Engineering Chemistry - 1

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Lecture - 2

Module 1: Atoms and Molecules

Particle in a Box (one and two dimension)

Welcome back to the lectures on chemistry as part of the National Programme on Technology Enhanced Learning funded by the Ministry of Human Resource Development. This is the series of lectures given to students in their college years in engineering and in basic sciences.

The Chemistry module we will continue today is the same as the atoms and molecules. In the last lecture if you recall, I introduced the idea that Quantum Chemistry is fundamentally important in understanding why molecules form, why molecules undergo transformations to form various newer species and how do we understand the structure, properties and the chemical transformations of molecules, how do we do this from first principles. If you ask these questions then Quantum Chemistry provides the answers. Therefore, the first model on the atoms and molecules is meant to expose the use of Quantum Chemistry techniques. I was categorical in the last lecture that we are not trying to understand Quantum Chemistry or Quantum Mechanics but rather we are trying to follow through a prescription or a procedure by which we use the rules of the mechanics and hopefully over a period of time that we will understand why such rules came into place.

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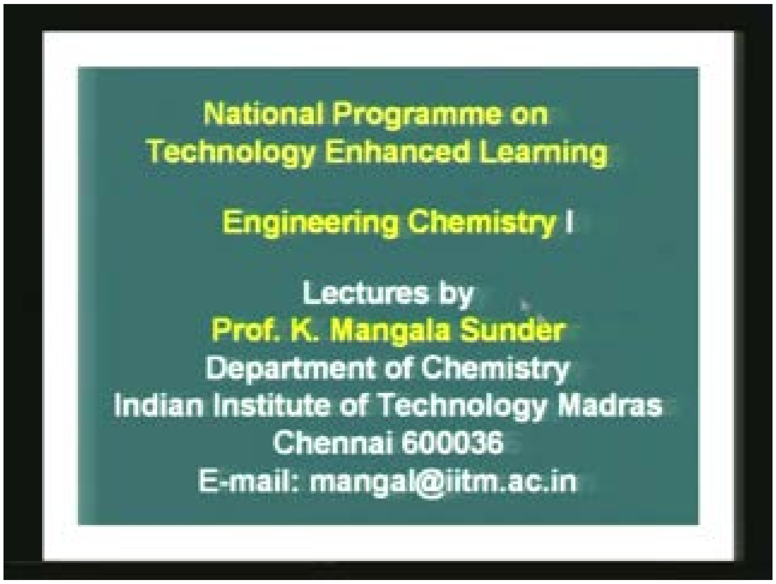

National Programme on
Technology Enhanced Learning

Engineering Chemistry I

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Before I begin my lecture let me welcome you with this acknowledgement to the National Programme on Technology Enhanced Learning, my name is Mangala Sunder, Department of Chemistry Indian institute of technology Madras in Chennai.

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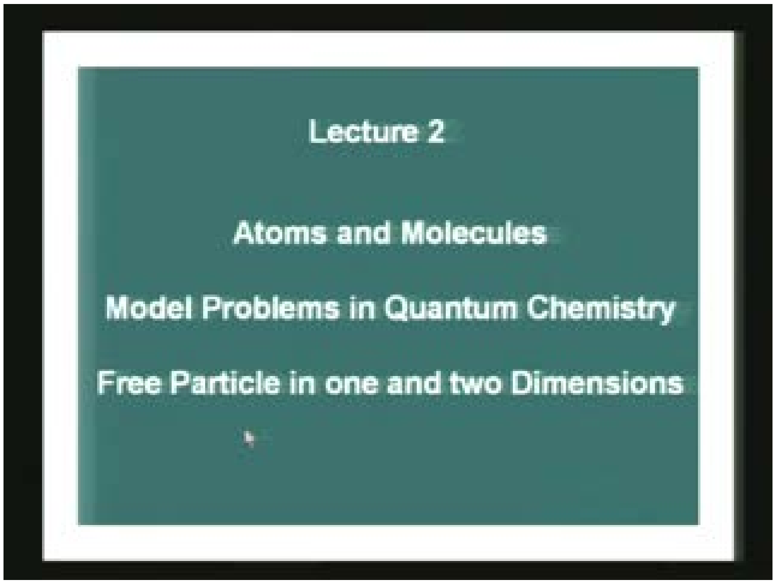

Lecture 2

Atoms and Molecules

Model Problems in Quantum Chemistry

Free Particle in one and two Dimensions

We will start studying model problems in Quantum Chemistry and we will start with the simple free particles in one and two dimensions. But before we do that, let me just recollect to you some of the most important names in Quantum Mechanics. In today’s lecture I will give you names of some of the important founders of the mechanics and in subsequent lectures I will also introduce you to the illustrious Chemists who have contributed to all our knowledge as of today.

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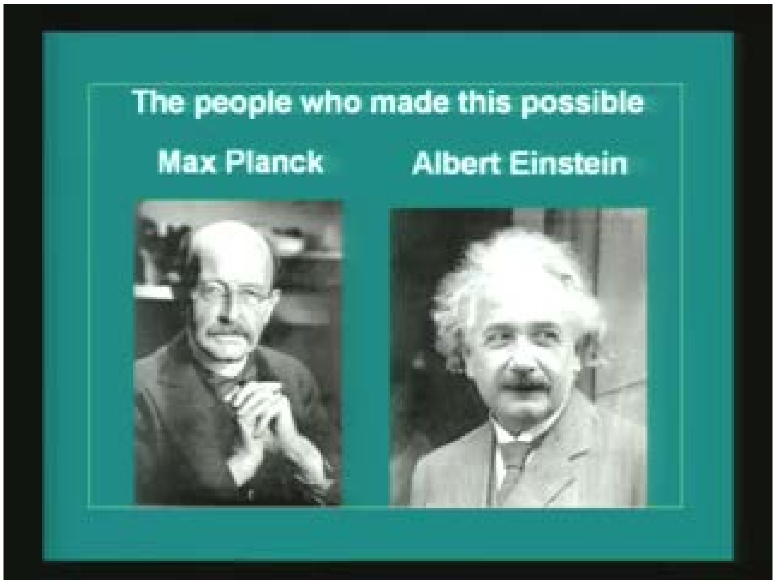

The people who made this possible

Max Planck

Albert Einstein

The people who made our understanding of the atoms and molecules possible, a few names most important ones Max Planck, we introduced Max Planck in the last lecture through his constant and his phenomenon of the black body radiation. Albert Einstein, undoubtedly the most famous Physicist ever to have lived in the last century whose contribution to Physics in general and to Quantum Mechanics in particular are unparalleled.

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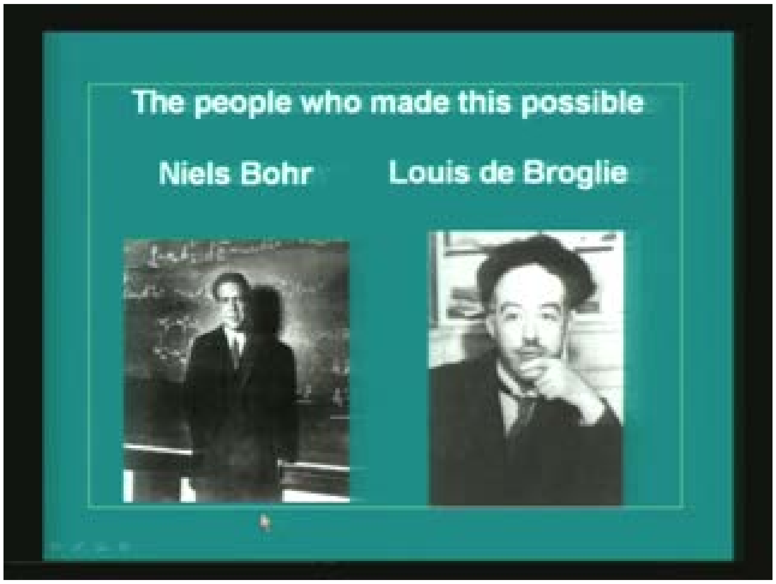

The people who made this possible

Niels Bohr

Louis de Broglie

Niels Bohr, a Danish Physicist whose name is familiar to all of you from your high school textbooks on the planetary model of the hydrogen atom the orbits of the electrons in the hydrogen atoms. We recall Niels Bohr who was the first to apply the quantum hypothesis to understand the spectra of hydrogen, the line spectra of hydrogen in terms of the lyman series, the balmer series, the paschen series and so on. We recall that there was a famous constant called the Rydberg constant which Neils Bohr explained through fundamental methods. Louis de Broglie, a French Physicist brought in the idea that matter can be treated as both particulate as well as wavelike. So this wave particle duality eventually led Erwin Schrödinger the Austrian Physicist to ask questions such as what are the governing dynamical equations for substances which behaves both wave like and particle like. Louis de Brogile was the founder of this matter the wave ideas.

