta function at that point but it's a super position of two eigenstates. So the delta function would be at the – h cross k_n and the +h cross k $_n$. so the important lesson is because the momentum does not commute with the Hamiltonian, a Hamiltonina eigen state is not an eigen state of the momentum in general but each eigen state can be written as a superposition of two plane waves. Looks like super position of two momentum eigenstates which is perfectly consistent with the classical picture but you see quantum mechanics is a very tricky subject. So what we should do is to check this if it's really true or not. i have already proved the wave function is square integrable. It's in L 2 and phi n of x is a member of L 2 but we just proved the theorem that if phi n of x is in L 2, phi n tilde of p should be also be L 2.

What would you do with something which is a delta function? They are not square integrable. The only way to settle this problem is actually to find the Fourier transform of this quantity and see what it does.

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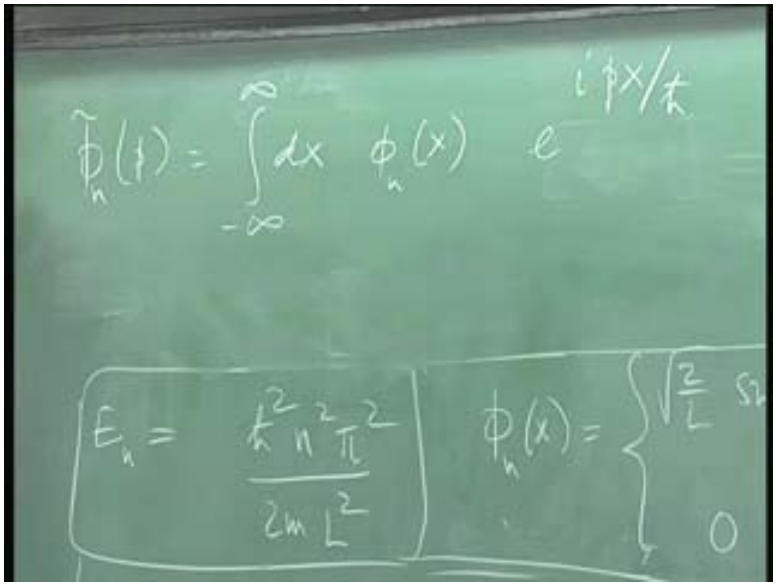

phi n tilde of p is integral minus infinity to infinity dx phi n of x multiplied by a phase factor which was the overlap function between x and p. so its e to i px over h cross.

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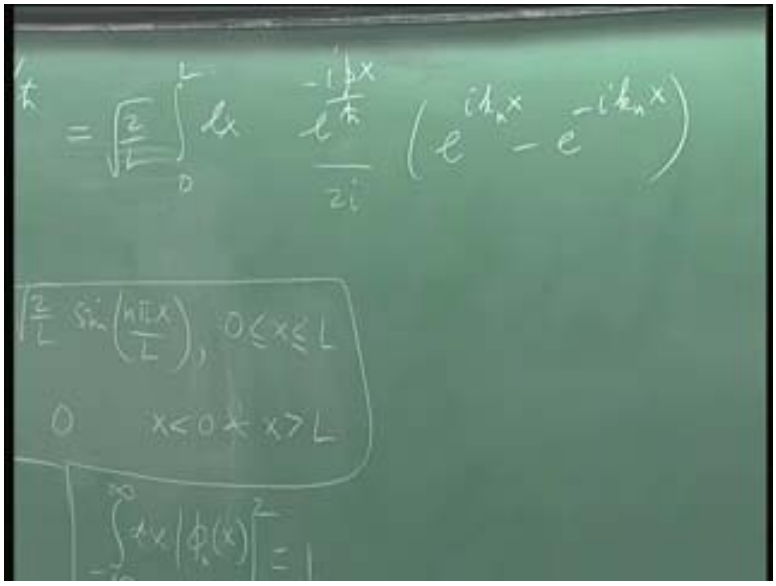

I should substitute for phi n of x and when I do that, the integral becomes 0 to L. had it been minus infinity to infinity, then each of the quantities gives you a delta function at p = plus or minus h cross k_n. but unfortunately or fortunately for us, it is 0 to L and so are not delta functions. e to the i kx integrated over x from - infinity to infinity is delta of k but you going to integrate over a finite range, so it's not true. That's why you must be careful to write the wave function as a sine function inside and zero outside.

