Engineering Chemistry - 1

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Lecture - 3

Module 1: Atoms and molecules

Particle in a box (one and two dimensions) continued

Welcome back to the lectures on chemistry as part of the National Programme on Technology Enhanced Learning, a programme sponsored and funded by the Ministry of Human Resource Development.

I have been lecturing on the basic principles of Chemistry for the engineering students as well as the students of basic sciences. In the last two lectures we have got ourselves introduced to Quantum Chemistry principles, the principles that we will use again and again and the principles that we will become familiar by examples.

In the last lecture the first and the simplest example namely the particle in a box was discussed. The relevance of the particle in a one dimensional box if you recall I mean an association with the energy levels of electrons to be more precise in a conjugated polyene system. That is a linear system and motion is one dimension of it. Today we will generalize this to the motion of the particle in two dimensions.

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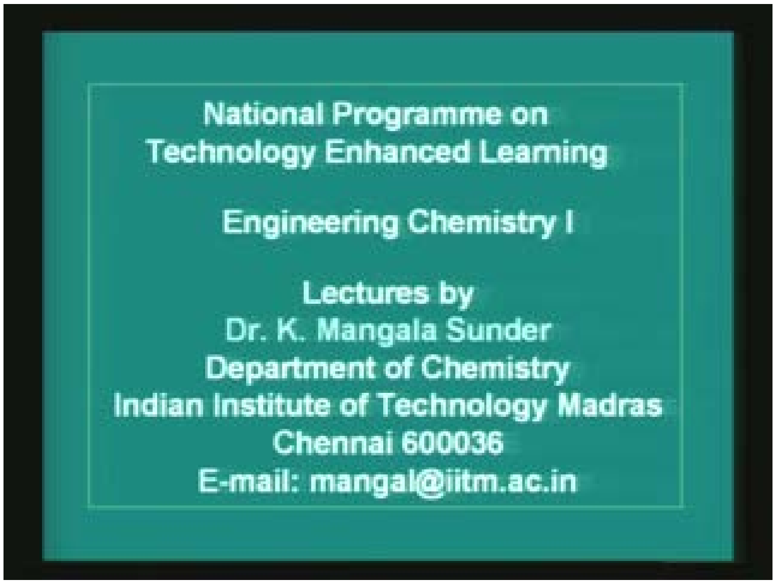

National Programme on
Technology Enhanced Learning

Engineering Chemistry I

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This is a course on Engineering Chemistry, my name is Mangala Sunder I am from the Department of Chemistry in the Indian Institute of Technology Madras Chennai and this is my electronic mail address mangal@iitm.ac.in

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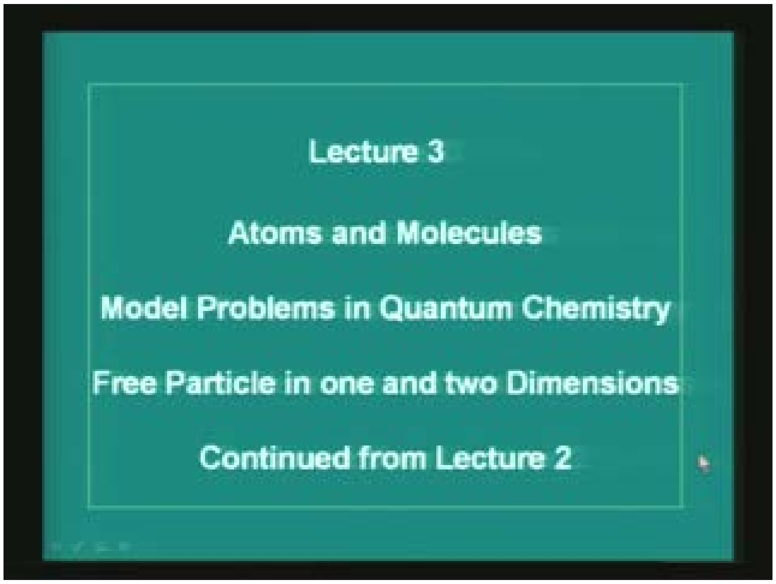

Lecture 3

Atoms and Molecules

Model Problems in Quantum Chemistry

Free Particle in one and two Dimensions

Continued from Lecture 2

This is the third lecture on the first module Atoms and Molecules. We are studying the model problems in Quantum Chemistry, the free particle in one dimension was discussed in the last lecture. We will discuss about the free particle energies in two dimensions today and the discussion continues from the last lecture.

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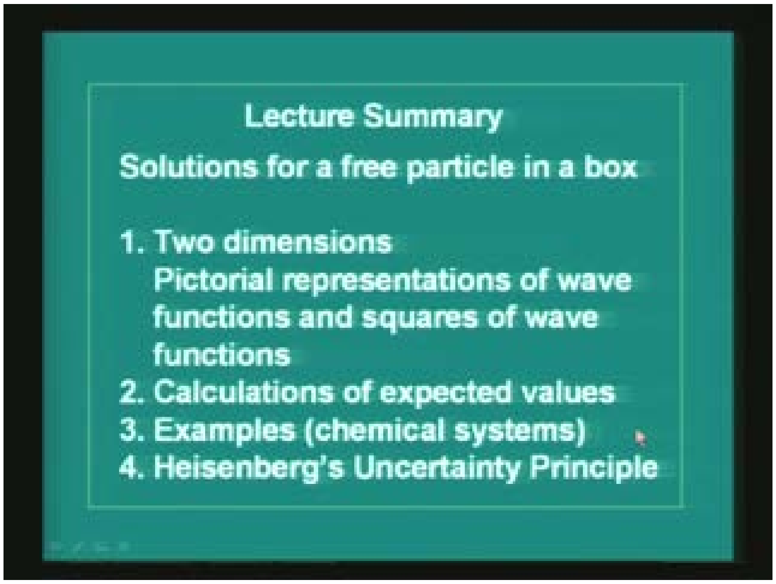

Lecture Summary

Solutions for a free particle in a box

1. Two dimensions
   Pictorial representations of wave functions and squares of wave functions
2. Calculations of expected values
3. Examples (chemical systems)
4. Heisenberg's Uncertainty Principle

The contents of today's lecture are the solutions for the particle energies in two dimensions and the wave function. This is the solution of the time independent Schrödinger equation.

The wave functions and the squares of the wave function will be represented by some pictures in this lecture. Pictorial representations or visualizations are very important in all of Science and all of Engineering. Wherever possible we will try to draw a graph or give a plot of the surface of the wave function if it is more than one dimensional and so on.

The second most important aspect of today's lecture will be the calculation of the expected values or the expectation values in Quantum Mechanics. From the last lecture please recall that when we talk about experimental measurements Quantum Mechanics comes up with the rule for the average or the excepted value of whatever we are trying to measure through a formula. We will illustrate that formula and follow that with one or two examples to chemical systems.

Given sufficient time I would try to explain the Heisenberg's Uncertainty Principle but in all likelihood this will go to the next lecture.

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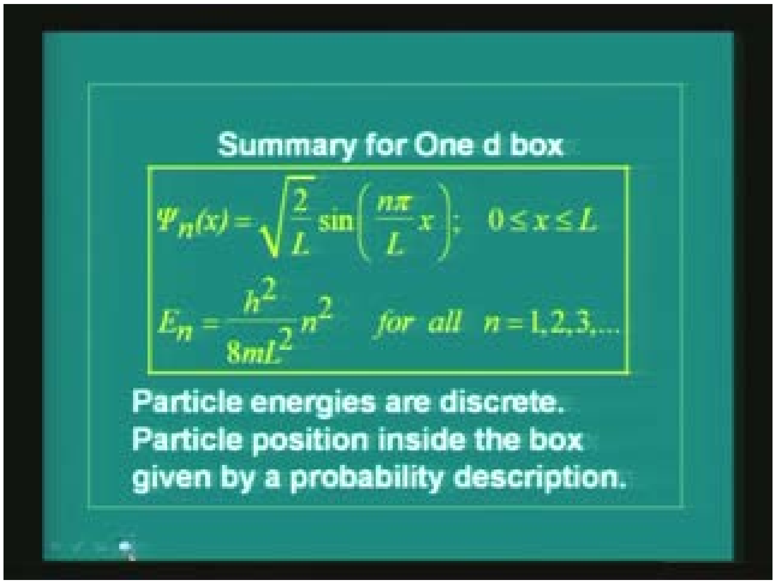

Summary for One d box

$$\Psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right);\quad 0\le x\le L$$

$$E_n=\frac{h^2}{8mL^2}n^2\quad \textit{for all}\quad n=1,2,3,\ldots$$

Particle energies are discrete.
Particle position inside the box
given by a probability description.

Recall for yourself the one dimensional particle in a box results. Let me quickly summarize these things from the last lecture.

For a box of length L and the particle with no potential inside the box the wave function was derived from the last lecture as 2/Lsin(nπ/L) where n is 1, 2, 3 etc integers.

The energy of the particle in the solution of the wave equation $\hat{H}\psi = E\psi$ the energies turn out to be quantized, discretized by the n's with a unit for the energy $h^2/8mL^2$ where m is the mass of the particle, h is Planck's constant. So the result was particle energies are discrete, particle position inside the box is given by a probability description which we saw in the last lecture.

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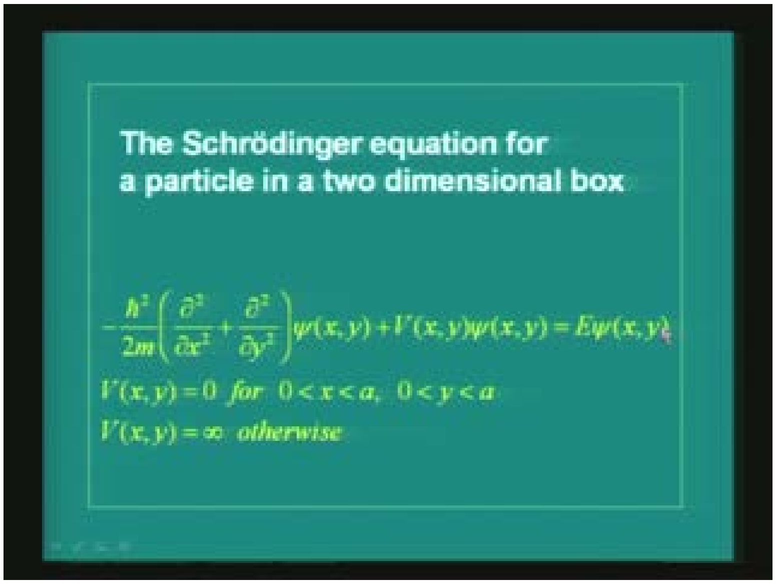

The Schrödinger equation for
a particle in a two dimensional box

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y)+V(x,y)\psi(x,y)=E\psi(x,y)$$

$$V(x,y)=0\quad \textit{for}\quad 0<x<a,\; 0<y<a$$

$$V(x,y)=\infty\quad \textit{otherwise}$$

In the last lecture I also introduced the Schrödinger equation for the particle in a two dimensional box in a manner analogous to the particle in a one dimensional box. Remember, that the motion, the one dimension refers to motion in one direction which we call as a coordinate x. A two dimensional box refers to motion in two orthogonal directions namely a planar motion the particles position anywhere in a plane, the particles energy due to the two degrees of freedom that it has, the wave function corresponding to these two degrees of freedom for the special case that the potential in a certain region is 0 and it is ∞ everywhere else.

So the model was that we will solve this particular problem $-\hbar^2/2m\,(\partial^2/\partial x^2 + \partial^2/\partial y^2)\,\psi(x,y)$ which is nothing but the kinetic energy times $\psi(x,y)$ + $V(x, y)$ times $\psi(x,y)$ which is the potential energy times the wave function. so what we have on this side is the Hamiltonian acting on the wave function ψ giving you the energy times the wave function ψ, this 'a', so it is $0<x<L$, $0<y<L$ and the potential is infinity everywhere except the box this is the model. (Refer Slide Time: 08:09 min).

Let us do a little bit of writing to see how we solve this problem. Inside the box the equation that we want to solve is $-\hbar^2/2m\,(\partial^2/\partial x^2 + \partial^2/\partial y^2)\,\psi(x, y) = E\,\psi(x, y)$. This is linear second order partial differentiation equation. $\partial^2/\partial x^2$ it is linear there are no cross terms involving x and y. There is a method in Mathematics called the method of separation of variables which allows these equations to be solved quickly.

Separation of variables: The variables here are x and y for the solution.