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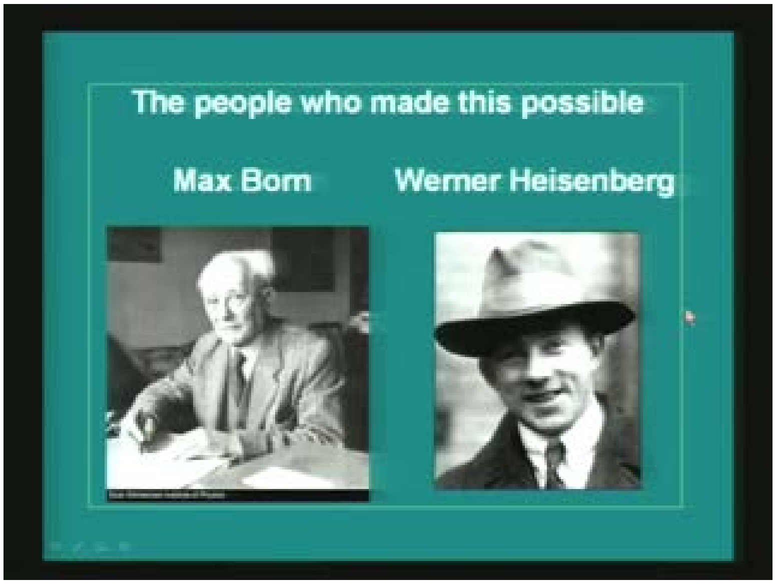

The people who made this possible

Max Born

Werner Heisenberg

Max Born is seen on the left hand side. Max Born's contributions in Physics in general are very well known but in this particular reference to the Chemistry it is his interpretation of the quantum mechanical wave function. This absolute square of the wave function is being identified with the probability density of the system. We will see those things a little bit more in detail. Werner Heisenberg, very well known for his uncertainty principle, we must have heard the joke that the Heisenberg may have been here to indicate the uncertainty associated with position and velocity, position and momentum, it is a corner stone of Quantum Mechanics.

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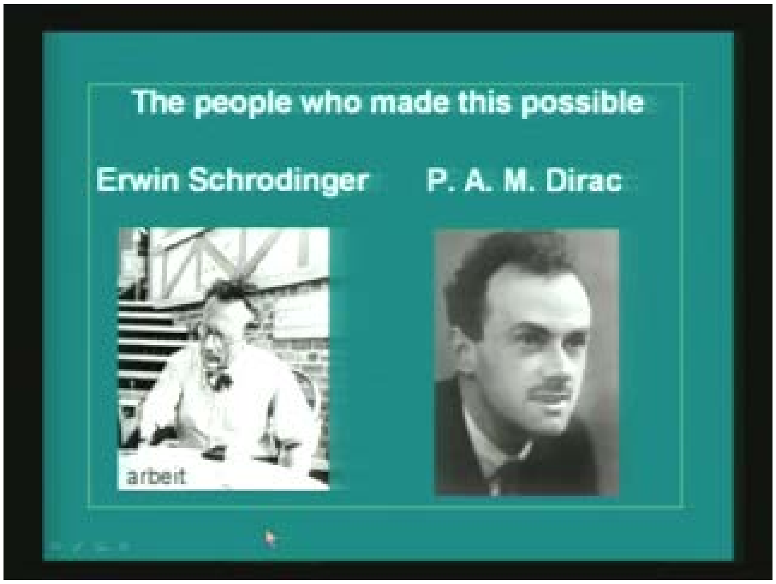

The people who made this possible

Erwin Schrodinger

P. A. M. Dirac

Erwin Schrödinger, the most important name for all the chemist because all the chemists quantum chemist, computational chemist, the ones who do theory the ones who tries to understand Chemistry from first principles have to solve the Schrödinger equation , have to understand how to solve Schrödinger equations both analytically and through the use of computers.

Paul Dirac, the man on the right hand side contributed to the development of Quantum Mechanics through His relativist theory of electrons. His contributions, in fact he made such a famous statement that all of the mechanics as is necessary for the applications of the Chemistry are well known and it is only a question of computational difficulty that we will have to surmount. Paul Dirac’s name is very famous among computational chemistry for the statements he made and for the developments in computational chemistry which has happened in the last 50 or 60 years. People understand that Dirac gave the basic formulation in terms of unifying Quantum Mechanics through his ever famous book called the Principles of Quantum Mechanics.

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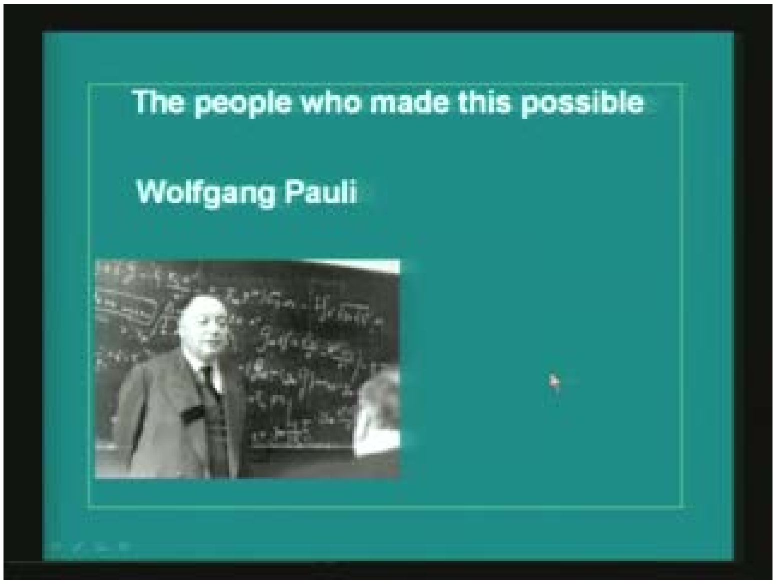

The people who made this possible

Wolfgang Pauli

Wolfgang Pauli is the other person that again Chemists know. Pauli’s exclusion principle in your high sdhool when you build up the electronic structure of an atom by adding electrons to various orbitals you are told that no more than two electrons for any orbitals, no two electrons can have all the same four quantum numbers. That is one of the many important things that Wolfgang Pauli did and which is fundamental to the atomic structure in Chemistry. Let us go back to the lecture that we have today, namely the model solutions of the quantum problems that we introduced, the Schrödinger equation that needs to be solved for simple models and from the models we try and understand the results in terms of simple physical pictures. And we see that the pictures that come out of the solutions are quite different from what we are familiar from our realization of what happens around us, what happens in the atoms, in sub atomic, in microscopic domain, microscopic dimensions seen so strange that we have to see this only through the Mathematics and the corresponding solutions of the mathematical equation as proposed by Erwin Schrödinger.