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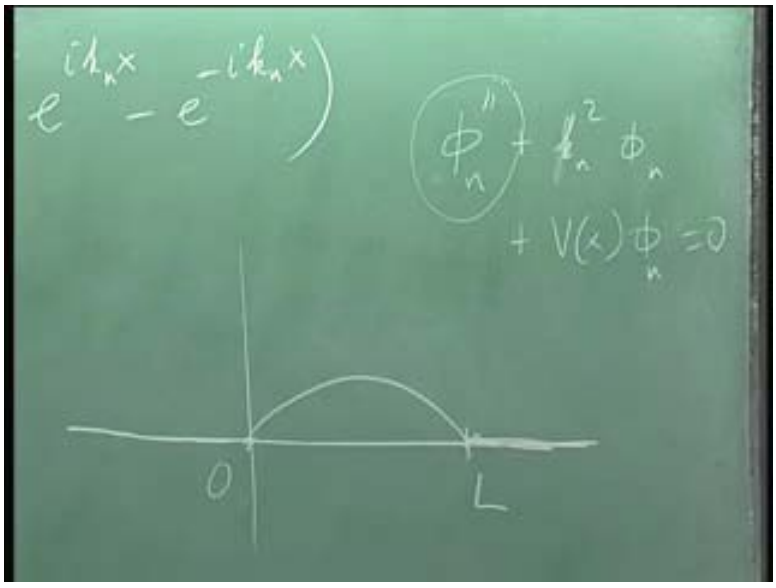

For instance, in the n =1 case, the wave function would look like this (Refer Slide Time: 33:43). The function is continuous at these points but the slope is discontinuous. So the second derivative of the wave function would have an infinite discontinuity at these two end points. The curvature is very different and the slopes are not continuous.

The wave function must satisfy phi n double prime + k_n squared phi n + V of x phi n = 0. it satisfies that but V of x has an infinite discontinuity at 0 and l. that's has to be compensated for by an infinite discontinuity in phi double prime. Otherwise the equation is not satisfied at the boundaries. After all, what's the meaning of a boundary condition anywhere in the in the natural science? You have an equation and you have some situation obtaining at the boundary, you want the equation to be valid at the boundary. So the difference between the two, you call it 0. That's what you mean by applying the boundary condition and that's exactly what's going on here. V of x has to compensate for phi n double prime of x. so the consequence of this is that the Fourier transform is not equal to a sum of two delta functions. It's some exponentials. That function will extend from p = - infinity to = + infinity. After all, you are familiar with the fact that if you take a very sharp pulse in time and you do Fourier analysis, it has a very broad frequency spectrum.

In fact, the pulse is infinitely spread out in frequency. And conversely if it's a monochromatic wave, then it goes like this from - infinity to infinity. So it's infinitely spread out. The more you try to press in one curvature, the more the other one spreads out and that's a basic fact of life, which in quantum mechanics is called the uncertainty principle. This means even in wave motion, except that in quantum mechanics, you get a dimensional constant playing a role which is the Planck's constant.

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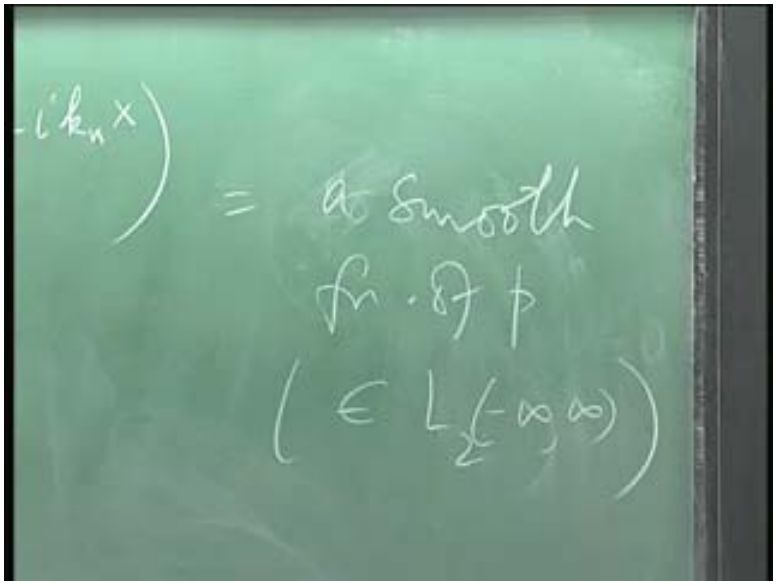

So it's equal to some function, which is a smooth function of p. its an element of L_2 from minus infinity infinity. And the upshot of it is that you don't have two delta function peaks when you compute that momentum space wave function.