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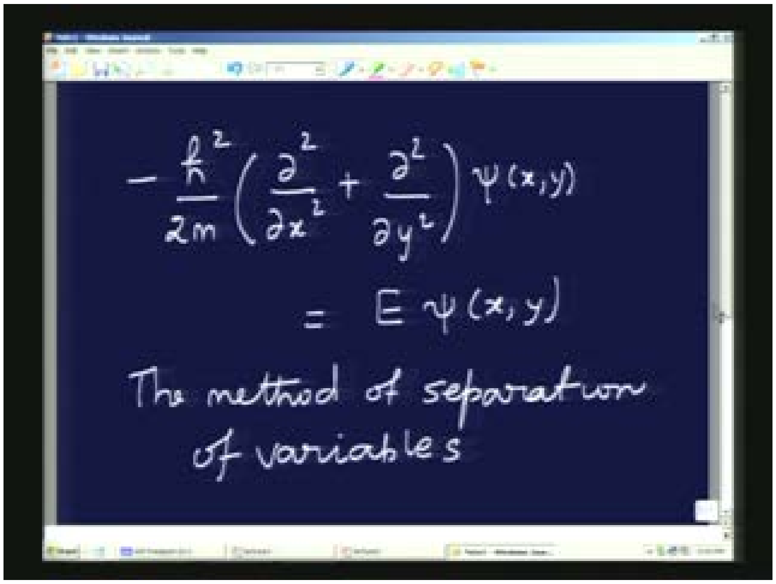

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E\,\psi(x,y)$$

The method of separation of variables

According to this method if we write $\psi(x, y)$ as a function, let me write the function using an appropriate symbol X which depends only on x multiplied by another function Y which depends only on y. This is possible by an examination of this equation and this is from the calculus of the solution of the differential equation.

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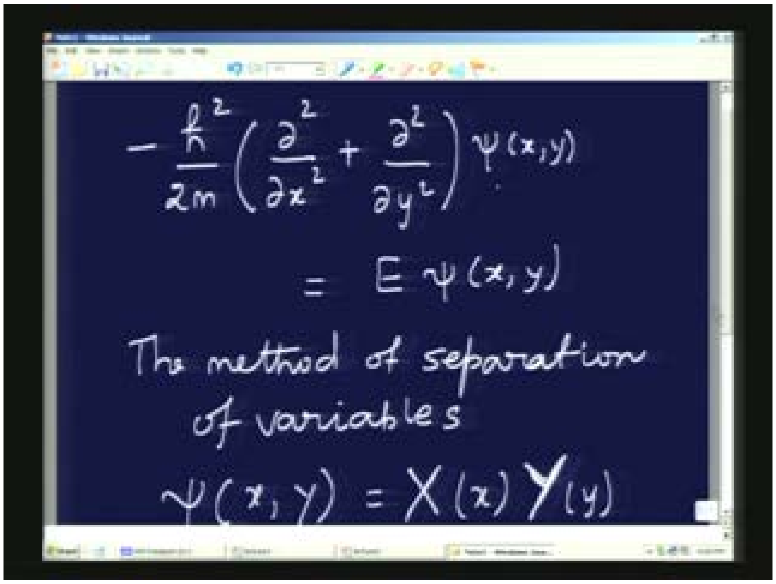

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y)$$

$$= E\,\psi(x,y)$$

The method of separation of variables

$$\psi(x,y) = X(x)\,Y(y)$$

We will adopt that and we will write down the solution for the wave function almost immediately. What is the role of $\psi(x, y) = X(x)\ Y(y)$? The wave function is expressed as a product of two functions each of which is a function of only one variable and this when you substitute in the differential equation it allows you to simplify the differential equation very quickly. Therefore, when you write $-\hbar^2/2m\ (\partial^2/\partial x^2 + \partial^2/\partial y^2)$ acting on a function $X(x)\ Y(y)$ giving you $E\ X(x)\ Y(y)$ this is a proposal for the wave function that we assume that the wave function ψ is expressed as a product of two one variable functions one variable dependent functions.

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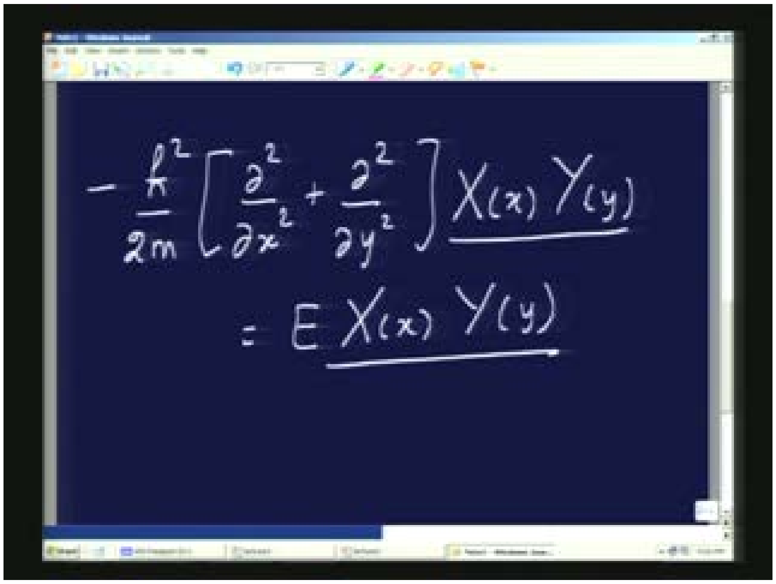

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]\underline{X(x)\,Y(y)}$$

$$= \underline{E\,X(x)\,Y(y)}$$

If we do that what are that consequences.

You know this is a partial derivative and the partial derivative on x, of course does not change function y. The partial derivative of y does not change function of x. Therefore this equation can be immediately written as $-\hbar^2/2m\,[(\partial^2X/\partial x^2)Y + (\partial^2Y/\partial y^2)X] = E\,X(x)\,Y(y)$ where Y is a multiple, X is a multiple. (Refer Slide Time: 12:41 min).

Now, if you divide both sides by the product X and Y the result will be $-\hbar^2/2m\,[1/X\,(\partial^2X/\partial x^2) + 1/Y\,(\partial^2Y/\partial y^2)]$ this is the X which is the function and this is the x which is the variable where this X is dependent on. Y is a function of the variable y. Therefore this quantity is equal to E. It is a very simple method of separation of variables and the argument now is that these two terms $1/X\,(\partial^2X/\partial x^2) + 1/Y\,(\partial^2Y/\partial y^2)$ are two independent quantities. Therefore this equation can be satisfied only when this whole thing first term is equal to a constant and this whole thing second term is equal to another constant such that the two constants add to give you the value E.

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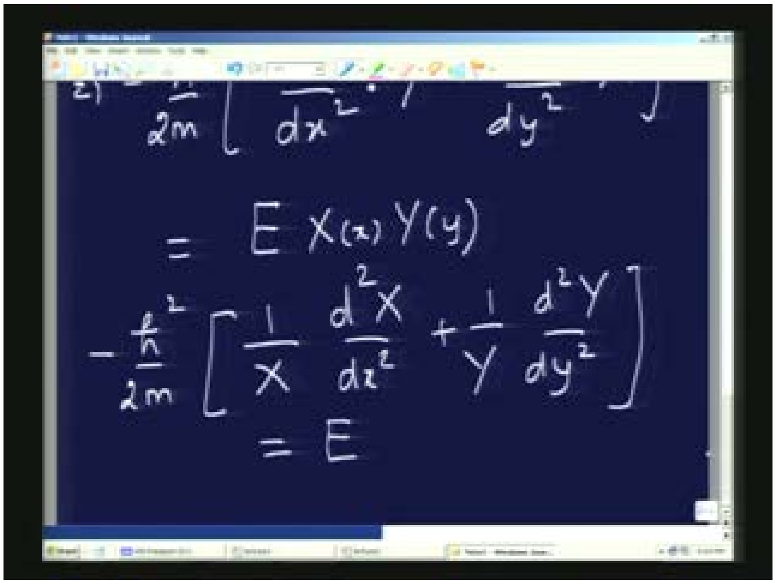

$$= E\,X(x)\,Y(y)$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2}\right] = E$$

Therefore the equation turns out to be $-\hbar^2/2m\,(\partial^2X/\partial x^2)\,1/X = E_1$ a constant, $-\hbar^2/2m\,(\partial^2Y/\partial y^2)$ times $1/Y = E_2$ a constant such that $E_1 + E_2 = E$ the total energy. The solution is $-\hbar^2/2m\;1/X\,(\partial^2X/\partial x^2)$ this whole thing is a constant E_1. Likewise the other term is another constant E_2 such that $E_1 + E_2$ = the total E. Now, what is this? This is the variable x between 0 and L the length of one side, y is also a variable in the other orthogonal direction between 0 and L for a square box. You can have any other arbitrary box but let us stay with the square box to simplify things.

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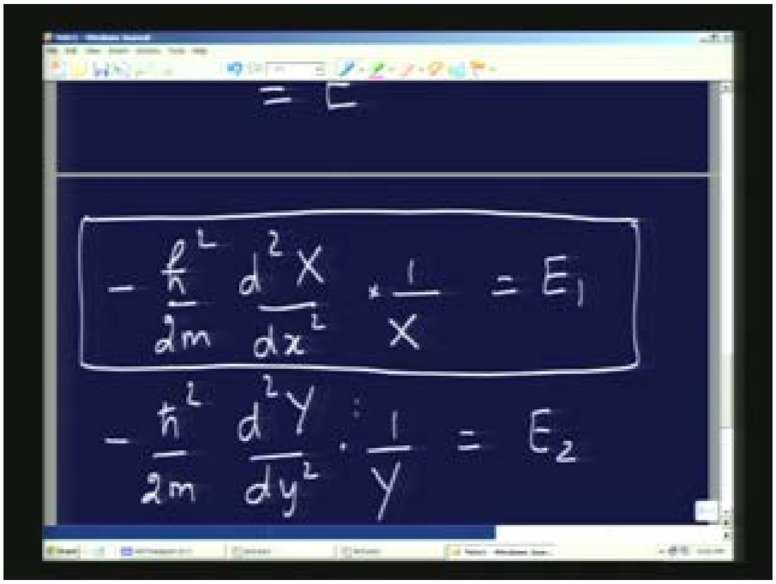

$$= E$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}\cdot\frac{1}{X} = E_1}$$

$$-\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2}\cdot\frac{1}{Y} = E_2$$

So what you have here is now two one dimensional problems, two particles in one dimensional box problems exactly similar to what you had in the last lecture. Therefore the solutions of this can be immediately written down with one exception, the exception is that E_1 and E_2 each of which are given by independent quantum numbers you recall that the energy is $h^2/8mL^2$ times n^2. These two equations are two independent equations. Therefore there are two independent quantum numbers E_1 is proportional to n_1^2 and E_2 is proportional to n_2^2 another quantum number, it does not have to be the same except that the sum of the two energies should be equal to the total energy E.

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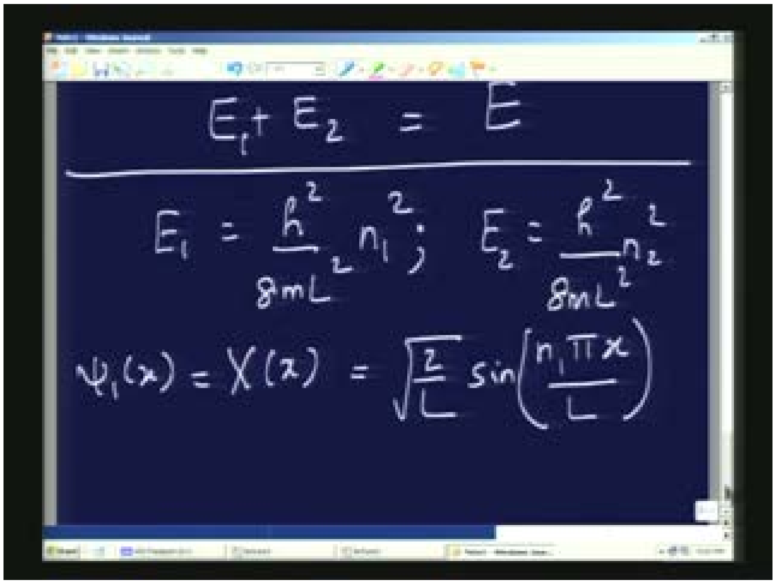

$$E_1 + E_2 = E$$

$$E_1 = \frac{h^2}{8mL^2}n_1^2; \quad E_2 = \frac{h^2}{8mL^2}n_2^2$$

$$\psi_1(x) = X(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_1\pi x}{L}\right)$$

So the result is immediately obvious namely E_1 is $h^2/8mL^2$ times n_1^2 and E_2 is $h^2/8mL^2$ times n_2^2 $\psi_1(x)$ which is $X(x)$ you remember that is our notation and that is going to be $\sqrt{(2/L)}\ \sin(n_1\pi x/L)$

exactly the same as the one dimensional problem $\psi_2(y)$ which is the function $Y(y)$ is $\sqrt{(2/L)}$ $\sin(n_2\pi x/L)$ such that the overall wave function $\psi(x,y)$ is $X(x)$ times $Y(y)$ and the overall energy E is $E_1 + E_2$.