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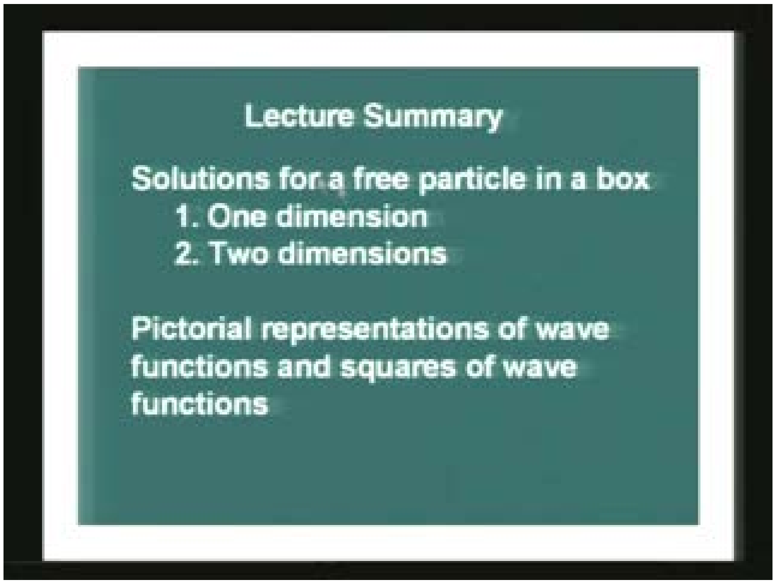

Lecture Summary

Solutions for a free particle in a box

1. One dimension
2. Two dimensions

Pictorial representations of wave functions and squares of wave functions

So, let we summarize the contents of today's lecture before we go into the details. We will solve the free particle in the box in one dimensional model problem and also in a two dimensional problem. And given some time, I would like to give you pictorial representations of the wave functions and squares of the wave functions. Let me recollect from the previous lecture the Schrödinger equation that we wrote down for a particle in the one dimensional box. You recall that there was a kinetic energy term $-\hbar^2/2m\ (d^2/dx^2)$, the operator corresponding to the kinetic energy plus the potential energy, $V(x)$ of the particle or of the system that we are interested in the potential energy experienced by the particle. All of this was called the Hamiltonian, H which represents in classical mechanics this total energy of the system. Quantum mechanical kinetic energy plus the quantum mechanical potential energy acting on the wave function $H\psi(x) = E\ \psi(x)$.

This is the equation governing the wave function $\psi(x)$. If we know the particle's mass and if we know the potential energy that the particle is facing then we are able to formulate the Hamiltonian of the system but then we have to solve the differential equation $H\psi = E\psi$ where E is a constant. This is a model problem.

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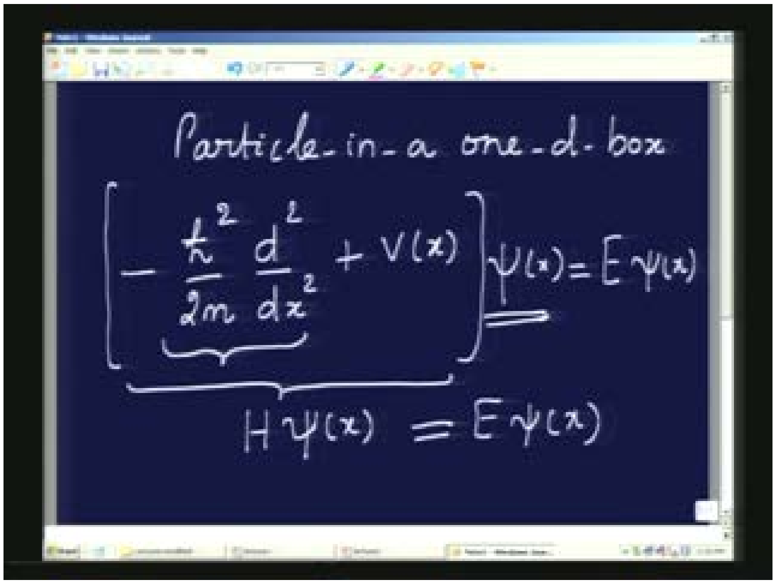

Particle-in-a one-d-box

$$\underbrace{\left[-\underbrace{\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}+V(x)\right]}\psi(x)=E\psi(x)$$

$$H\psi(x)=E\psi(x)$$

Now, why is particle in a 1D box for chemist? Think about a simple system like conjugated polyenes, alternating single and double bond structures. Polymeric if you want to the simplest structure for this is butadiene then of course you can put the hydrogen to ensure that the chemical bonding of carbon is taken care of. The π-electrons which are in the double bonded structure, the π electrons are easily modeled to a first approximation by an equation similar to that of a particle in a 1D box equation. If you want to know something about what these molecules do when they absorb light or when you excite them where the electrons go and things like that then to a certain approximation we can understand all of them by solving the Schrödinger equation for a one dimensional particle in a box. Therefore, the relevance is in trying to understand a corresponding chemical system.

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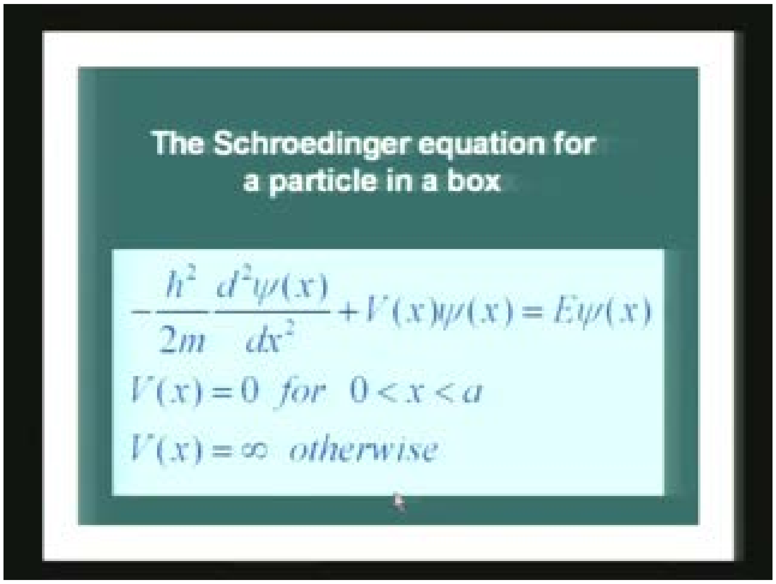

The Schroedinger equation for a particle in a box

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

$$V(x)=0 \;\; for \;\; 0<x<a$$

$$V(x)=\infty \;\; otherwise$$

The particle in a 1D model is of course $-\hbar^2/2m\,(d^2\,\psi(x)/dx^2)+V(x)\,\psi(x) = E\,\psi(x)$. But with a specific requirement that this potential vanishes in a small region $0< x <a$ is the region or the box or the length of the box. If the particle moves in one dimension x the length of box is a, you see that the potential is 0 in that region and the potential is infinite otherwise so that the particle does not escape the box.

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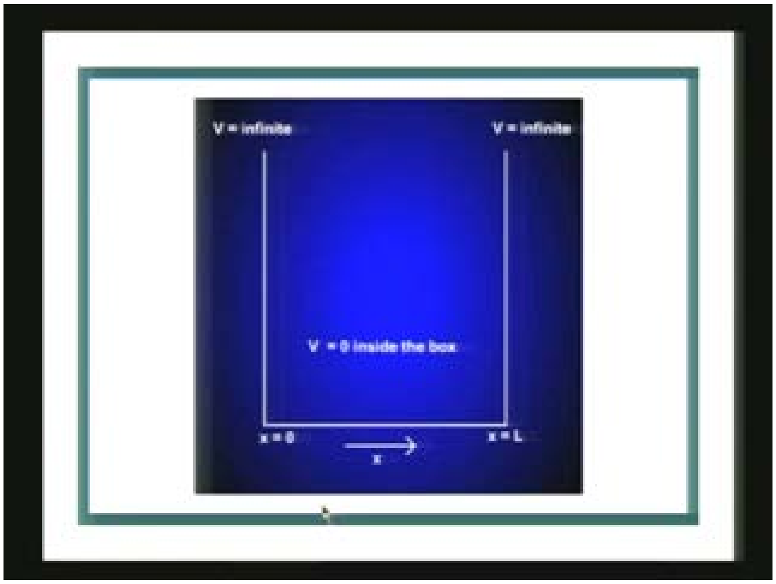

Simple pictorial representation of the box is something like what you see here. The particle moves inside this region, what I had is ‘a’ there in the equation is replaced now by L is length of the box, 0 to L, x is the variable the particle is moving in a one dimensional motion. We do not know where it is, we all know that it is inside the box it cannot escape the box in that the potentials at the ends of the box are infinity, infinite, repulsive so that the particles stays inside the box. This is the model we want to solve. Now let us go back to that equation. Since V is 0 inside the box we can simply rewrite this equation as $-\hbar^2/2m\,(d^2\psi/dx^2) = E\,\psi$ or we can bring the constant to other side and then bring the whole thing back to write this equation as $d^2\psi/dx^2 + (2mE/\hbar^2)\,\psi(x) = 0$.