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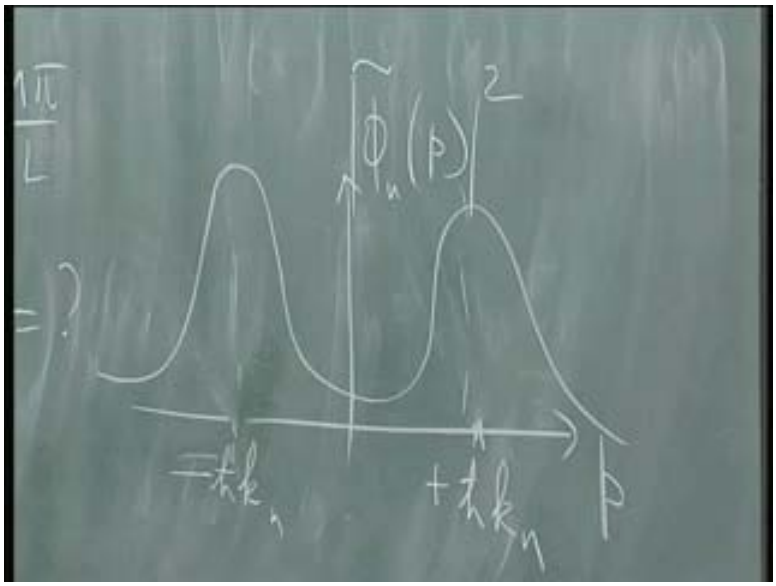

When you calculate mod phi n of p squared, the probability that the momentum is something or the other from minus infinity to infinity, the wave function looks like this(Refer Slide Time: 37:36). It has peaks about these points and that's in a nod to the classical case. When they have just two sharp values of momentum but the momentum of the particle inside the box, it could actually have any value. The average value is the probability density which is zero since the particle is inside the box. But the mean square is not zero. So our next task now is to calculate mean square.

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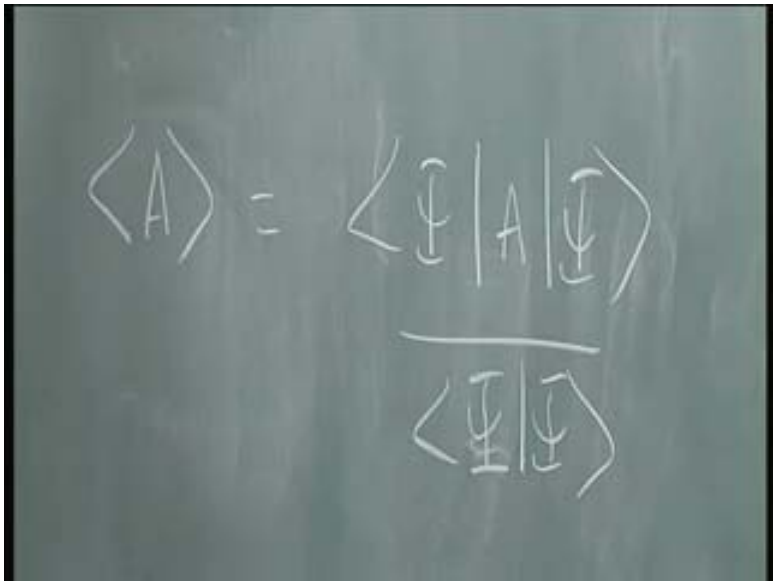

So what is x average in the n'th eigenstate? The general formula for the expectation value for an operator A in any state is psi A psi divided by psi psi. We have to apply that to the present situation. The denominator is always normalized to unity. So we have set it equal to one. All the eigen states are normalized to unity. We are going to compute the numerator now. It's time independent because you are in a stationary state. The average value of any physical quantity which is not explicitly time dependent is constant. That's the reason for calling it a stationary state. So I insert a complete set of states in the numerator.

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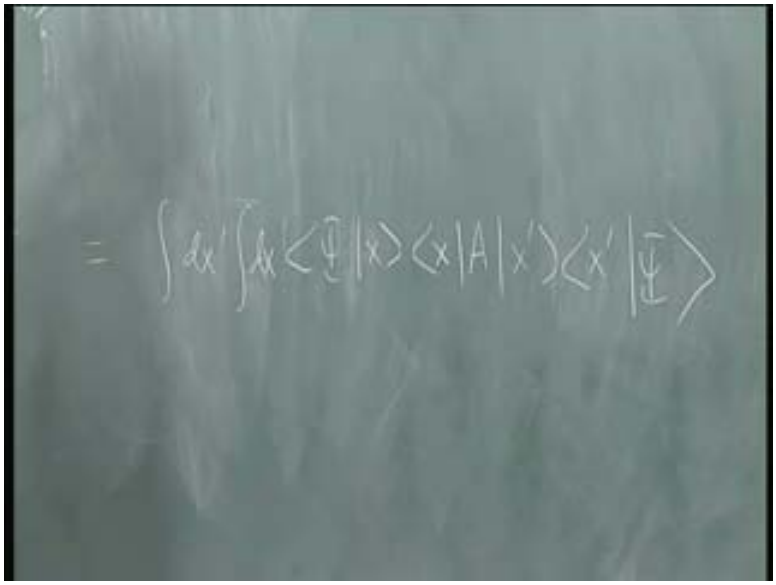

So let's write this as psi x x and integrate over dx. Then you have psi x, x A x prime, x prime psi. You have an integral dx prime as well. That's what psi A psi was equal to. The last quantity is just the wave function but I want it in the state phi n, the energy eigenstate. So I can replace this by phi n of x prime.