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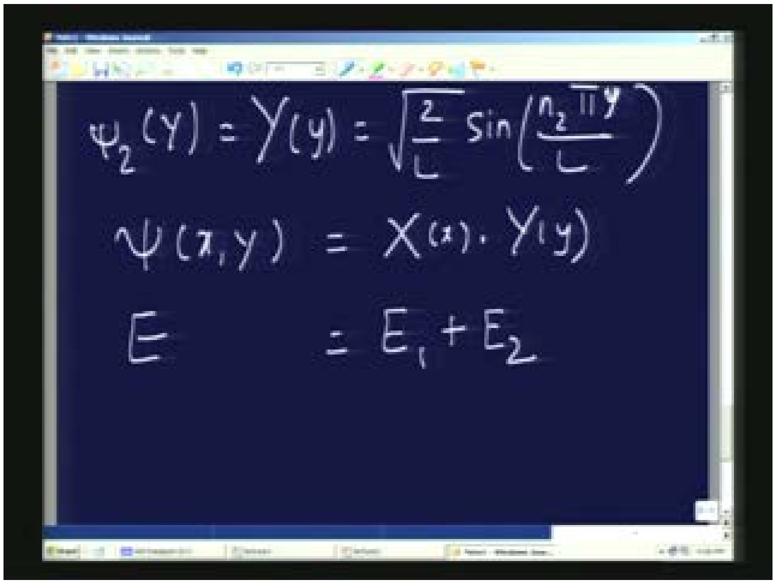

$$\psi_2(y) = Y(y) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_2\pi y}{L}\right)$$

$$\psi(x,y) = X(x)\cdot Y(y)$$

$$E = E_1 + E_2$$

This is a result that comes from the use of an appropriate mathematical technique known as the method of separation of variables which works well in this particular case because the equation is of that type, the partial second order linear differential equation in two variables does not have any cross terms therefore the solution comes out like this.

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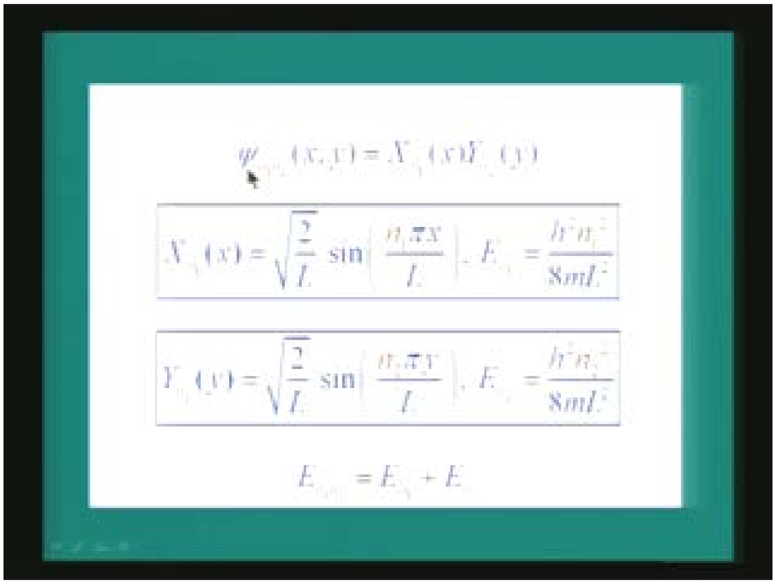

$$\psi_{n_1 n_2}(x,y) = X_{n_1}(x)Y_{n_2}(y)$$

$$\boxed{X_{n_1}(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_1\pi x}{L}\right),\ E_{n_1} = \frac{h^2 n_1^2}{8mL^2}}$$

$$\boxed{Y_{n_2}(y) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_2\pi y}{L}\right),\ E_{n_2} = \frac{h^2 n_2^2}{8mL^2}}$$

$$E_{n_1 n_2} = E_{n_1} + E_{n_2}$$

The summary of this result is, the wave function now depends on two quantum numbers n_1 and n_2 you recall that is because of the x dependent quantity depending on a quantum number n_1 the

Y dependent quantity depending on the quantum number n_2 and the wave function is the product of these two functions therefore it is indexed in general by two quantum numbers n_1 and n_2 such that it is $X(x)$ times $Y(y)$ and energies are the sums of the squares of the quantum numbers namely $h^2/8mL^2$ times $(n_1^2 + n_2^2)$ is what you have here.

Let us quickly see how to represent these wave functions in a simple pictorial form and how to represent the squares of the wave function in a pictorial form. And afterwards we will examine the consequences of this solution in terms of the most important concept for today's lecture namely degeneracy of the energy levels.

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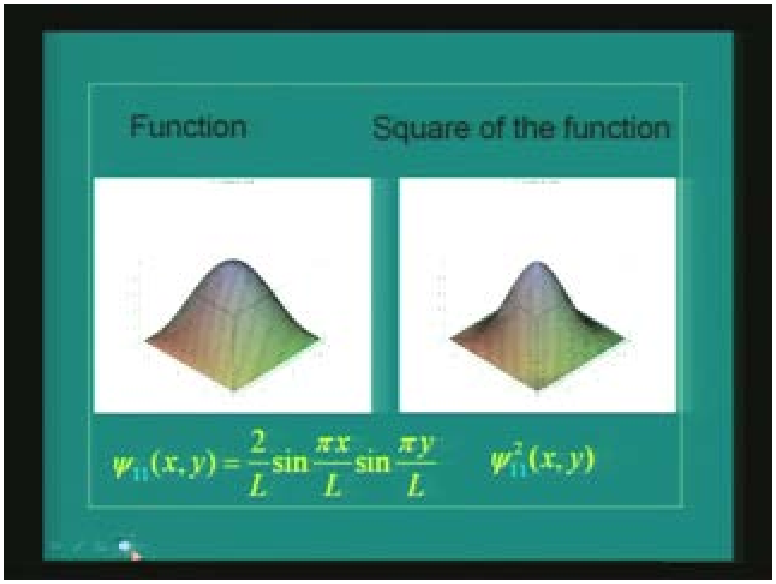

Function

Square of the function

$$\psi_{11}(x,y) = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L} \qquad \psi_{11}^2(x,y)$$

What I have here are two plots. Let me go back to my notes. Remember, $X_{n1}(x)$ is $\sqrt{(2/L)}\sin(n_1\pi x/L)$ since n_1 is 1,2,3,….etc you have obviously $X_1(x)$ you have $X_2(x)$, $X_3(x)$ and so on all possible functions.

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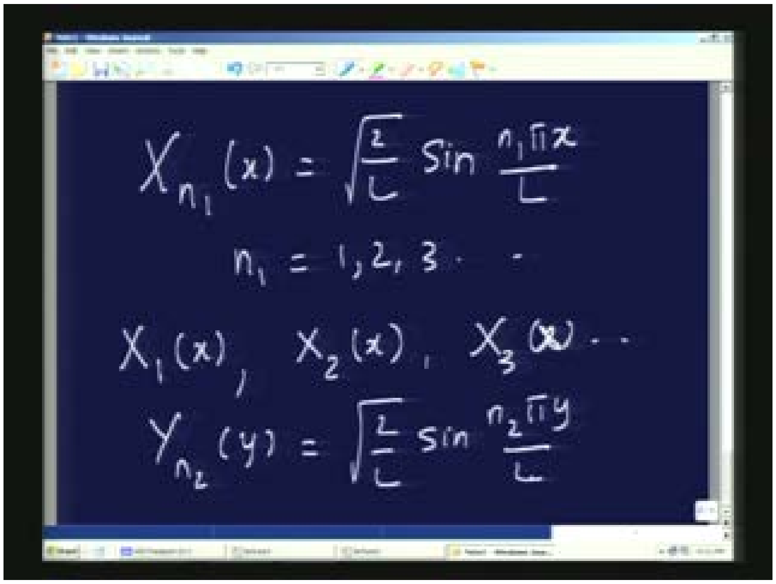

$$X_{n_1}(x) = \sqrt{\frac{2}{L}} \sin \frac{n_1 \pi x}{L}$$

$$n_1 = 1, 2, 3 \cdot \; \cdot$$

$$X_1(x), \quad X_2(x), \quad X_3(x) \ldots$$

$$Y_{n_2}(y) = \sqrt{\frac{2}{L}} \sin \frac{n_2 \pi y}{L}$$

Likewise you have the $Y_{n2}(y) = \sqrt{(2/L)} \sin(n_2 \pi x/L)$ also running into the indices $Y_2(y)$, $Y_2(y)$ and so on. Therefore the wave function ψ which is a function of n_1 and n_2 let us take the first one namely n_1 is 1, n_2 is 1 and x, y is obviously the product of $X_1(x)$ $Y_2(y)$. You remember that this $X_1(x)$ is a half sine wave, $Y_2(y)$ is a half sine wave and both these half sine waves you remember you plotted them in the last lecture in one dimension. (Refer Slide Time: 20:56 min). Now, since this is a two dimensional function to plot this function in two coordinates x and y the value of the function in the third coordinate the plot is obviously a three dimensional plot and not a two dimensional plot. That is the plot which is you now see here.

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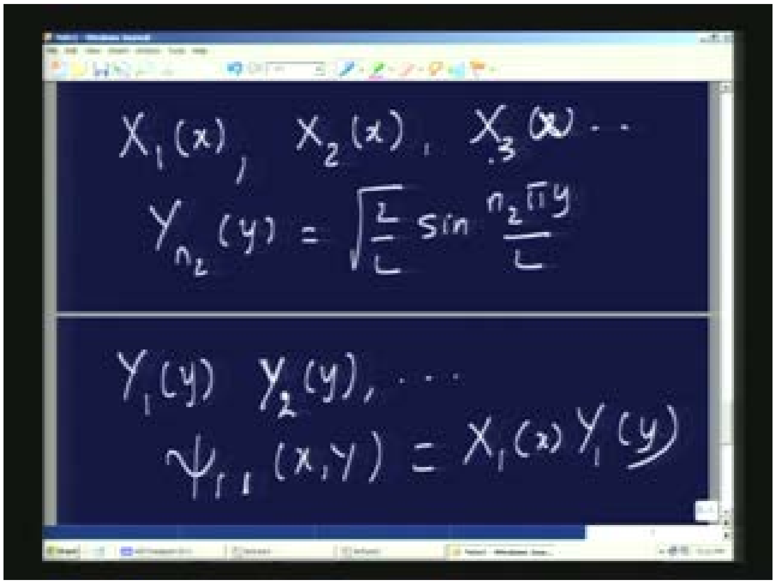

$$X_1(x), \quad X_2(x), \quad X_3(x) \ldots$$

$$Y_{n_2}(y) = \sqrt{\frac{2}{L}} \sin \frac{n_2 \pi y}{L}$$

$$Y_1(y) \quad Y_2(y), \ldots$$

$$\psi_{1,1}(x,y) = X_1(x) Y_1(y)$$

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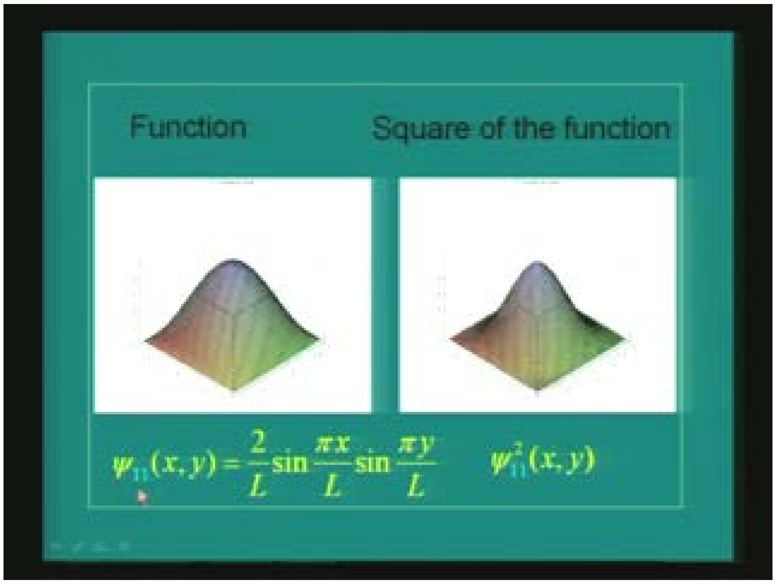

Function

Square of the function

$$\psi_{11}(x,y) = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L} \qquad \psi_{11}^2(x,y)$$

$\psi_{11}(x, y)$ meaning n_1 is 1 and n_2 is 1 is equal to $2/L \sin(\pi x/L) \sin(\pi y/L)$. In this first one is a half sine wave so if you are looking at this direction this is the x direction the other is orthogonal direction the y direction. Therefore if you plot this function $\sin(\pi x/L) \sin(\pi y/L)$ in the graph in the computer what you will get is a half sine wave like when you project this plot on this plane you get a half sine wave here when you project this on this plane you get a half sine wave so you get a surface plot. It is a surface plot because it is a function of two variables.