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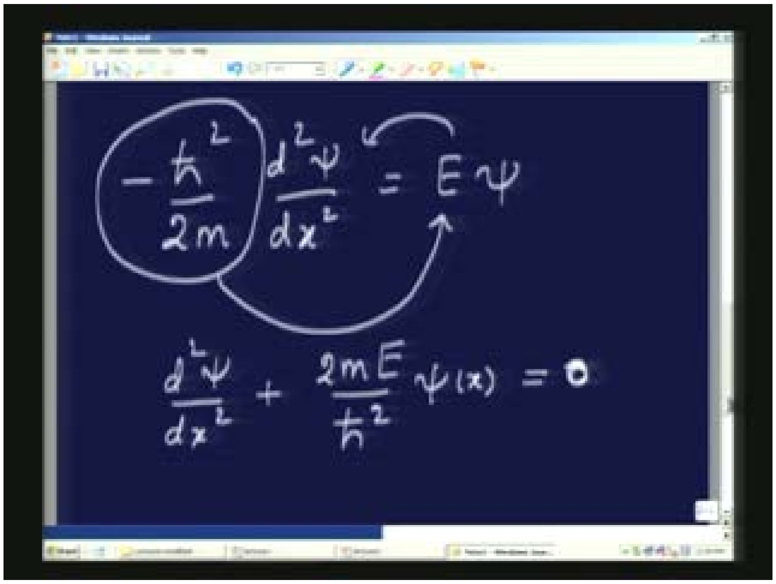

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

The energy of a moving particle is always positive and therefore this particular constant is $2mE/\hbar^2$ where $\hbar$ is $h/2\pi$ where h is a Planck's constant. So this equation is, to represent it in simple term is $d^2\psi/dx^2 + k^2\psi = 0$. The particle in the one dimensional box gives you with this kind of an approximation gives you the simplest Schrödinger equation to solve. Even from the simplest Schrödinger equation some of the consequences that you draw from the solution are rattling, they are difficult to recognize as anything familiar. Therefore, even a simple model like this has in it the newness, the discreteness of the energy coming out of it as we see in a few minutes. The solution of this equation is a simple mathematical equation. It is $\psi(x) = A\cos(kx) + B\sin(kx)$, using the real functions, where k is of course I have told you k^2 is $2mE/\hbar^2$. If you do not know how to get this solution, my suggestion is that you substitute this solution in the above equation and see that this $\psi(x)$ satisfies this equation.

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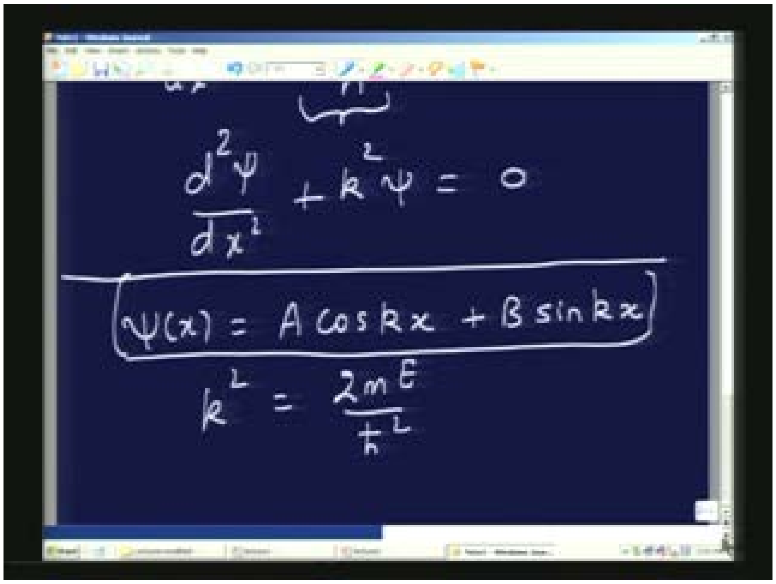

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

$$\boxed{\psi(x) = A\cos kx + B\sin kx}$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$d\psi/dx$,if you recall when ψ is $A\cos(kx)+B\sin(kx)$. You know what is $d\psi/dx$. It is $-kA\sin kx + kB\cos kx$. Therefore, the derivative $d^2\psi/dx^2$, the second derivative is $-k^2A\cos kx - k^2B\sin kx$. Which is nothing other than $-k^2\psi(x)$. Therefore, you see that the equation is the same as what we started with $d^2\psi/dx^2 + k^2\psi = 0$. Therefore the solution makes sense, the method of solving how we get all these things is not necessarily part of the Chemistry course but you have to learn Mathematics at the same time to solve simple differential equations, let me leave that. Our point is to make sense out of the solutions as said earlier.

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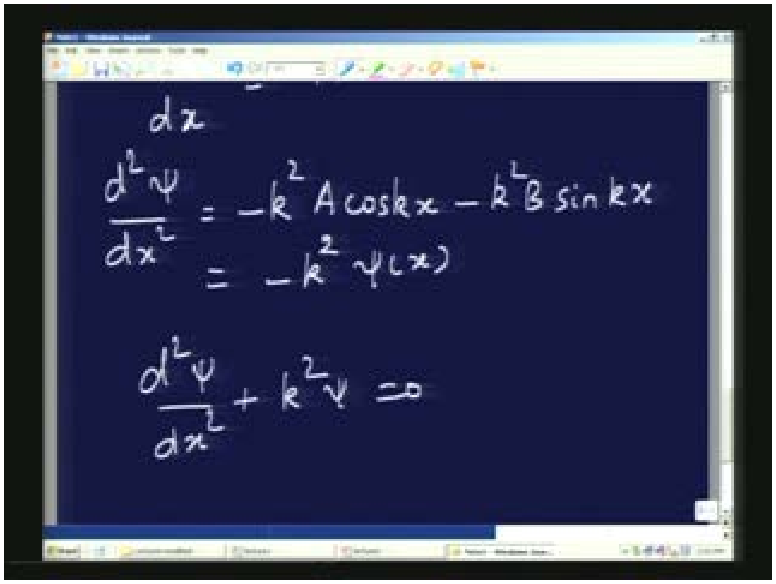

dx

$$\frac{d^2\psi}{dx^2} = -k^2 A\cos kx - k^2 B\sin kx$$

$$= -k^2\psi(x)$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

Now, given that the wave function is A cos kx + B sin kx. And given the model if you recall the model V is ∞ at the ends of the box, x = 0 and x = L. And if we are solving the Schrödinger equation for the particle inside the box and we say that ψ(x) is the solution. Then the presence, this is infinite potential means the wave function goes to 0 at x = 0, the wave function vanishes, goes to 0 at x = L that is a model. Therefore the two conditions that we have ψ(x) =0 at x = 0 and ψ(x) = 0 at x= L. These are the two conditions that we have to remember. Since these two conditions refer to the motion of the particle with respect to a boundary. You can also call these as boundary conditions because the particle is bounded by these two limits.