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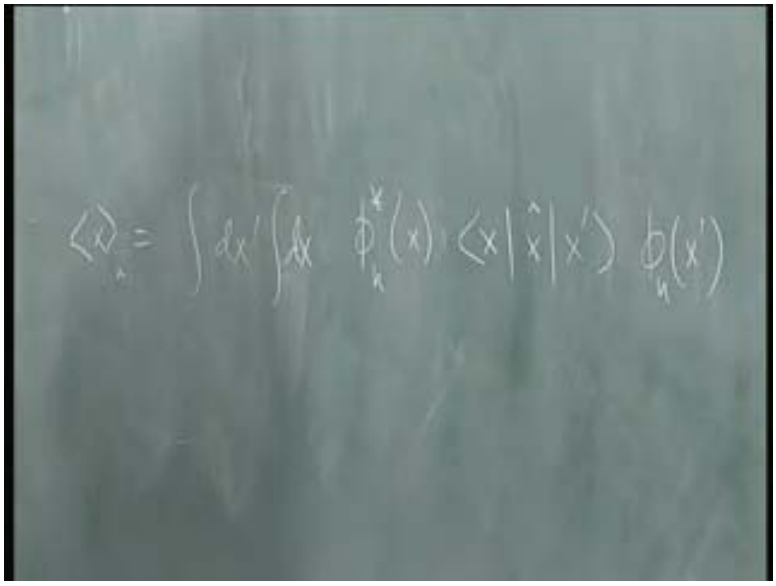

The first term is phi n star of x. But i still have two integrals to do and I want to look at the position eigen states. So I want to look at x in the n'th eigenstate which we have computed. And the operator A is x. So it is x operator acting on x which gives you just the number x. Then I have an x with x prime but it's a delta function because it's an orthonormal basis. So it becomes a delta of (x - x prime). Now I can do the x prime integral. So i get rid of the x prime integral and I'm left with phi n x phi n star of x.

So the expectation value of x becomes equal to 0 to L, because phi vanishes outside the box. Otherwise it's minus infinity to infinity. This wave function vanishes outside so its dx 2 over L sin squared (n pi x over L), multiplied by x. And that's a trivial integral to do.

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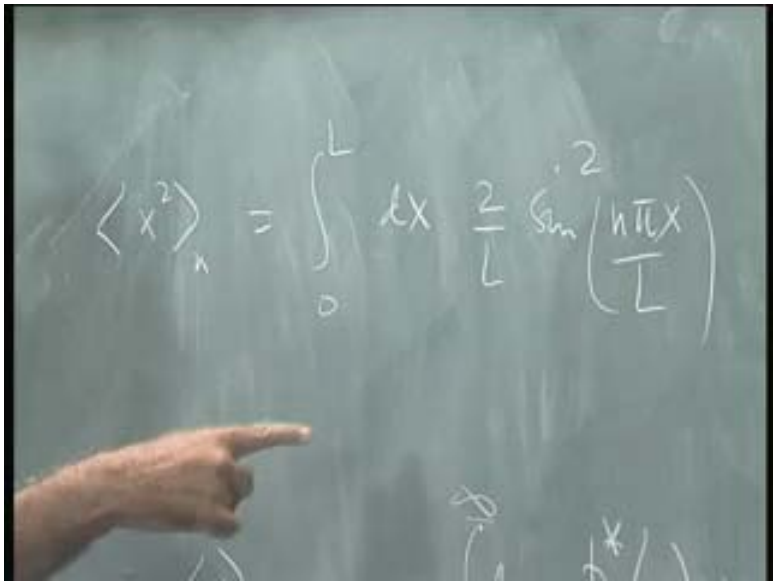

X squared average is equal to the entire expression except for the x replaced by x squared. We integrate by parts to arrive at this expression.

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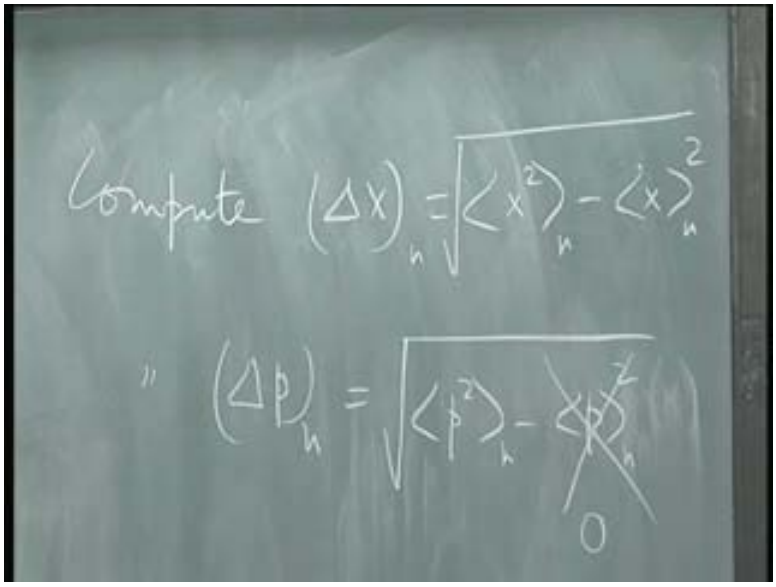