It is going to be a much more complicated plot if we are going to discuss the motion in three dimensions like in the case of hydrogen atom it is where we are going to go soon. If we take the square of the wave function which you know represents the probability density the square of the wave function in a small region gives you the probability of finding the system in that region. Therefore, if we plot the square of this wave function you see also get more or less similar plot except to that there is a little bit shallow on the ends because sin square goes to 0 very quickly on both sides and that is why you see the plot is slightly different.

What is the next wave function? The $\psi_{12}(x, y)$ is $\psi_{n1n2}(x, y)$ meaning n_1 is 1 and n_2 is 2 along the x direction the wave function is $\surd 2/L \sin \pi x/L$ along the y direction is $\surd 2/L \sin 2\pi y/L$ therefore you get a 2/L. So what you have is a $\sin(\pi x/L) \sin(2\pi y/L)$ which tells you that along the x axis or the projection is a half sine wave whereas in the y axis or y direction if you project it is a full sine wave and that is exactly what you see in this graph namely it is a full sine wave in the y direction with up and down. And in the case of x direction it is a half sine wave that it goes through minuses and plus because this function takes those values. But you see when you project to this on this orthogonal direction side you get a complete sin wave and you get a half sin wave on x-axis.

Now, if you square this function there is no negative part to this function everything will become positive and therefore the negative part which is a dip that you see here now becomes a nice positive node. This is now you see that it is a sin square wave. You recall the one dimensional plot again. You recall the one dimensional plot for $\psi_2(x)$. Here it is a line joining two ends here and this there is a node at center therefore the wave function is a sine wave and $\psi_2^2(x)$.

If you remember the probability was that there is no negative part to it and it is again in the middle you have something like that and the negative part is squared up and of course the shallow continues like that and this is the kind of plot that you see long the y direction and along the x direction you obviously see the half sin wave. So, this right side is the surface plot for the square of the wave function representing the probability density ψ_{22}.

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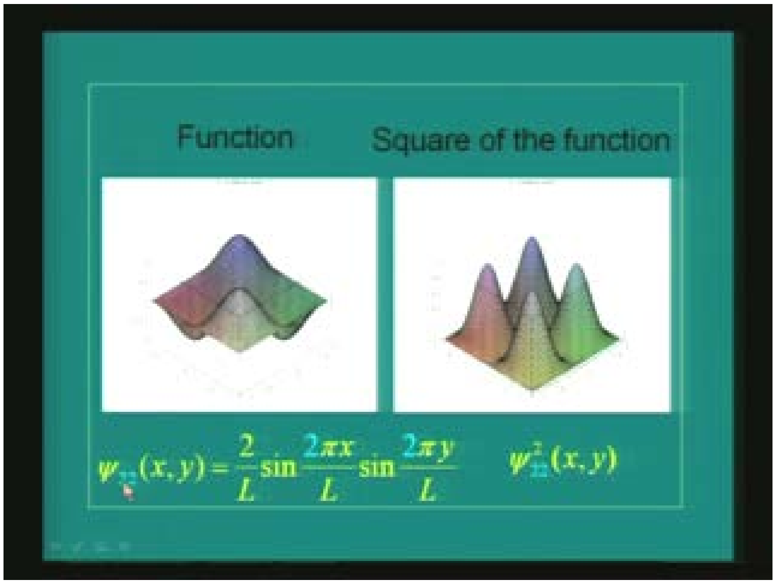
Function

Square of the function

$$\psi_{22}(x,y) = \frac{2}{L}\sin\frac{2\pi x}{L}\sin\frac{2\pi y}{L} \qquad \psi_{22}^2(x,y)$$

Now you know that it is 2 in the x direction the quantum number n_1 is 2 the quantum number n_2 is also 2 therefore it is a full sine wave in both directions and therefore you see the full sine wave form in both directions and when you square them up correspondingly you see the two hums here, the negative parts becoming positive throughout because the function is squared up and you see the two hums. In x direction it is quantum number 2 and in y direction also it is quantum number 2. So the probability density now is very seriously changed from region to region from place to place.

In a plane there are regions where the particle is likely to be found much more certainly and there are regions where the particles where less likely to be found. There is only a point or nodal line where the density goes to 0 that is the square of the wave function goes to 0. You never talk about the probability of finding the particle at a point or on a line for a problem where the variable is continuous. You always take the probability density to be represented in a small region of space.

Therefore the probability density is never ever 0 in a region it is very small it is 0 at point or along a line but there probability in a certain region for finding the particle whether it is one dimensional or two dimensional is never 0 and is never negative.

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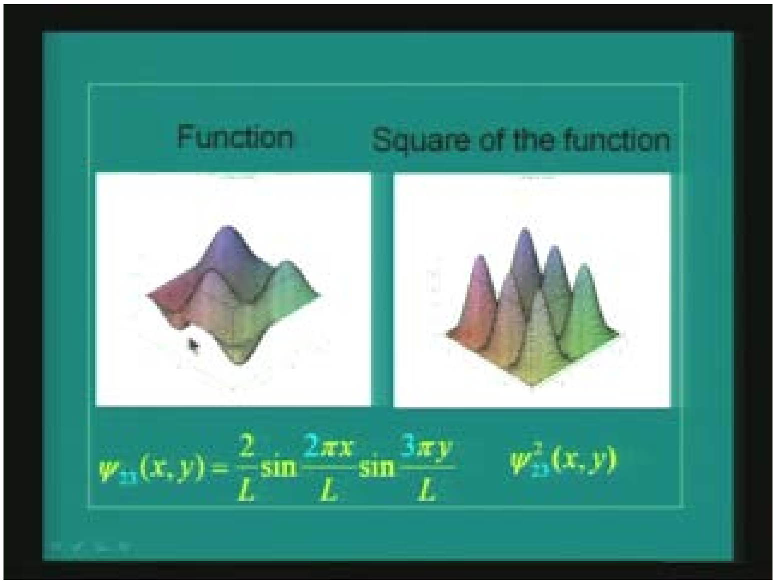

Function

Square of the function

$$\psi_{23}(x,y) = \frac{2}{L}\sin\frac{2\pi x}{L}\sin\frac{3\pi y}{L} \qquad \psi_{23}^2(x,y)$$

Likewise for ψ_{22} quantum number in the x direction is 2, the first one and the quantum number in y direction the second one is 3 therefore you should see a three sine half waves in the y direction and a two sine half waves in the x direction and if this is not clear when you square the function when you square this particular function you see immediately that there are three hums along the y direction when you see that and along the x direction you see these two hums indicating that this is the probability density function for the particle in a two dimensional box, a square box with quantum numbers $n_1 = 2$ and $n_2 = 3$.

What is the other important consequence? Let us write the energy level expression once again E is $h^2/8mL^2$ $(n_1^2 + n_2^2)$ for $\psi_{11}(x, y)$ here the quantum number n_1 is 1 n_2 is 1 therefore E, let me also put n_1n_2 here to index the energies according to the numbers that we put in here. Therefore E_{11} is two times the $h^2/8mL^2$.

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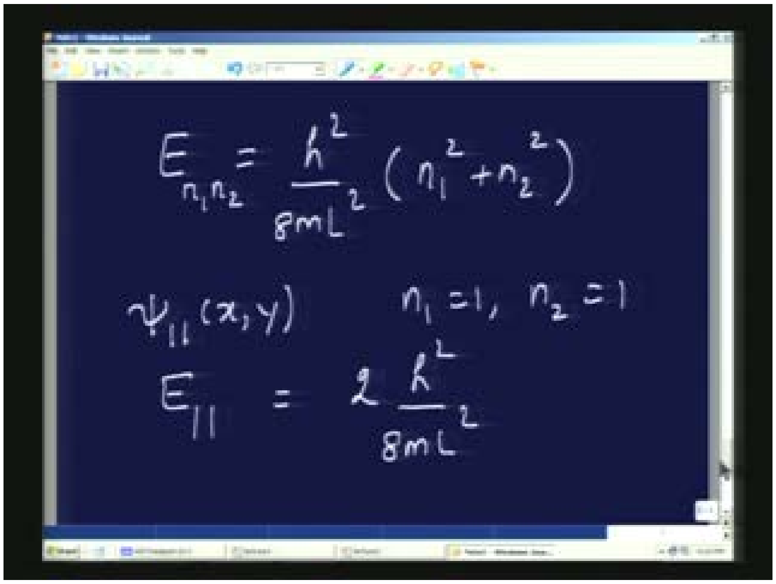

$$E_{n_1 n_2} = \frac{h^2}{8mL^2}(n_1^2+n_2^2)$$

$\psi_{11}(x,y)$ $n_1=1,\ n_2=1$

$$E_{11} = 2\frac{h^2}{8mL^2}$$

ψ_{11} is obviously $2/L \sin(\pi x/L) \sin(\pi y/L)$.

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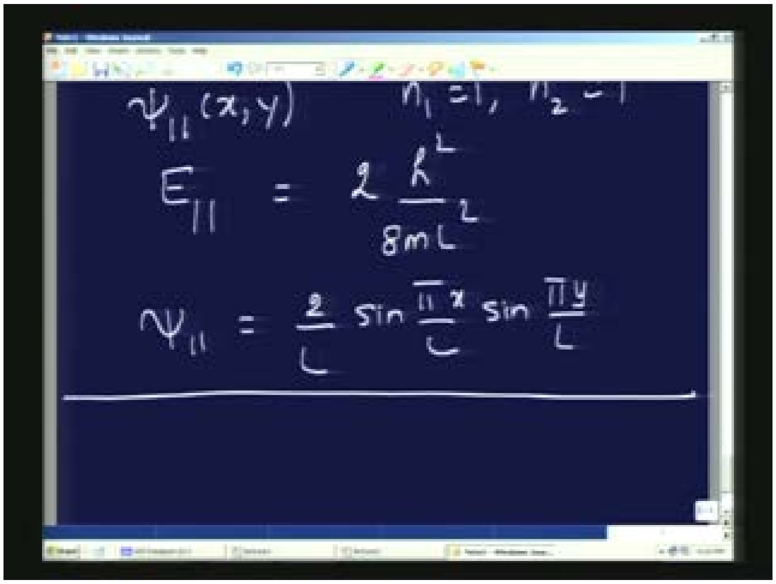

$\psi_{11}(x,y)$ $n_1=1,\ n_2=1$

$$E_{11} = 2\frac{h^2}{8mL^2}$$

$$\psi_{11} = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}$$

What about the next? The ψ_{12} is $2/L \sin(\pi x/L) \sin(2\pi y/L)$. What about E_{12}? It is $h^2/8mL^2$ and n_1^2 is 1, n_2^2 is 4 so you get $5h^2/8mL^2$.