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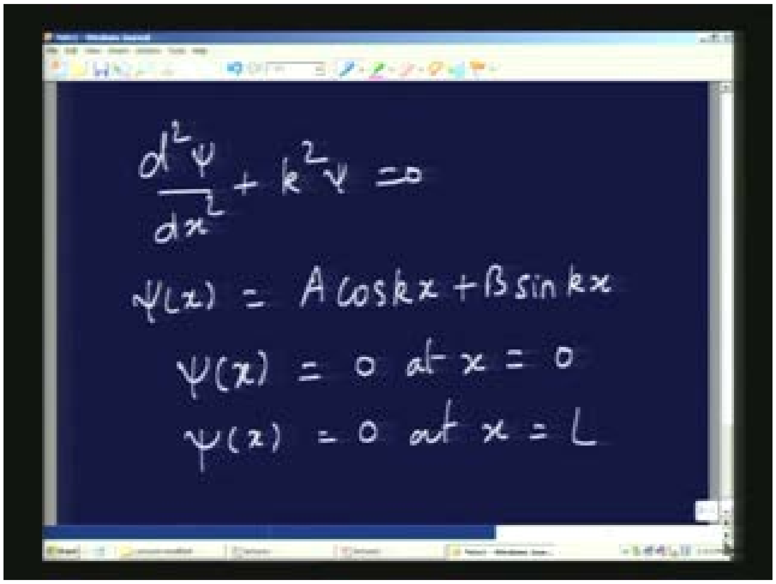

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

$$\psi(x) = A\cos kx + B\sin kx$$

$\psi(x) = 0$ at $x = 0$

$\psi(x) = 0$ at $x = L$

Therefore, let us apply these the boundary conditions to the solution that we have $\psi(x) = A \cos(kx) + B \sin(kx)$ is such that it vanishes at both the boundaries of the box. Let us take x = 0, $\psi(0)$ should be 0 and that means $A \cos(0) + B \sin(0)$ and $\sin(0)$ is 0 therefore this term goes away. $\cos(0)$ is 1. Therefore this is A implies A = 0. One of the two constants is removed by one of the boundary conditions. The next condition is $\psi(L) = 0$ and that implies now since A is 0 you recall $\psi(x)$ is B sin kx only. Therefore what is $\psi(L)$?. $\psi(L)$ is B $\sin(kL)$ and this has to be 0 as required by the boundary condition. $\psi(L)$ is 0, the wave function vanishes at the other boundary.

Again it is a very simple choice if you want to make, now B can be 0, but the point is if B is 0 and $A = 0$ then ψ is a trivial solution is a useless solution. After all this differential equation is always satisfied by the trivial requirement that ψ is 0. We are not looking for trivial solutions. We are looking for non trivial solutions. Therefore with the condition that B is not necessarily 0 then $\psi(L)$ goes to 0 only if $\sin(kL)$ goes to 0. And that is easy to understand because you what a sin function does. A sin function when you plot sin of x as you go from x = 0 or to all the way up you see $\sin(0)$ is 0, $\sin(\pi/2)$ is 1, $\sin(\pi)$ is 0, $\sin(2\pi)$ is 0, $\sin(3\pi)$ is 0 and so on. Therefore you see that the condition $kL \sin(kL) = 0$ implies $kL = n\pi$, where n = 1, 2, 3, 4 etc. Again n = 0 is not acceptable for the same reason that B = 0 is not acceptable. So $kL = n\pi$ is the requirement that you get by solving the Schrödinger equation with the boundary conditions that the wave function vanishes at one end of the boundary as well as at the other end of the boundary.

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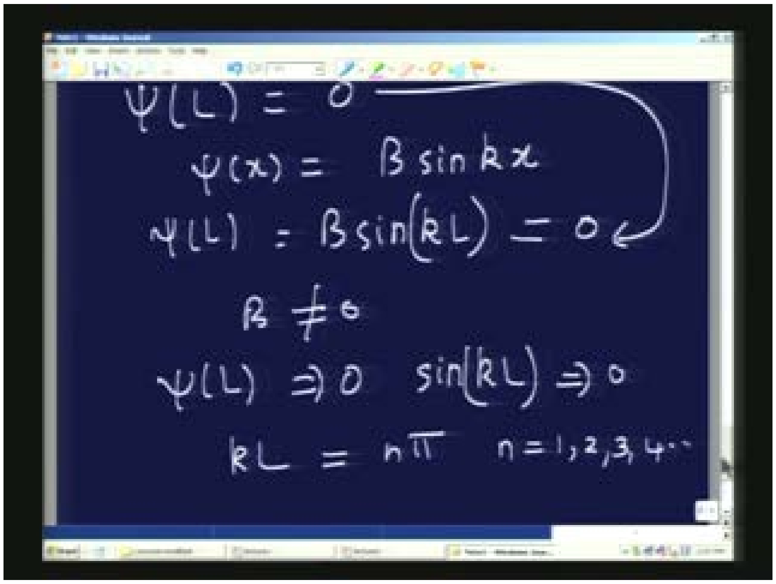

$$\psi(L) = 0$$

$$\psi(x) = B \sin kx$$

$$\psi(L) = B\sin(kL) = 0$$

$$B \neq 0$$

$$\psi(L) \Rightarrow 0 \quad \sin(kL) \Rightarrow 0$$

$$kL = n\pi \quad n = 1, 2, 3, 4 \cdots$$

So let us write the solution carefully. Therefore $k = n\pi/L$, $k^2 = n^2\pi^2/L^2$. Now these are purely mathematical equations. Now, the equation was $\psi(x) = B \sin (n\pi /L)x$.

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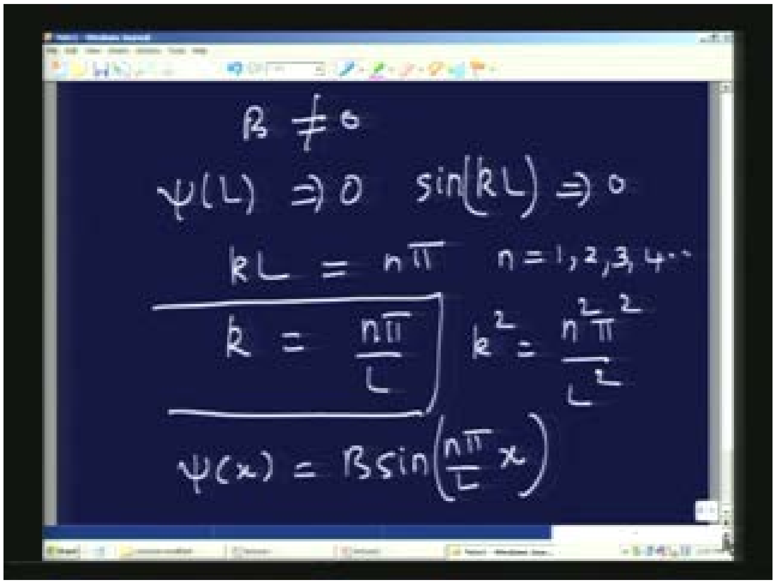

$$B \neq 0$$

$$\psi(L) \Rightarrow 0 \quad \sin(kL) \Rightarrow 0$$

$$kL = n\pi \quad n = 1, 2, 3, 4 \ldots$$

$$\boxed{k = \frac{n\pi}{L}} \quad k^2 = \frac{n^2\pi^2}{L^2}$$

$$\psi(x) = B\sin\left(\frac{n\pi}{L}x\right)$$

Interesting thing is k^2 which we wrote earlier for $2m\,E/\hbar^2$ is now $n^2\pi^2/L^2$ where n = 1, 2, 3 etc. Values of n other than integers are not allowed and what is this I told you the total energy, $E = \hbar^2 n^2\pi^2/L^2\, 2m$. Now you know that $\hbar^2$ is $h^2/4\pi^2$, where $\hbar$ is $h/2\pi$. Therefore, the final expression for the total energy, $E = n^2\, h^2/8mL^2$. So the energy of the particle is the possible solution for the equation $\hat{H}\psi = E\psi$.