Now let's compute delta x which is the uncertainty. It is the standard deviation in the position. It is given by square root of x squared average - x average the whole squared. We follow the same argument to compute the standard deviation in the momentum except that you would have the momentum operator acting on this wave function here (Refer Time Slide: 44:35). The momentum operator acting on the wave function is - i h cross d over dx phi n of x.

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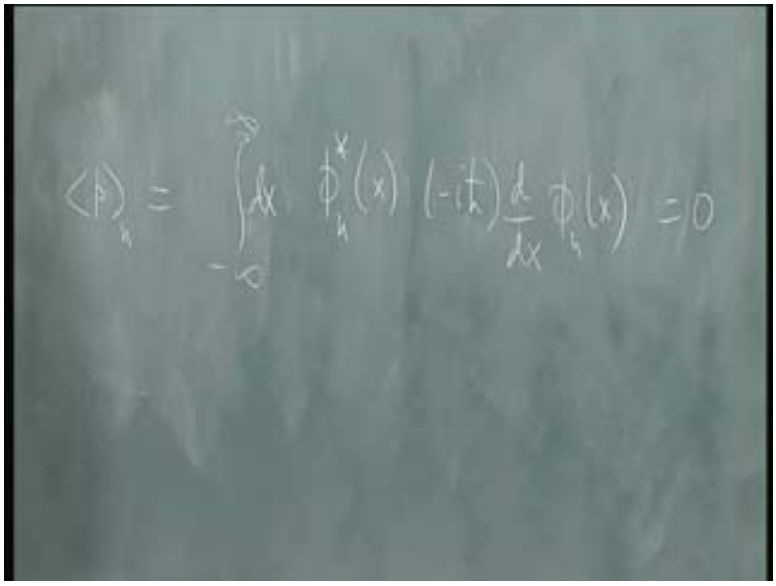

So this is some root over L sin n pi x over L. you would then get a cosine and the product integrates to. Then delta p n equal to square root of p squared n – p n average squared and we just discovered that p n average squared is 0 in this problem. Now what is p squared average equal to? It's just the energy because energy is just kinetic. So we can write it as the expectation value of the energy.

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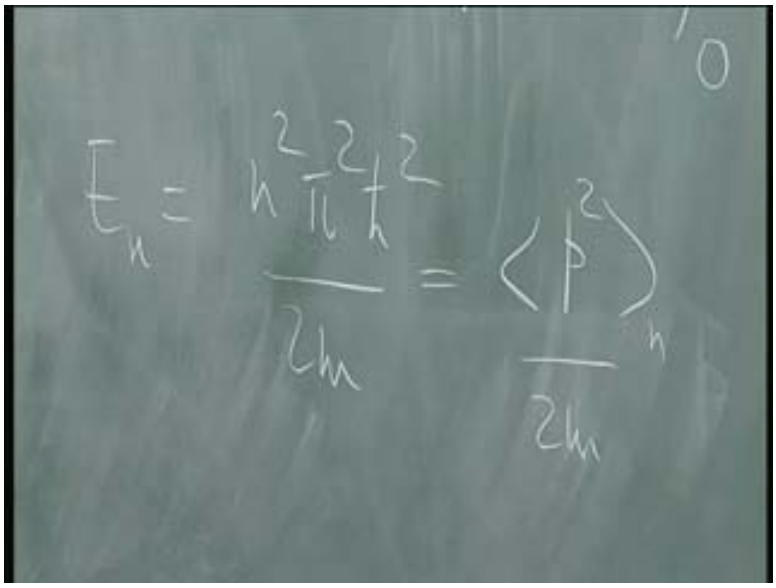

En is equal to n squared pi squared h cross squared over 2 m. but that's also equal to p squared. There is no potential energy in this problem. So we wouldn't have to compute the integral. But we have to be very careful when you say the energy is just kinetic

energy. That is not certainly true. Since there is a potential outside which is infinite and zero inside, it so happens that this integral is contributed to only by what's inside.