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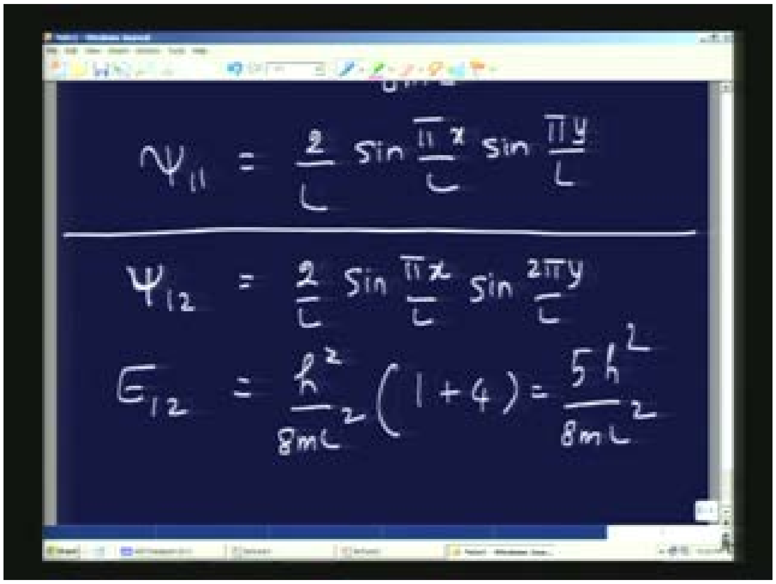

$$\psi_{11} = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}$$

$$\psi_{12} = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}$$

$$E_{12} = \frac{h^2}{8mL^2}(1+4) = \frac{5h^2}{8mL^2}$$

This is for $n_1 = 1$ and $n_2 = 2$. Now let me look at the case $n_1 = 2$ and $n_2 = 1$. These are the possible quantum numbers for the system. The wave function for this state $n_1 = 2$, $n_2 = 1$ is different from the wave function for the state $n_1 = 1$ and $n_2 = 2$.But what about the energies? E_{21} is obviously $5h^2/8mL^2$. But ψ_{21} is not equal to ψ_{12}. This is precisely what is called the degeneracy of the energies the system that may have more than one wave function that may be represented by more than one state but both of which have or all of those states have the same energy. Such states are called degenerate states.

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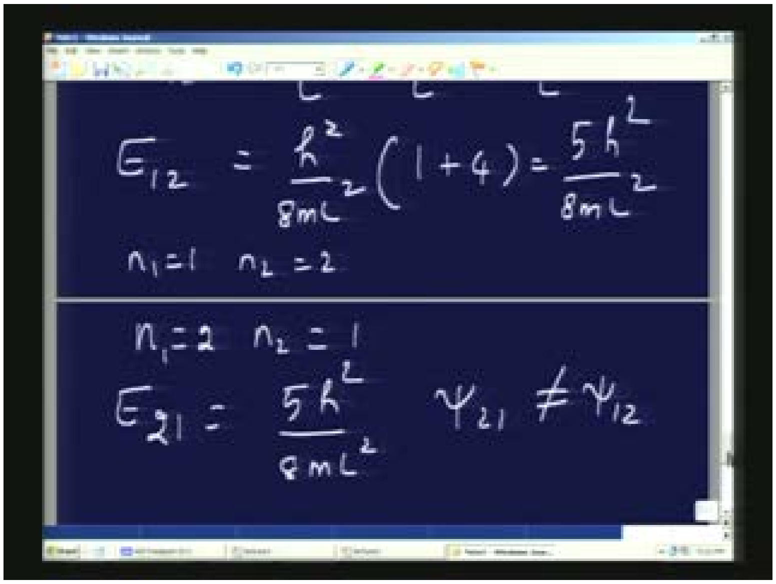

$$E_{12} = \frac{h^2}{8mL^2}(1+4) = \frac{5h^2}{8mL^2}$$

$n_1 = 1 \quad n_2 = 2$

$n_1 = 2 \quad n_2 = 1$

$$E_{21} = \frac{5h^2}{8mL^2} \qquad \psi_{21} \neq \psi_{12}$$

$E_{21} = E_{12}$ represents the degeneracy of order 2. It is not possible to have higher degeneracy here because we started with a two dimensional problem. The degeneracy in the case of a three dimensional system and of order 3, you recall in a case of hydrogen atom from your elementary descriptions of the hydrogen atom the 1S orbital is non degenerate, the 2S orbital is of course and the 2P orbital all four them have the same energy. You know that the degeneracy in the case of the hydrogen atoms is n^2 where n is the principle quantum number that is associated with the hydrogen atom. You have studied that in high school. Those conclusions will come out of this Mathematics neatly when we do these hydrogen atoms as we go through this process now from a particle in a 1D to 2D to a hydrogen atom you will see how the degeneracy is and this quantum numbers build up.

The next important aspect for the model problems is how do we calculate average values for the quantities that we measure? The energy we know, energy is a solution of the Schrödinger equation we do not need to calculate the average values of energy. You will get already when you do that you will get the energies that you get out of the solution of the Schrödinger equation. But there are the other things and there is no momentum in this model of course then the average position of the particle, then how do we calculate the average position of the particle using the prescriptions of the quantum mechanical principle.

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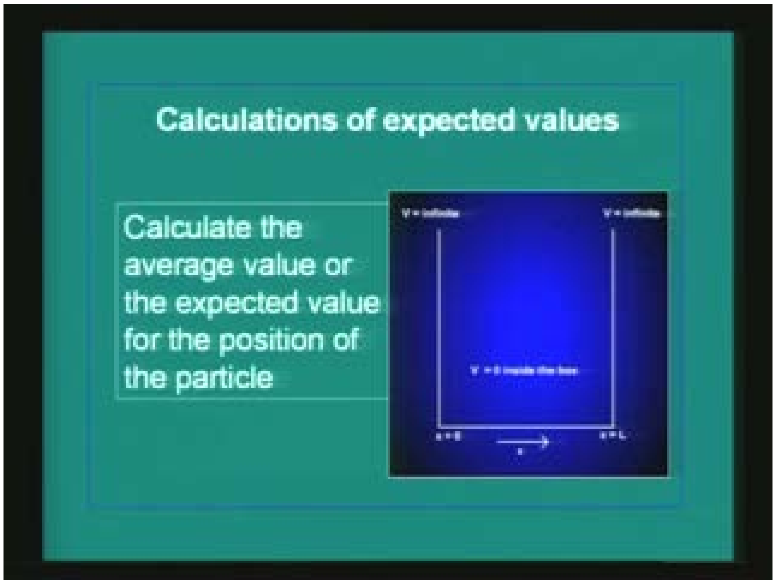

Calculations of expected values

Calculate the average value or the expected value for the position of the particle

So how do we calculate the expected values or expectation values? For a particle in a one dimensional box we will start with that and then extend the same thing for 2D and 3D model.

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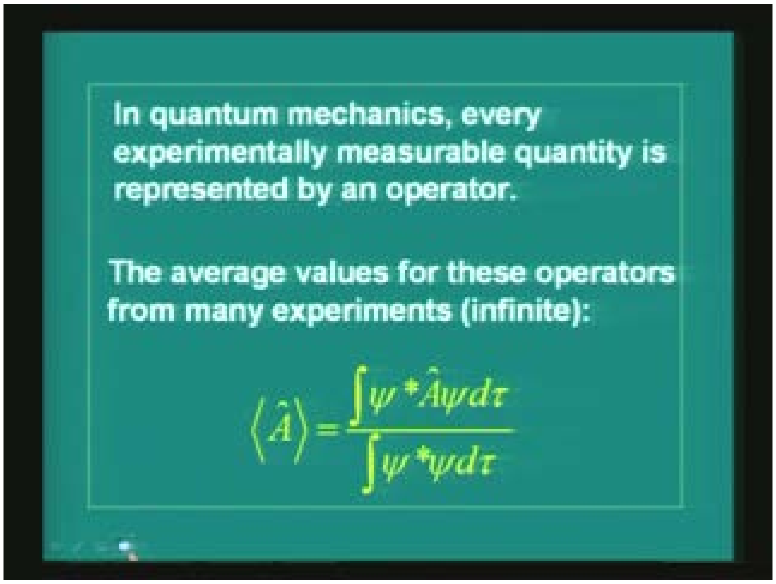

In quantum mechanics, every experimentally measurable quantity is represented by an operator.

The average values for these operators from many experiments (infinite):

$$\langle \hat{A} \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

Remember that in Quantum Mechanics every experimentally measurable quantity is represented by an operator. This is a statement from first lecture. The average values in that lecture was also given as the $\int\psi^*\hat{A}\,\psi\, d\tau/\int\psi^*\psi\, d\tau$ the operator $\hat{A}$ corresponding to what you are measuring. (Refer Slide Time: 33:11 min)

How do we do this for a particle in a one dimensional box what is the average value for the position of the particle. The verbatim formula if you substitute is the $\int\psi^*(x)\, x\, \psi(x)dx/\int\psi^*(x)\, \psi(x)\, dx$. Now, we have to put all the integrals in the appropriate form. Now you recall what is $\psi^*(x)$ or $\psi(x)$. It is $\sqrt{2/L}$ for the particle in a one dimensional box it is $\psi(x)$ is $\sqrt{2/L}\, \sin n\pi x/L$. What are the values for x? So, x goes from 0 to L in one dimension. Therefore the integral when you talk about the integral dx the average value x is now from x = 0 to x = L is $2/L \int\sin \pi x/L$.

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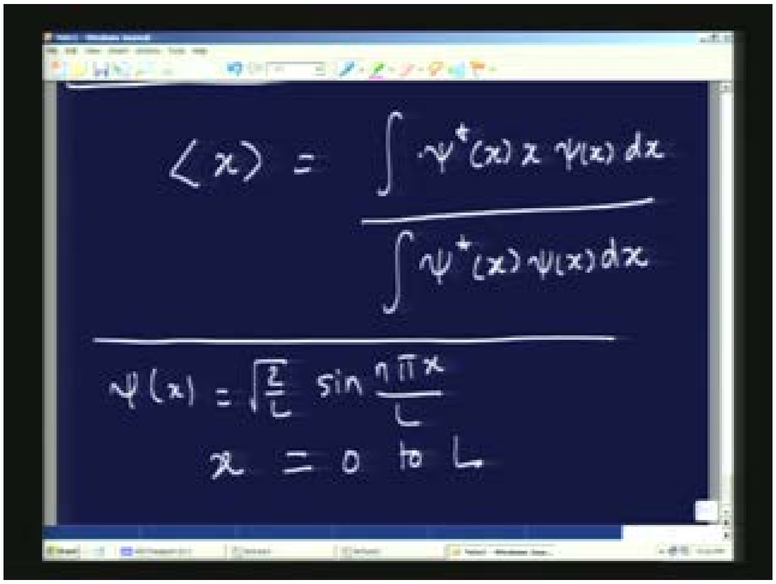

$$\langle x \rangle = \frac{\int \psi^*(x)\, x\, \psi(x)\, dx}{\int \psi^*(x)\, \psi(x)\, dx}$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

$$x = 0 \text{ to } L$$

If you want to put in an n you can put an n for the arbitrary state ψ_n, x that is the operator corresponding to the position, sin nπx/L dx / (x = 0 to x = L) 2/L∫sin(nπx/L) sin(nπx/L)dx. So <X> = 2/L∫sin(πx/L) x sin (nπx/L) / 2/L∫sin(nπx/L) sin(nπx/L)dx in between the limits x = 0 to x = L.

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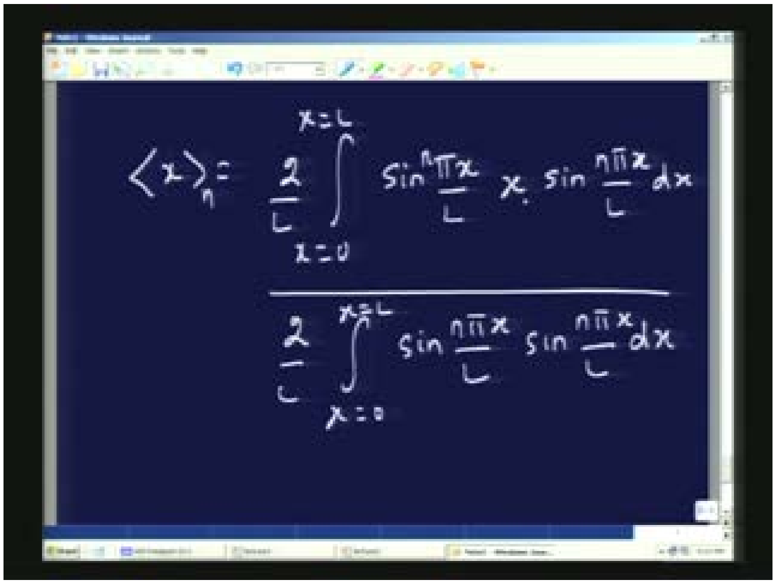

$$\langle x\rangle_n = \frac{\frac{2}{L}\int_{x=0}^{x=L} \sin\frac{n\pi x}{L}\, x\, \sin\frac{n\pi x}{L}\,dx}{\frac{2}{L}\int_{x=0}^{x=L} \sin\frac{n\pi x}{L}\, \sin\frac{n\pi x}{L}\,dx}$$

If we have to calculate the average value for the momentum operator you have to put the operator for the momentum between the two wave functions that is sandwiched by the two wave functions. The operator for momentum is –iħ d/dx.