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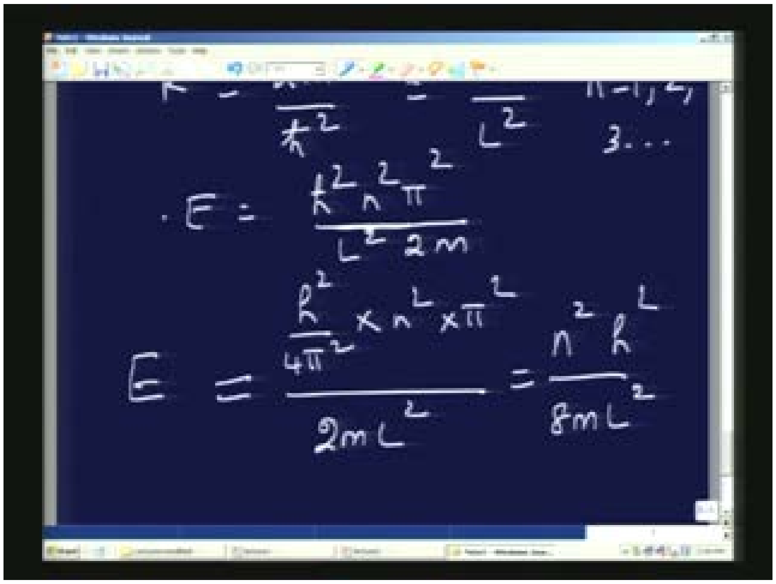

$$\hbar^2 \qquad L^2 \qquad 3\ldots$$

$$E = \frac{\hbar^2 n^2 \pi^2}{L^2\, 2m}$$

$$E = \frac{\frac{h^2}{4\pi^2} \times n^2 \times \pi^2}{2mL^2} = \frac{n^2 h^2}{8mL^2}$$

Now for this particle in a box model with the boundary conditions that $\psi(x)$ is a sin function vanishing at the ends of the boundary. But the possible energies that the particle can have now are discrete values, not possible for any value of n but only n = 1, n = 2, n = 3 and so on. So the energy solution for the particle is $h^2/8mL^2$ times n^2, an integer. Therefore it is 1, 4, 9, 16, 25 times this constant $h^2/8mL^2$. These are the possible energies for the particle. Therefore the discreteness of the energy of the particle appears immediately as a requirement of the boundary conditions.

The quantization of the energy of the particle, the quantization of the moving electron in a conjugated diene, the electron cannot have any arbitrary energies but if it is bounded by the requirement that it stays with the molecule that it does not fly off from the molecule. That boundedness requires the electrons to have only specific energies. We are talking about Chemistry that we are not talking about the particle in a box only. That is some model which is applied to the chemical problem should give you results which are in tandem with the chemical observations.

Therefore the simple model which gives you discretization or quantization of the energy arises, this discretization arises because of the requirement of the boundary conditions. Therefore boundary conditions impose quantization. The second thing, we have solved for $\psi(x)$ as some constant, we still do not know what that constant is, we have $B \sin n\pi x/L$ and energy is given by that. But before I do that let us just check when we write the energy as $h^2/8mL^2$ times n^2. h is Planck's constant, typically of the order of 10 raised to – 34 joules second, h is joules sec and you recall joule is kg $(\text{meter})^2(\text{second})^{-2}$. Therefore h is kg $(\text{meter})^2(\text{second})^{-1}$. h^2 has a dimension that $[\text{kg}(\text{meter})^2(\text{second})^{-1}]^2$, m mass of the particle in kilograms.

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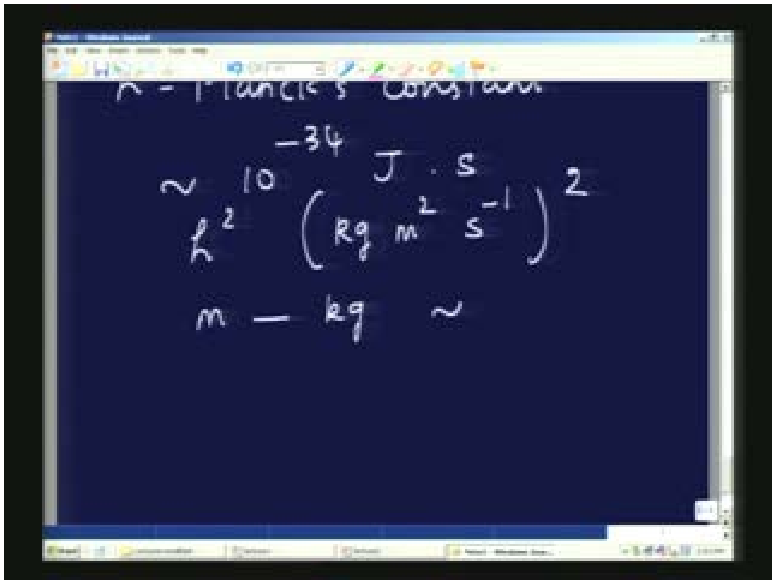

h – Planck's Constant

$\sim 10^{-34}$ J . s

$h^2 \; (\text{kg}\; m^2\; s^{-1})^2$

m — kg $\sim$

If you talk about atoms if you talk about electrons the mass is approximately of the order of 10 raised to – 30 kilograms. If you talk about atoms the masses are approximately in the range of 10 raised to – 27 kilograms again extremely small. But you see that these numbers are no longer so small or so big compared to the height of the Planck's constant. m has the dimension of kilogram, L length with the atomic dimensions, all of you know is of the order of the Angstroms 10 raised to – 8cms, i.e. 10 raised to – 10 meters. this unit h square by m L square leave the eight out what is the dimension kilogram square meter to the power four second to the minus two by kilogram mass L square is meter square so get all this things out you a get kilogram you get a meter square kilogram meter square per second square . So, if L has the dimension of meter and h is kg $(\text{meter})^2$ $(\text{second})^{-1}$ and mass is kilogram. (Refer Slide Time: 30:00 min) By substituting all these dimensions, we get the unit as kg $(\text{meter})^2$ $(\text{second})^{-2}$. Therefore that has the same dimension as the energy.

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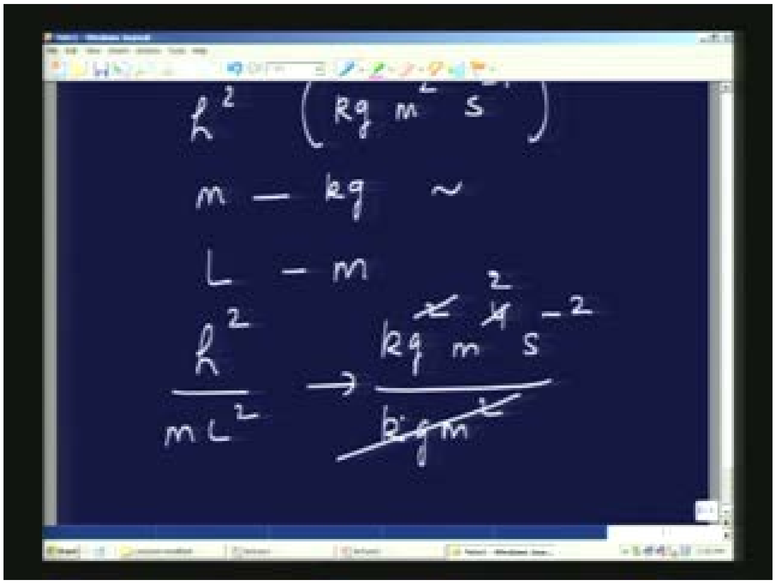

This is the unit of energy for the particle in a box, $h^2/8mL^2$ is the unit times n^2. The quantum number, n the discrete integer with 1, 2, 3 as the possible values which we call as quantum numbers because it represents the quantization of energy gives you the energy of the particle inside the box. Then what about the wave functions? Here, $\psi_n(x) = B \sin (n\psi x/L)$. Let us do this for $n = 1$, $\psi_1(x)= B \sin 1\pi x/L$ meaning that whatever is the value of n that is the same value. So, $\psi_1(x) = B \sin \pi x/L$.