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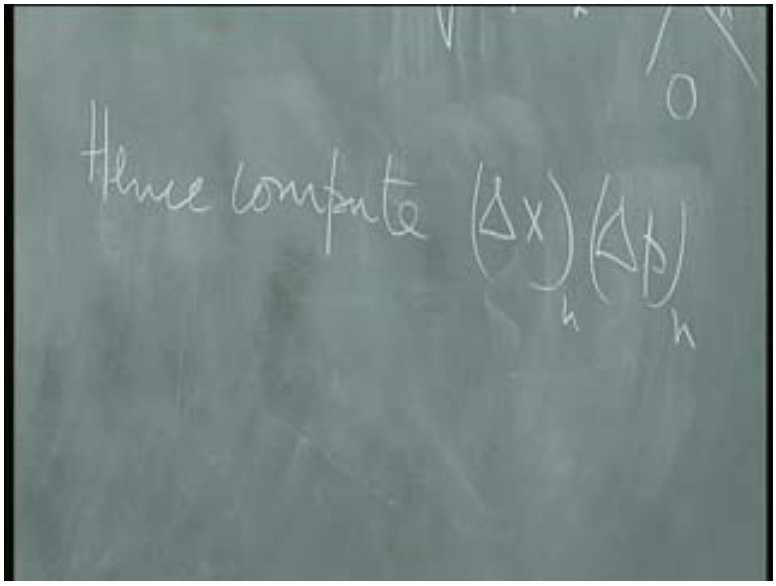

Hence compute del x del p and this should be greater than h cross over 2. In fact, you should work this out and becomes larger and larger as n increases. You will discover that it is dependent on n. the smallest value is for n =1 which is the ground state and even in that case, it's bigger than h cross over two.

So the ground state of this problem is not a minimum uncertainty state. Whenever this uncertainty bound is saturated, delta p delta x is exactly equal to h cross over 2. I would call that the minimum uncertainty state. This problem doesn't have a minimum uncertainty state at all. So this is the way you compute the uncertainties in the problem. And that more or less tells us everything we need to know about the particle in a one dimensional box.

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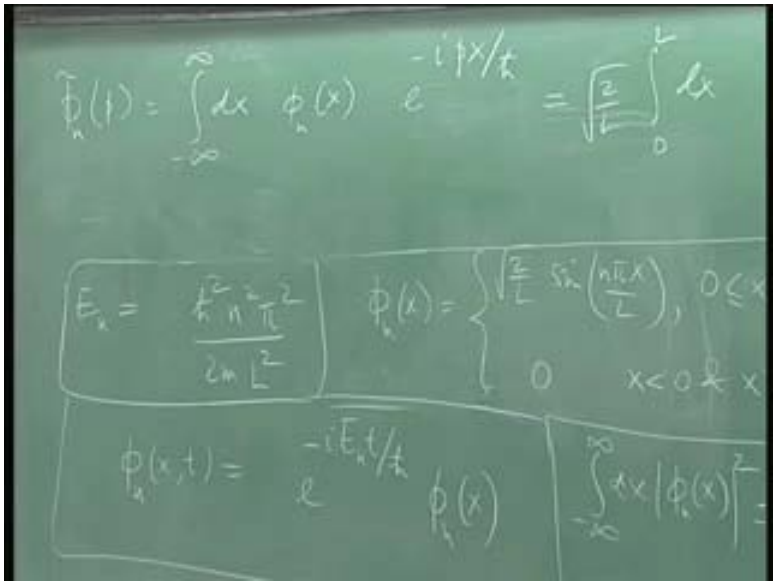

There are certain other aspects which we should ask which we will talk about a little later but I want to ask again if the energy levels are degenerate or not. In this problem they are not. Now as an exercise, I would like you to do the following one dimensional problem. Imagine this particle is not inside a one dimensional box but is living on a one dimensional on a ring.

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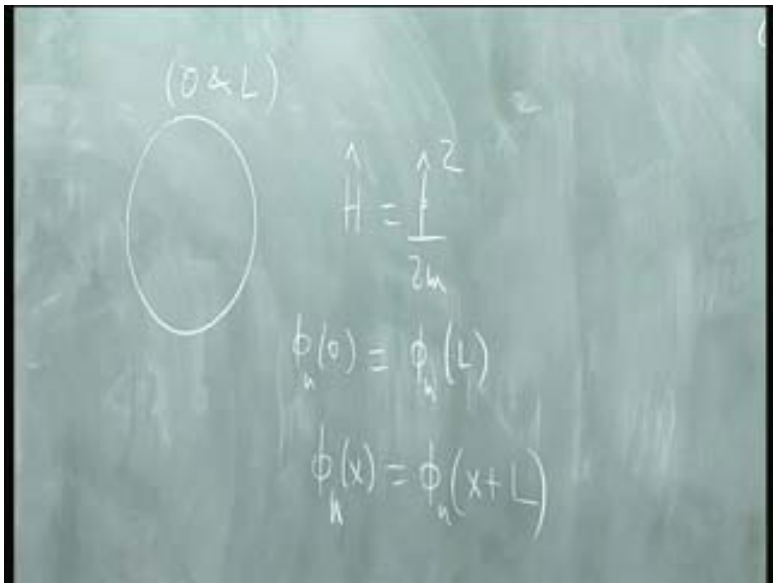