Therefore it is extremely important where you put that operator and quantum mechanical rule tells you that the operator should be placed in the middle of these two wave functions ψ^* on one side ψ on the other side, do not ask me why, that works, there are no problems with that kind of a prescription when we calculate the averages experimentally we seem to have no inconsistencies of any kind. This is an elementary integral for you to solve. The average value of x in terms of the integral on the numerator and the integral on the denominator, of course this you know, this is how you got 2/L sin(nπx/L)sin(nπx/L)dx was nothing but the ψ^2dx which is the probability of finding the particle in a small region. And when you integrated the probability completely you got 1.

Therefore this automatically is equal to 1 from your previous calculations. You only have to calculate the other, I will leave the result as for you to calculate but the average value of x will turn out to be for no ones surprise L/2 which is the middle of the function, no surprises here. What is the average value for a particle which is moving with a constant energy kinetic energy between the ends of the box right in the middle but what is the average value for the momentum of the particle? The average value for the momentum p is exactly the same problem 2/L∫sin(nπx/L) form 0 to L, now the operator for p is – iħ d/dx sin(n π x/L) times dx. So, <p> = 2/L∫sin(nπx/L) (–iħ d/dx) sin(nπx/L)dx from 0 to L.

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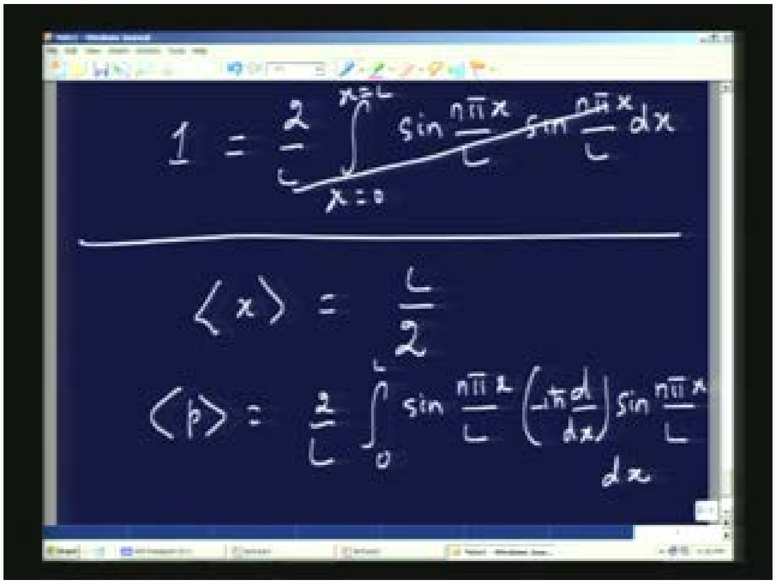

$$1 = \frac{2}{L}\int_{x=0}^{x=L} \sin\frac{n\pi x}{L} \sin\frac{n\pi x}{L}\, dx$$

$$\langle x \rangle = \frac{L}{2}$$

$$\langle p \rangle = \frac{2}{L}\int_{0}^{L} \sin\frac{n\pi x}{L}\left(-i\hbar\frac{d}{dx}\right)\sin\frac{n\pi x}{L}\, dx$$

You do not need the denominator because the denominator where I showed you is already 1. So if you calculate this value for the momentum which I would give you as problem for solve the answer is 0. The average value for the particle's momentum as it is moving in the box is at every point the particle's momentum can either be in this direction or in that direction. And therefore it looks like the momentum vector is all added up to give you on the average when you make infinite measurements.

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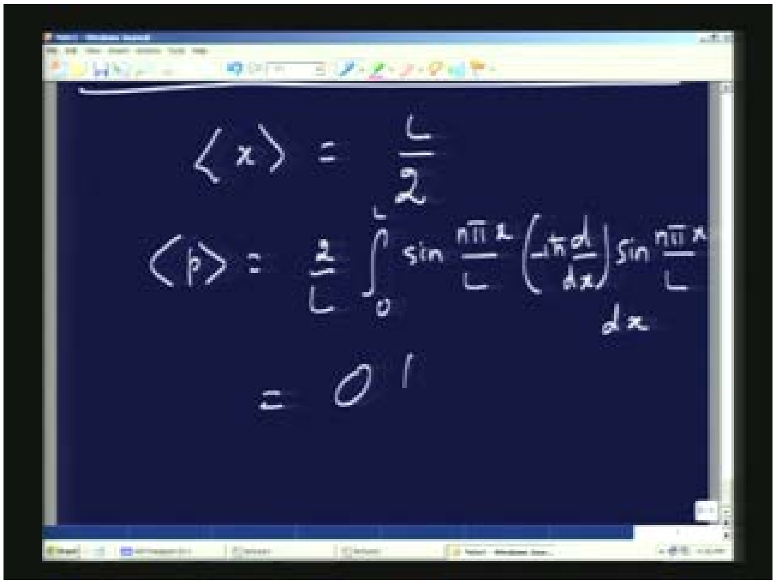

$$\langle x \rangle = \frac{L}{2}$$

$$\langle p \rangle = \frac{2}{L}\int_{0}^{L} \sin\frac{n\pi x}{L}\left(-i\hbar\frac{d}{dx}\right)\sin\frac{n\pi x}{L}\, dx$$

$$= 0\,!$$

This angular bracket refers to the fact that it is an average over many theoretically or in principle infinite number of measurements. The average value for the momentum turns out to be 0. So this how we become sort of operational in Quantum Mechanics.

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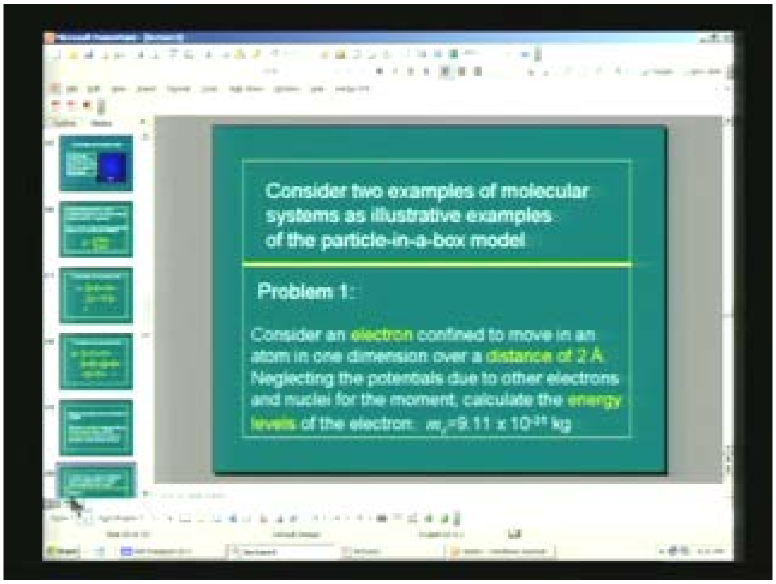

Consider two examples of molecular systems as illustrative examples of the particle-in-a-box model

Problem 1:

Consider an electron confined to move in an atom in one dimension over a distance of 2 Å. Neglecting the potentials due to other electrons and nuclei for the moment, calculate the energy levels of the electron. m_e=9.11 x 10^{-31} kg

Now, let us consider two numerical examples for the rest of lecture. To illustrate why we have to worry about these things in the molecules and why we do not have to worry about these things in real life, in day-to-day life. Let us take two examples, let me read two examples again with the particle in a one dimensional box model, the calculations for the two dimensional boxes are very similar.

So let us consider two examples of molecular systems as illustrative examples of the particle in the box model. The first problem: let us consider an electron confined to move in an atom in one dimension over a distance of 2 A^0 Angstroms. So this gives since it is constrained to move in one dimension over a distance of 2 A^0 Angstroms the interpretation is that the box length is 2 A^0 Angstroms neglecting the potentials due to other electrons and nuclei for the moment which is equivalent to saying that inside the box that the particle is moving with no potential experience by it. Of course in the atom there is a positively charged nucleus and the electron moving in the absence of the positively charged nucleus is a fictitious problem. It is an imaginary problem.

What we want to show is where Quantum Mechanics is important and where it is not. So let us assume for the moment the electrons and the nuclei do not interact with each other. It is a very non chemical assumption but we will do that. Let us calculate the energy levels of the electron how are they composed of, you remember that the energy level for the particle in a one dimensional box is $h^2/8mL^2$ times n^2. So let us calculate that with the mass of the electron given as 9. 011 times 10 raised to – 31 kilograms, so near substitution of the numbers.

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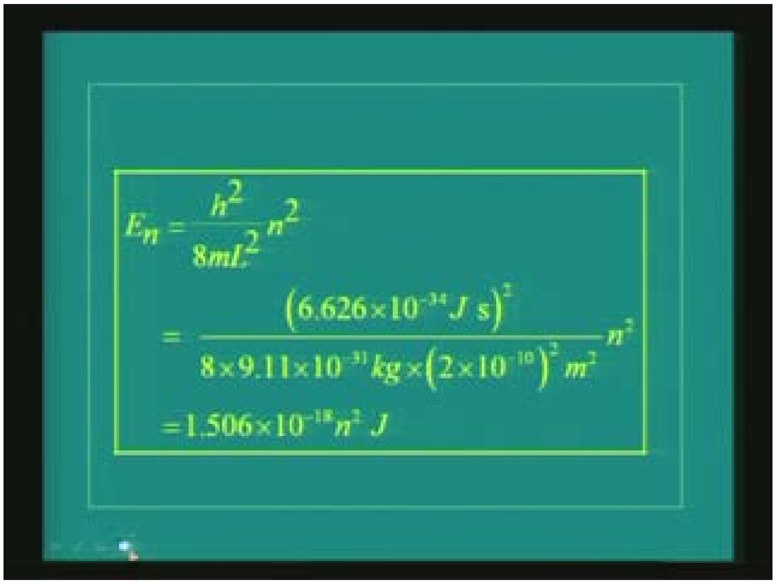

$$E_n = \frac{h^2}{8mL^2}n^2$$

$$= \frac{(6.626\times10^{-34} J\ s)^2}{8\times9.11\times10^{-31} kg\times(2\times10^{-10})^2 m^2}n^2$$

$$= 1.506\times10^{-18} n^2\ J$$

E_n is of course given by $(h^2/8mL^2)n^2$, h is 6.626 times 10 raised to – 34 joules second and h^2 is square. And the mass of the electron is 9.011 times 10 raised to – 31 kilograms. The dimension given to you is 2 A^0 Angstroms or 2 × 10 raised to – 10 meters it is L^2. Therefore you have the meter square here. So you have kilogram meter square and we want to calculate the energy. And at the top you have kilogram $(\text{meter})^2$ $(\text{second})^{-2}$, joule is $(\text{second})^{-2}$ times second therefore this unit is $(\text{kilogram})^2$ $(\text{meter})^4$ $(\text{second})^{-2}$. The result is number of joules, 1.506 times 10 raise to – 18 n square joules where n is the quantum number. Therefore the energy levels are separated by this factor. (Refer Slide Time: 41:56 min)

Now let us draw the energy levels E_1 is $h^2/8mL^2$, E_2 is $h^2/8mL^2$ times 4, E_3 is nine times this whole quantity $h^2/8mL^2$ and so on. So in units of this if you call this as a unit of energy E_2 is $4E_1$, E_3 is $9E_1$, E_4 is $16E_1$ and so on. Therefore the energy level diagram if you draw and if this is the increasing values of energy this is E_1 and E_2 the difference between E_1 and E_2 is 3. E_2 and E_3 is 5, the difference between these two is 5 because E_3 is 9 times the E_1. This is the difference 3 E_1, E_3 is nine times E_1 and E_2 is $4E_1$ so the difference between the two is $5E_1$. The next is of course E_4 is 16 E_1. So the difference is 3, 5, 7, 9, 11, and so on. So the energy levels increase with the spacing between the energy level increasing.

The difference between any pair of successive energy level which is 2n + 1 where n is the quantum number associated with that pair. Here it is 3 so n is 1, 2n + 1 is 3. So n is 2, 2n + 1 is 5, n is 3, 2n + 1 is 7 and so on. Therefore the energies of the particle here are functions of n^2 and the energy levels difference is of the order of n. With this energy for the electron in the atom 1.506 times 10 raised to – 18 joule it is a measurable energy it is possible to distinguish such energies.