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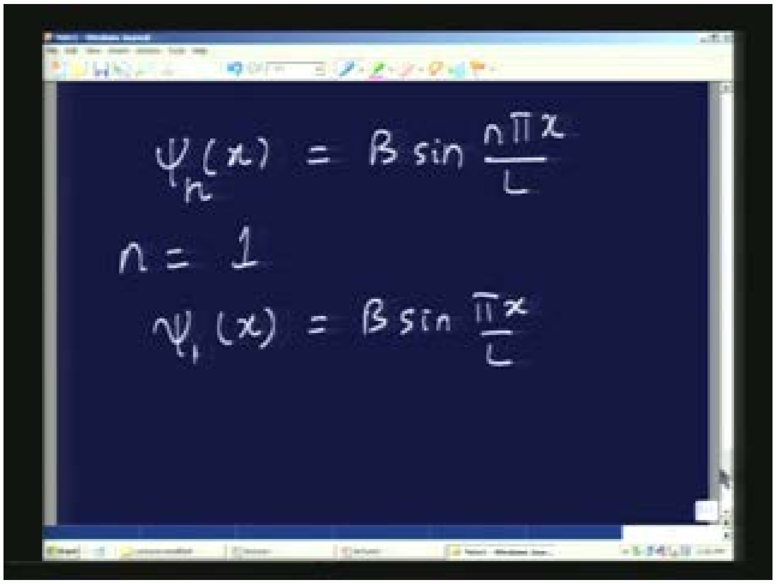

$$\psi_n(x) = B \sin \frac{n\pi x}{L}$$

$$n = 1$$

$$\psi_1(x) = B \sin \frac{\pi x}{L}$$

It is easy to plot this equation, and it is a sin graph between the limits 0 and L. It is a half sin wave vanishing at both ends and by this we get the value of B. (Refer slid time 31:54 min). What is the meaning of ψ? Nobody knows that ψ has an interpretation. When we solve the Schrödinger equation we will have a lot of difficulty in trying to understand the solutions of the Schrödinger equation but with a clear conscious mind that ψ does not have an interpretation and that the solution we have obtained does not have a meaning. Using ψ but rather the ψ^2, i.e. $\psi \times \psi$ and if the wave function is complex using the absolute ψ^2, Max Born provided the interpretation that ψ^2 evaluated in a small region of space is same as the probability of finding the system in that space.

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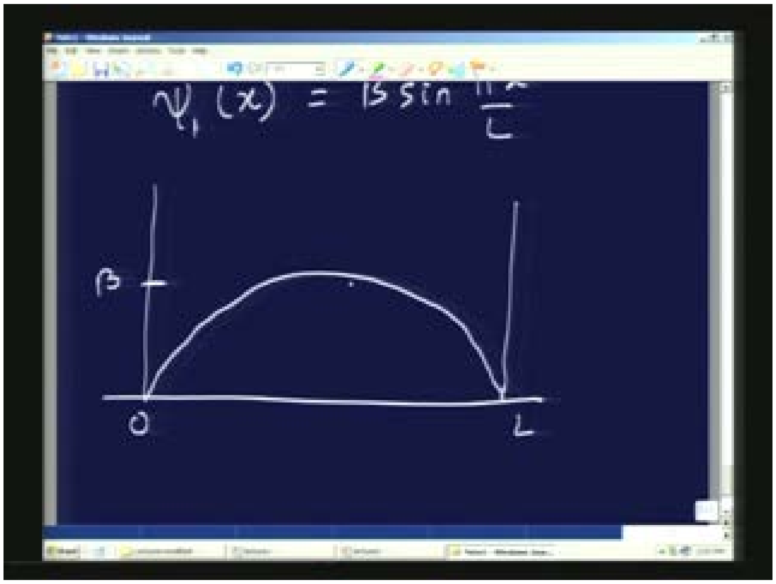

What is the meaning ψ?

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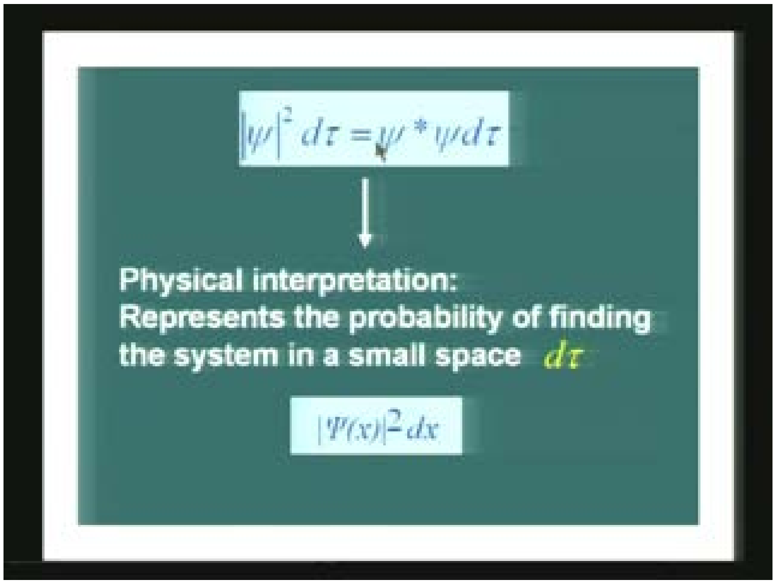

$$|\psi|^2 d\tau = \psi^* \psi d\tau$$

Physical interpretation:
Represents the probability of finding the system in a small space $d\tau$

$$|\Psi(x)|^2 dx$$

If the wave that we have right now is a sin function but if it is a complex for the some other problem the absolute square of ψψ* calculated in a small region of space dτ represents the probability of finding the system in a small space dτ. This is the interpretation provided by the Max Born. And if you think it is hard you must also understand that Erwin Schrödinger who proposed this equation for solving the atomic systems dynamics as well as the stationary energy levels. Schrödinger himself did not get the role of ψ correctly. His proposal of what ψ means was in fact turned down.

And several years later it was Max Born who gave the correct interpretation which is now accepted universally as the interpretation for the wave function. The ψ does not have a meaning but the absolute value of square has a meaning related to the probability.

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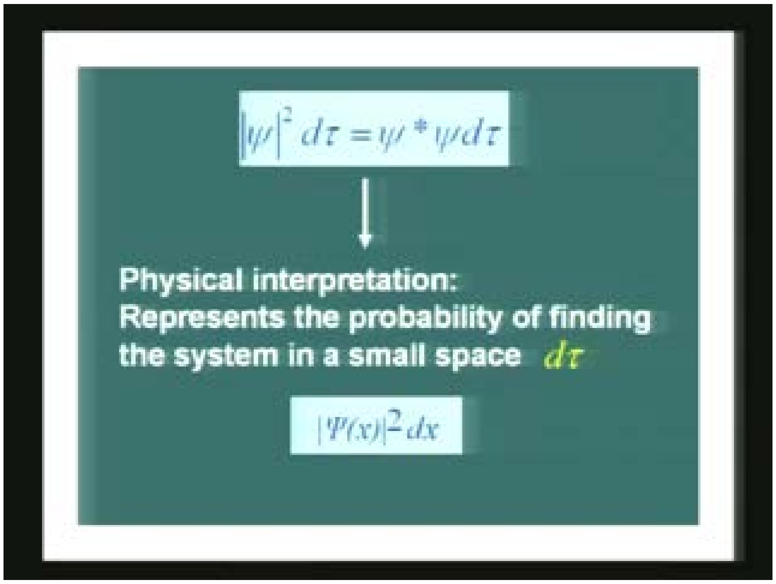

$$|\psi|^2 d\tau = \psi^* \psi d\tau$$

Physical interpretation:
Represents the probability of finding the system in a small space $d\tau$

$$|\Psi(x)|^2 dx$$

Now, we talk about this small space here, if you recall the particle moves in the box between x = 0 to L. Therefore for this coordinate any small region is dx, the length dx is intermediate. Therefore you calculate the wave function ψ(x) at that point and then interpret the absolute square of the wave function. $|\psi(x)|^2dx$ represents the probability of finding the particle in the small space between x and x + dx. The meaning of ψ is none, the square of the absolute value of ψ (since in our case it is a real function) is $\psi^2(x)dx$, represents the probability of finding the particle in the region bounded by x and x + dx. It is $\psi^2(x)$.