So let's suppose its living on a ring of circumference L. so this is the point 0 and L (Refer Slide Time: 50:10). So it's a circle of circumference capital L just to be able to compare with what happens in the box of length L. It's exactly the same problem as before no

potential energy no question of any potential at all in this cases just kinetic energy h is p squared over 2 m. therefore would you or would you not expect the Hamilton eigenstates to be the same as the eigenstates of the momentum? In this problem you would expect that every energy eigenstate is also the momentum eigen state. What boundary condition would you put here? After all, the equation is exactly the same as before? You would solve exactly the same equation as before but what boundary condition would you put? So I would say here phi n of 0 = phi n of L. This is actually more than a boundary condition because this is towards every x. In fact what you are saying is that the wave function here is the same as a function wave function. And therefore it's equal to phi n of x= phi n of (x + L) and so on. These are called periodic conditions. It's not a boundary condition. And the effect of this is that when I say the function here is equal to function at x + L, it means every derivative of the function here is every derivative of the function there.

So it's an infinite set of conditions. The functions must match the slopes, the curvature, all derivatives etc. so imposing a thing like this is like putting an infinite number of conditions. So this is very strong and this condition is sufficient to the find the unique solution here. What do you think the wave function is going to look like in this case? It is just going to be a sin n pi x over L. will it just be an exponential? It will be a super position but will it be a finite superposition? Remember you need to satisfy the boundary condition. So it will end up with a fairly complicated superposition and it's not trivial.

Would they be degenerate? They are doubly degenerate in this problem because one of them would correspond to momentum in the clockwise direction and the other would correspond to momentum in the anticlockwise direction. Now very often in text books you will see the statement that in one dimensional problems, you don't have degeneracy. This is true provided the underlying space is simply connected. A circle is not simply connected. So topology plays a role here and in this problem definitely there is double degeneracy even in one dimension. We will try to come back and give this is an exercise to work out fully. We will see what the wave function looks like for a particle moving in a circle. This is crucial because these are the kinds of problems one would encounter in applications. We will take up two dimensions and I will do the rest of it tomorrow.

If you recall in the classical physics course, all closed loops cannot be shrunk to a point without leaving the space. So it's actually infinitely connected. It is like taking the problem of putting a rubber band on a cycle wheel rim. You can encircle completely once or twice or thrice or -1, -2, -3 times in infinite number of distinct ways of mapping. So in the technical sense, it's not a simply connected space but physically the circles boundary conditions as periodicity are such that there is truly no potential. Hamilton does commute with the momentum in this problem. The consequence of it is that you don't have to solve Schrodinger equation. You can solve the one dimensional momentum eigen function equation. You could solve the equation p on wave function equal to number times wave function. That's the first derivative equation and you superpose all possible solutions.

They are guaranteed then to be simultaneous eigenstates of momentum as well as the total energy. So we will return to that now, you can do what we did for one dimension in a two dimensional box.

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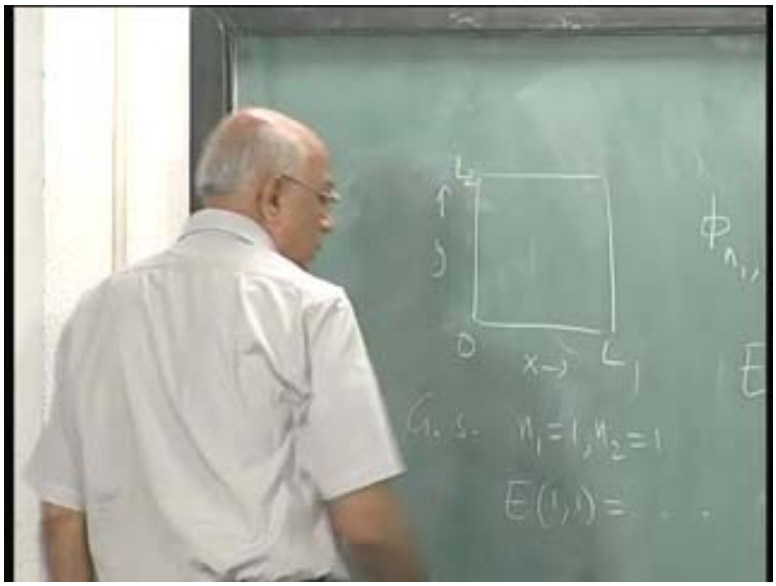

So now I have a wave function inside a square box in the x direction and in the y direction, 0 to L. as usual, I say the wave function is identically 0 outside and non-zero inside. And I can now separate the Schrodinger equation in Cartesian coordinates and what would the solutions look like in this case. Let us suppose that you have two quantum numbers now, n_1 and n_2 because you get two degrees of freedom. So phi would be labeled by two quantum numbers, n_1 n_2 and it will be a function of x, y. this is square root of 2over L in each of the directions. So it is sin n_1 pi x over L and sin n_2 pi over L.