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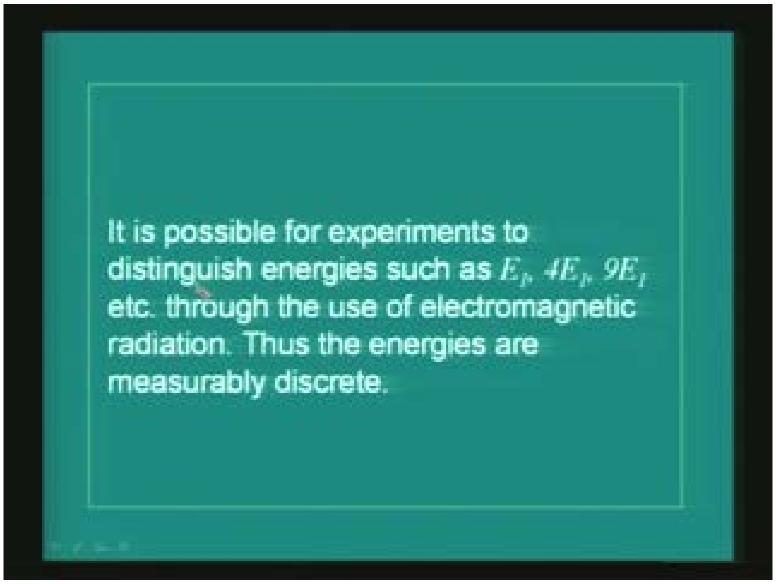
It is possible for experiments to distinguish energies such as E_1, $4E_1$, $9E_1$ etc. through the use of electromagnetic radiation. Thus the energies are measurably discrete.

So E_1, $4E_1$, $9E_1$ can be easily separated can be understood you can see them through spectroscopic measurements. Thus the discreteness that you have in terms of the energies can be directly seen by a spectrometer by a spectroscopy experiment. Therefore the proof of the pudding is in the eating as we say in English the proof of the Quantum Mechanical calculation is the result that it gives are measured or observed by the experiments and confirmed by the experiments. So these are perceptibly different energies. Let us take the next case where it is not possible to have such clear distinction.

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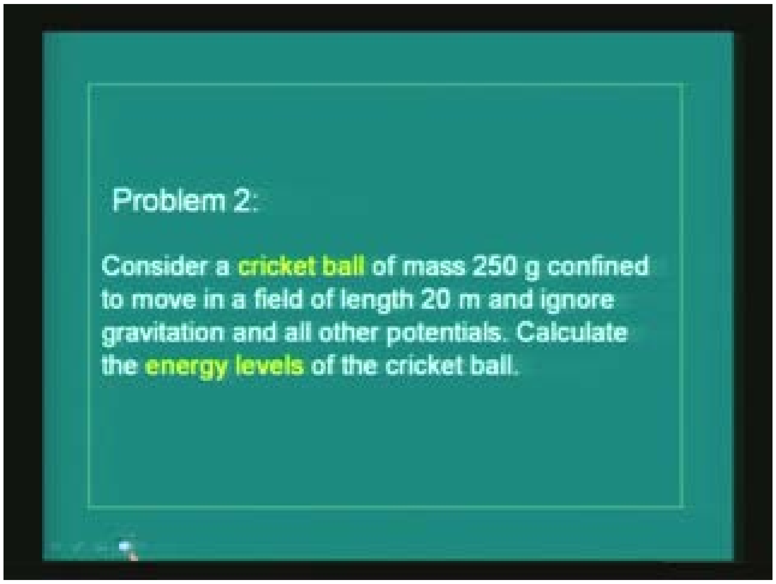
Problem 2:

Consider a cricket ball of mass 250 g confined to move in a field of length 20 m and ignore gravitation and all other potentials. Calculate the energy levels of the cricket ball.

This country is mad after cricket so let us take the cricket ball as an example. This is an approximate distance I am not a player of cricket therefore I do not know the actual distance between the two ends of the stumps and so on so approximate figure I am going to give you 20 meters may be it is not, 22 yards I do not even remember what it is. Let us consider a cricket ball of mass of 250 grams may be it is heavy or light but it is of the order of magnitude a ¼ kg confined to move in a field of length 20 meters. Let us assume that the ball never flies off the batsman or off the bowler that the ball is only between those regions and let us ignore the gravitation and all other potentials. Let us assume that the ball has only kinetic energy between the batsman and the bowler.

Let us only try to know the energy levels of the cricket ball to give you an order of magnitude where Quantum Mechanics is important.

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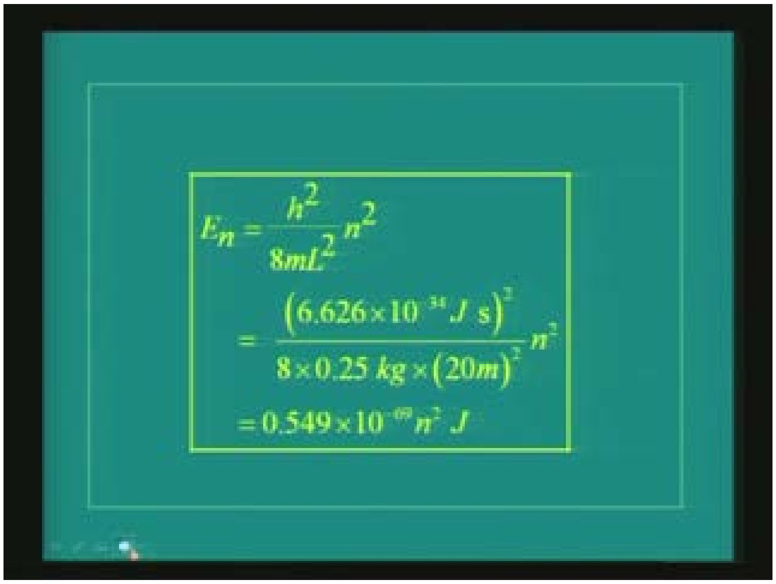

$$E_n = \frac{h^2}{8mL^2} n^2$$

$$= \frac{\left(6.626 \times 10^{-34}\, J\, s\right)^2}{8 \times 0.25\, kg \times \left(20m\right)^2} n^2$$

$$= 0.549 \times 10^{-69} n^2\, J$$

Again the energies are $(h^2/8mL^2)n^2$. So, what is our particle now? The particle is a cricket ball, what is the box now? It is a box of 20 meters and the two ends of the box are on one side is the batsman and other side is the bowler, the ball does not go off either of them. That is not a very interesting cricket but we will just see that what that example tells you in terms of energy levels of the macroscopic objects. Assuming that and also leaving aside all the interactions that the ball has with the ground and so on if we do this simple model calculation you see what kind of energies we get. Much as the model itself is ridiculous the energy levels are even more ridiculous.

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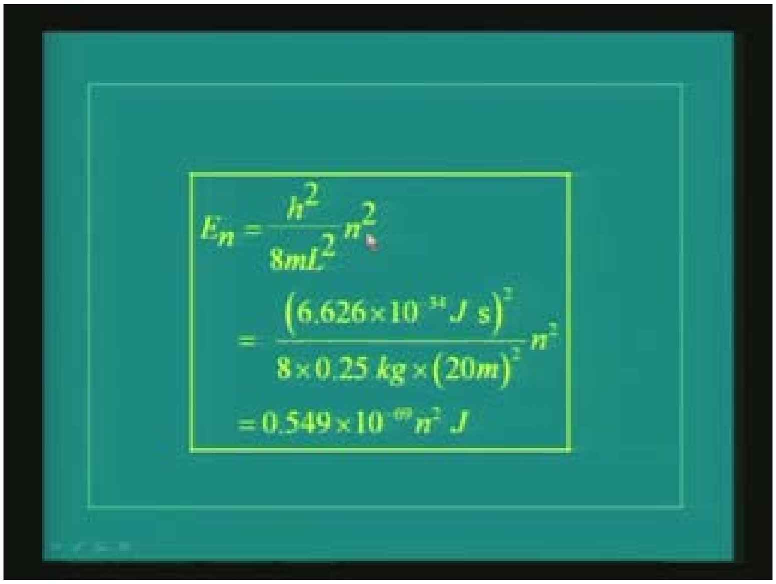

$$E_n = \frac{h^2}{8mL^2} n^2$$

$$= \frac{\left(6.626 \times 10^{-34} J\ s\right)^2}{8 \times 0.25\ kg \times \left(20m\right)^2} n^2$$

$$= 0.549 \times 10^{-69} n^2\ J$$

E_n is $(h^2/8mL^2)n^2$, h is a Planck’s constant, you see this is 10 raise to – 34 joule second square. Now the ball is 0.25 kilograms and the length of the box is 20 meters. Therefore the length is 20 $(\text{meter})^2$ times n^2. So, if you calculate all these things you see that the energy levels are a number 0.549 times 10^{-69} impossible to measure no matter what the values of n are so n has to be at least 10^{30} or 10^{40} in order for this energy level these types of energy levels to be perceptibly different which means that the discretization of the energies of this ball the kinetic energy of the ball when you consider Quantum Mechanics the discretization is so small so immeasurable that it is unimportant.

The motion of the ball can very well be considered by a simple classical mechanical problem we do not need the finer details of Quantum Mechanics. Since h is extremely small number 10^{-34} its smallness is a large measure for the atom where you have the other quantities also extremely small the mass of the electron is 10^{-31} kilograms. The length the atomic dimensions is 10^{-10} meters.

Therefore $h^2/8mL^2$ becomes a meaningful quantity for the small value of h only when the masses and the lengths that you talk about are very small. When the masses or the masses of realistic value the lengths or the dimensions that our eye can measure you see that this discretization is no longer important that the particle in a box is no longer relevant for the real physical macroscopic object problems. Perhaps, that the reason was never discovered.

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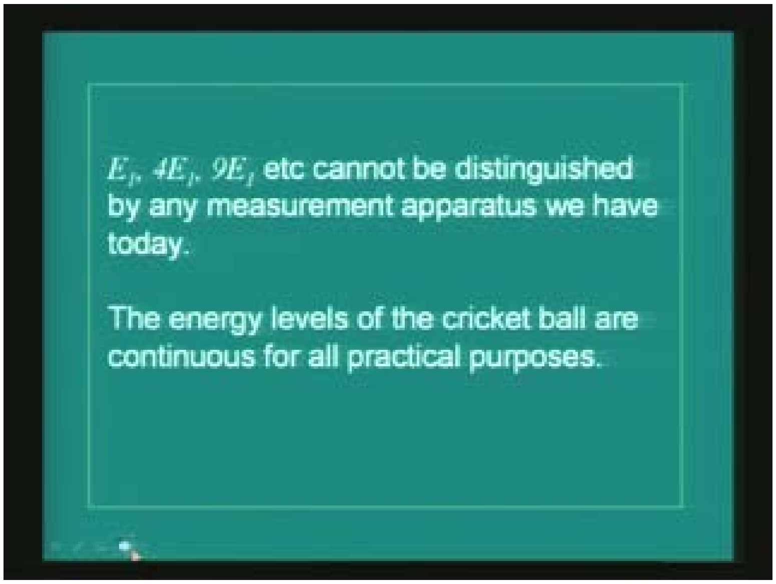

E_1, $4E_1$, $9E_1$ etc cannot be distinguished by any measurement apparatus we have today.

The energy levels of the cricket ball are continuous for all practical purposes.

So the conclusion is that E_1, $4E_1$, $9E_1$ what is $4E_1$ and $9E_1$ for this number? This is four times, this is nine times, this of course you cannot see any of these numbers therefore they cannot be distinguished by any measurement apparatus we have today.

The energy levels of the cricket ball are continuous for all practical purposes even within this trivial model. What this means is that for macroscopic objects we do not have to worry about the fineness the grained structure of the quantum mechanical equations we do not need them.

Classical mechanical equations are sufficiently accurate for us to follow the description.

Let us review having gone through the last three lectures some new ideas and concepts which are quite foreign to us. Let us review them and I suggest some problems for you to do as a back up exercise to the lesson that are being broadcast.

We suggest review problems based on what has been done up to now. The first one, derive the normalization condition for the wave function $\psi(x)$ particle in a one dimensional box. What does that mean? Show that the integral 0 to L, $\sin^2 n(\pi x/L)$ dx = L/2. This is the normalization condition and this is what we used in writing the wave function as $\sqrt{2/L} \sin n\pi x/L$.