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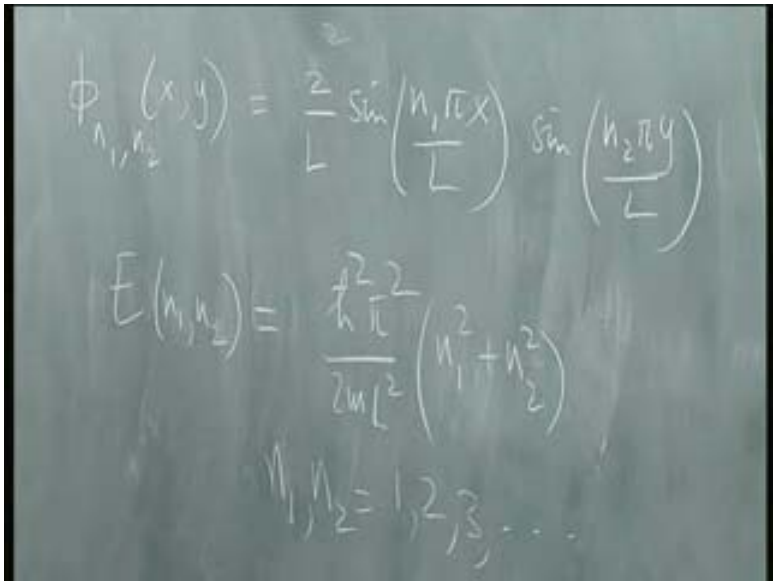

E is now a function of n 1 n 2 = h cross squared pi squared over 2 m L squared times (n_1 square + n_2 squared). Those would be the wave functions. The ground state is not degenerate. It's unique. You can't put either n 1 or n 2 zero because then there's no wave function at all. So this definitely is the ground state, the lowest energy state. The first excited state is degenerate. It could be either n_1 as 1 and n_2 is 2 or vice versa. So it's doubly degenerate. Of course you can do this numerology in the beginning but the interesting thing to ask is how does the degeneracy increase as n increases. What about three dimensions? Suppose the boxes were a rectangular box having L_1 and L_2 as sides, what would happen?

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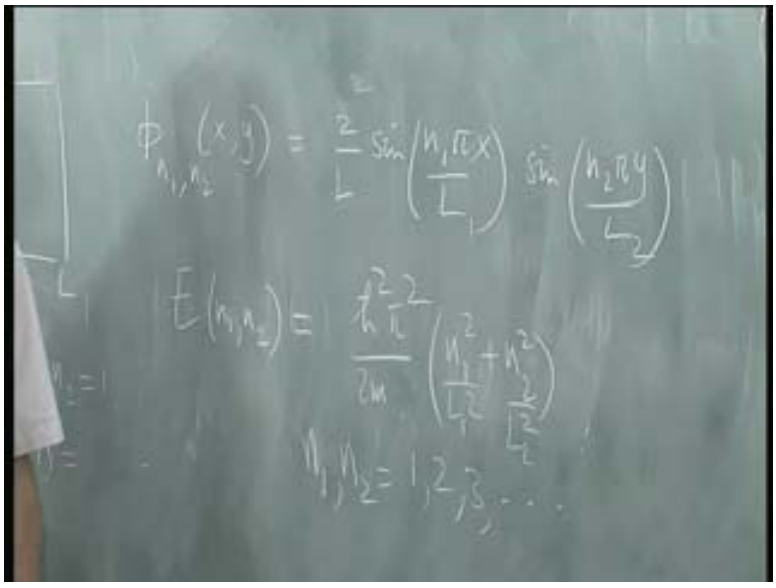

Well, it would be the same except that this (Refer Time Scale: 01:00:08) expression would have an L1 and an L2. The degeneracy depends on L_1 and L_2. So we are back to this thing about frequencies of two harmonic oscillators at right angles. So it depends on the geometry of the box. You can do a tetrahedral box, a spherical box, etc. They are of academic interest except that with the advent of nanotechnology and nanoparticles , it's become crucial now because you can actually produce metallic particles which are confined to boxes of particular geometrical shapes.

So it now becomes actually relevant to ask what do the energy levels look like in different shapes of boxes and how do they get quantize. That's an interesting problem look at. What I am going to do next is to take off from this problem and introduce a potential and show you how, if you relax this condition of an infinitely rigid value, then you start getting a spillover of the wave function outside. So we will talk about that tomorrow. Thank you!