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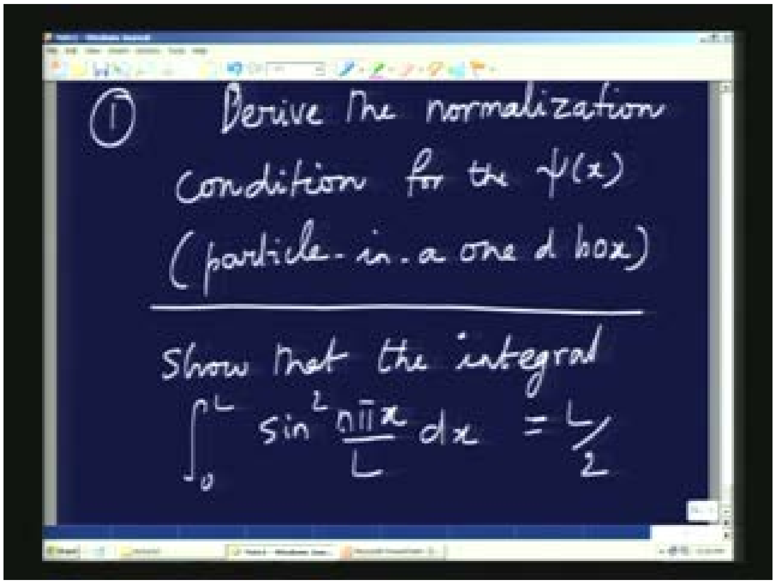

① Derive the normalization condition for the $\psi(x)$ (particle-in-a one d box)

Show that the integral $\int_0^L \sin^2 \frac{n\pi x}{L}\, dx = L/2$

The next problem is; does the wave function have a dimension like length, mass, time does it have any dimension? If it does then what are the dimensions for the wave function for 1d box and 2d box problems? Can you generalize this to n dimensions? The answer is the wave function has dimensions but you can find out what the dimensions are or please refer to text books accordingly. The third question is on the average values. The average value for the particle position x is given by the integral limits 0 to L in one dimension $2/L \int \sin^2 (n\pi x/L)\, x\, dx$.

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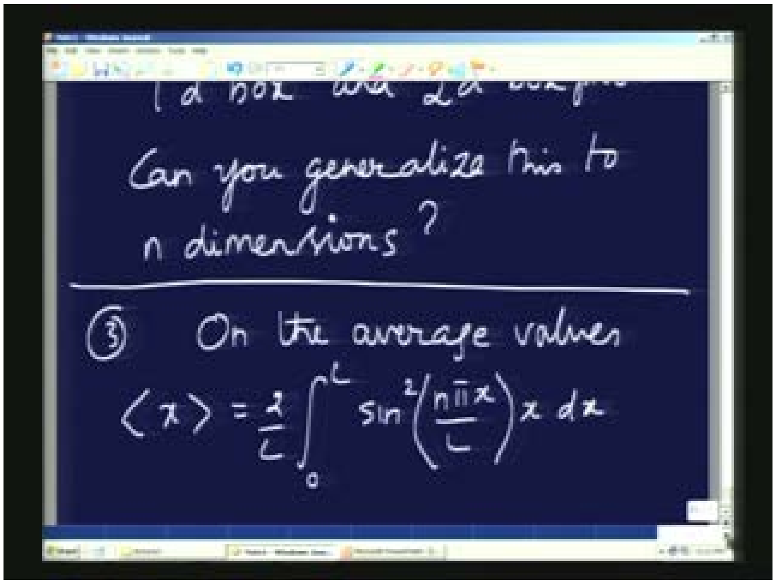

1 d box and 2d box

Can you generalize this to n dimensions?

③ On the average values

$\langle x \rangle = \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) x\, dx$

The value for x, what is <x>? The average value or if I give you the answer verify that the integral gives you that answer the answer is of course <x> is L/2.

The fourth one: think before you do this, what is the average value for the energy of the particle in the one dimensional box?

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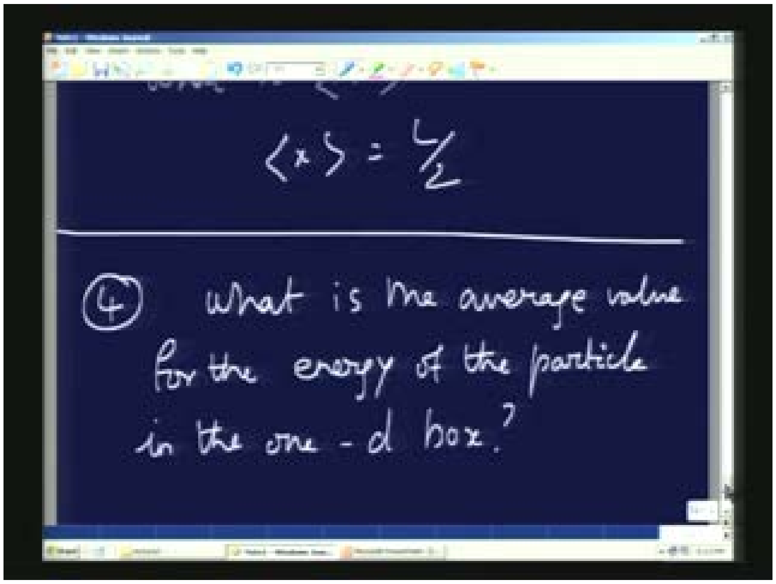

$$\langle x \rangle = L/2$$

④ what is the average value for the energy of the particle in the one-d box?

Now, if you recall our definitions for the <A> is ∫ψ*(x) A ψ(x)dx between 0 to L because for the particle in the 1d box denominator is of course is equal to 1. Let us write this out anyway, this is anyway is equal to 1.

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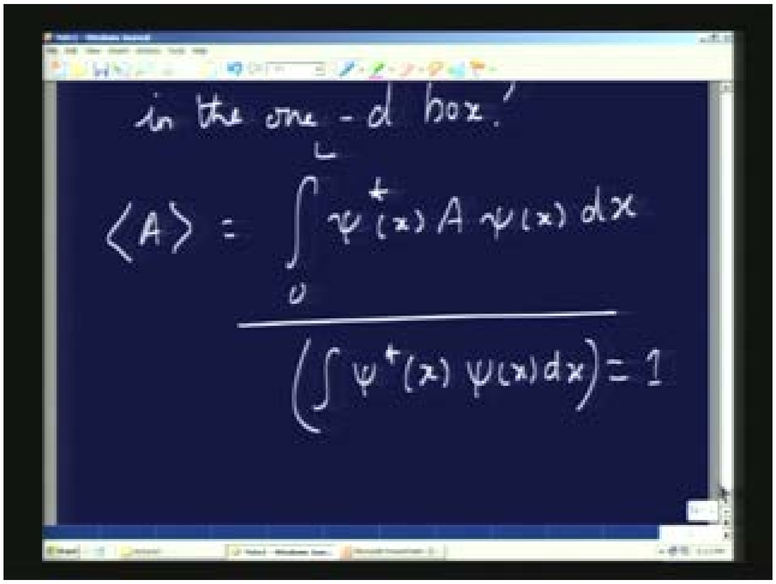

in the one-d box?

$$\langle A \rangle = \frac{\int_0^L \psi^*(x)\, A\, \psi(x)\, dx}{\left(\int \psi^*(x)\, \psi(x)\, dx\right) = 1}$$

So when you talk about the average value for the energy what is the operator that you want to use you have to use the Hamiltonian operator. The operator associated with the momentum is –iħ d/dx.

The operator associated with the energy is of course the Hamiltonian. The operator associated with the position is x. Likewise when you want to calculate the energy $<E>$ and if you put the Hamiltonian operator $\int\psi^*(x)\ \hat{H}\ \psi(x)dx$ between limits 0 to L you should not be deriving the integral but use the class lectures to write the answer immediately, that is the challenge. The fifth problem is calculating these quantities for the particle in a two dimensional box. These quantities like the average value of the position x the average value of the position y the average value for the momentum etc for the particle in a 2d box, 2d box problems.

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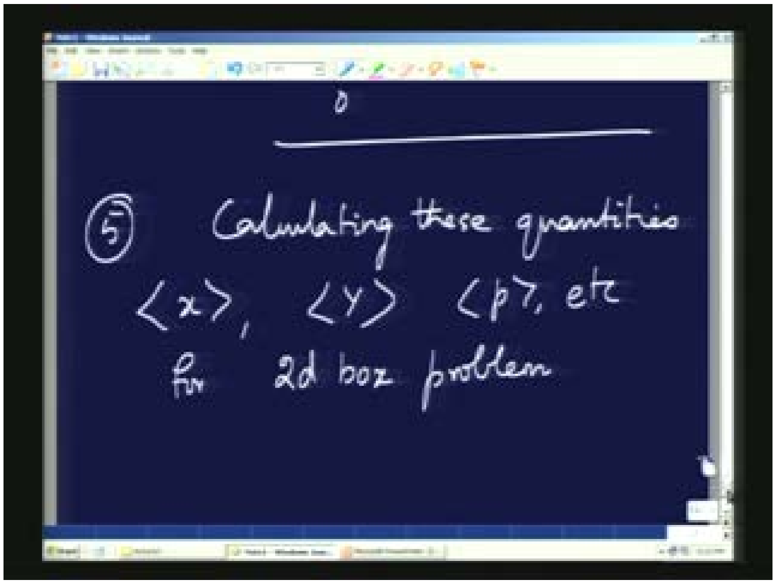

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⑤ Calculating these quantities

$\langle x\rangle$, $\langle y\rangle$ $\langle p\rangle$, etc

for 2d box problem

And lastly, of course as a model let me define an error in the position measurement by the quantity Δx the error as square root of the average of the square of the position minus square of the average value for the position, $\sqrt{(<x^2> - <x>^2)}$.

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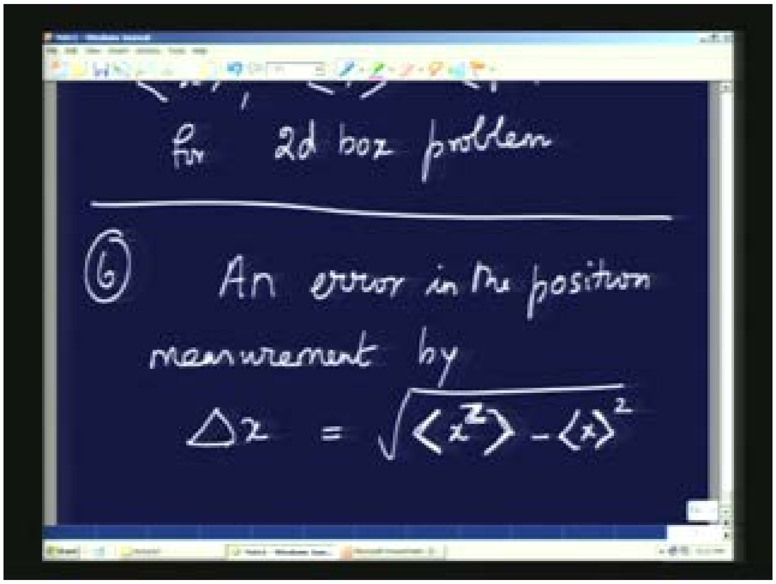

for 2d box problem

⑥ An error in the position

measurement by

$$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

Calculate Δx average I should write this as the average value for $<\Delta x>$ itself. Calculate Δx for the particle in a one dimensional box. Also defining the average value for the momentum Δp as $\sqrt{p^2}$ average value minus the average of p^2, calculate Δp.

What is your result for the product $<\Delta x>$ $<\Delta p>$?

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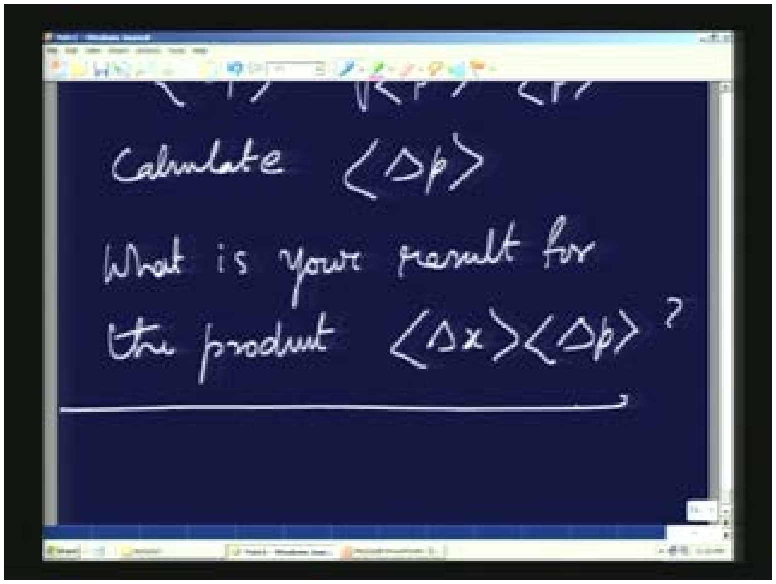

Calculate $\langle \Delta p \rangle$

What is your result for the product $\langle \Delta x \rangle \langle \Delta p \rangle$?