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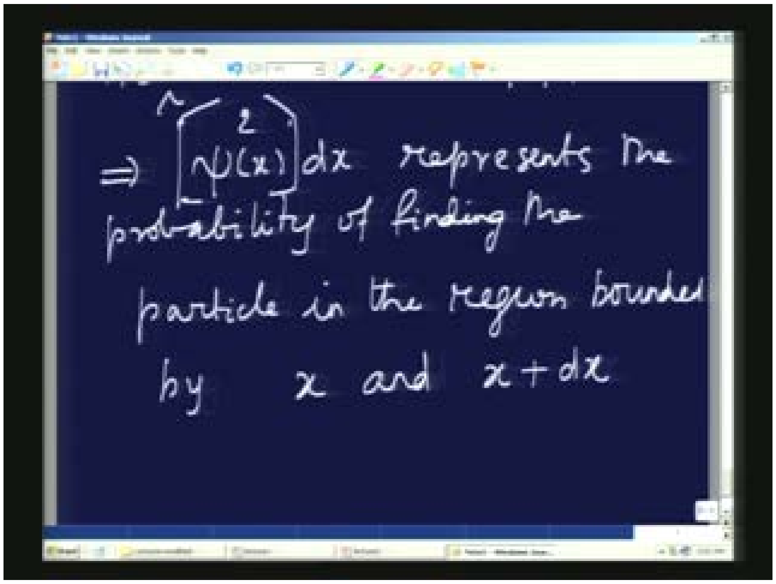

$\Rightarrow \left[\psi(x)\right]^2 dx$ represents the probability of finding the particle in the region bounded by x and $x+dx$

Therefore we have a wave function ψ which is a sin function. So we can calculate ψ^2 which is nothing but the $(\sin)^2$ function and we plot $(\sin)^2$ as a function of x and then you see that in each small region or a strip narrow space that the value of ψ^2 gives you the probability of finding the particle in that region. If $\psi(x)$ is $B \sin(n\pi x/L)$ where B is a constant then ψ^2 is obviously $B^2 \sin^2(n\,\pi\,x/L)$. So, if you plot that, this is nothing again another oscillatory function, it is a $\sin^2$ therefore it is between 0 and L which is probably something like that. Now, x-axis is x = 0 and x = L. What is on y-axis? The maximum value on y-axis is B^2 now. The probability of locating the particle in a small region between x and x+ dx, and for x is equal to some value here. This small region, $\psi^2 dx$ representing the area of the ψ^2 graph in this small space.

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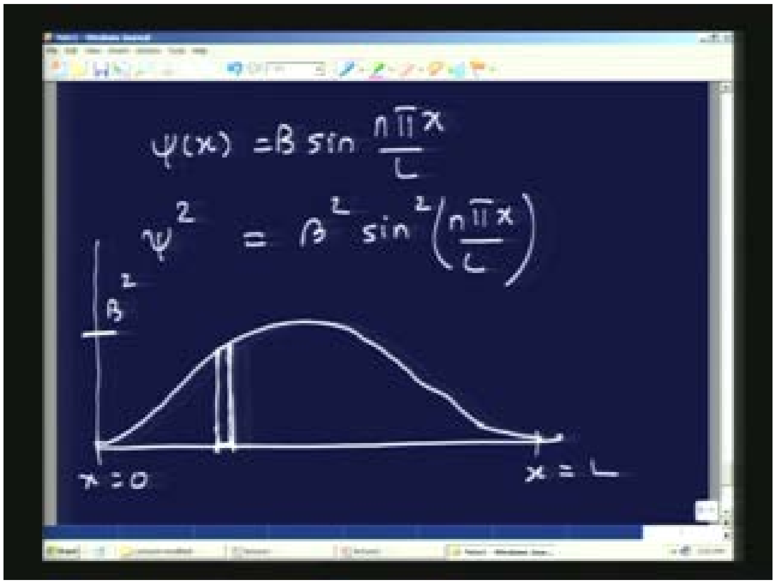

$$\psi(x) = B \sin \frac{n\pi x}{L}$$

$$\psi^2 = B^2 \sin^2\left(\frac{n\pi x}{L}\right)$$

Since x is a continuous variable you can represent the probability in any small region of space by choosing that value of variable. Therefore what happens is if we add all these probabilities that particle here is anywhere in these anyone of the small regions. (Refer slid time 38:17 min). Let us add all these probabilities what should we get? That is important because you recall that the potential was taken to be infinite at the ends of the box to ensure that the particle stays in the box.

Therefore, if you calculate all these probabilities in every region if you calculate the total area of this graph, it is like finding the particle anywhere between x = 0 and x = L which is absolute value absolutely certain value can be one. Therefore, when you add all these small areas that is equivalent to $\int\psi^2(x)\,dx$ between the limits x = 0 and x = L and that should give you an absolute value of 1, certainty. There is no leakage of this particle outside through the boundary, the boundary is too steep. Therefore this rigid model first of all gives us a picture of how things are different in the quantum world as suppose to the classical mechanical world.

Unfortunately for a chemist all the atoms and molecules that we talk about are microscopic in dimensions and they do follow the quantum principles. You have to excite the atoms and molecules to a very large value before you think about applying the classical physical laws. Spectroscopy for example you have to study this quantum principle in order to understand basic standards of spectroscopy. Now, $\psi^2(x)\,dx = 1$. This tells you immediately that between x = 0 to x = L. $B^2 \sin^2(n\pi x/L)$ should be equal to 1. This is an elementary integral.

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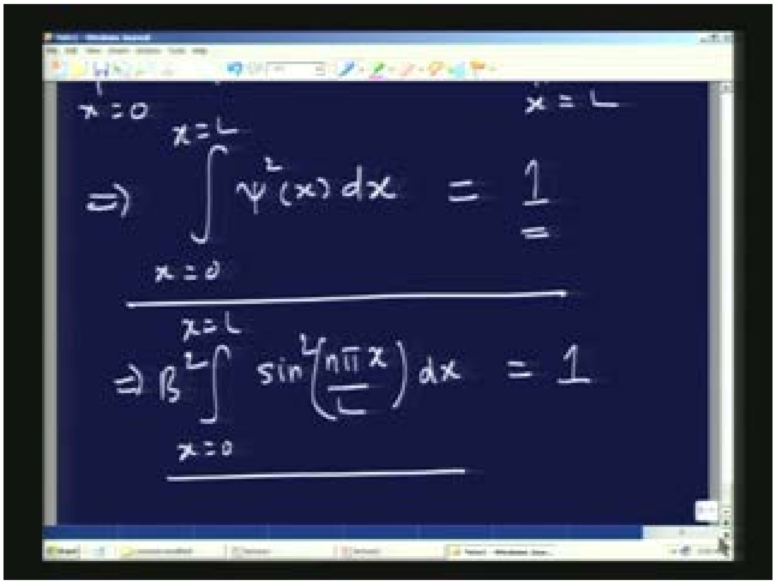

$x=0$ $\qquad x = L$

$$\Rightarrow \int_{x=0}^{x=L} \psi^2(x)\, dx = \underline{\underline{1}}$$

$$\Rightarrow B^2 \int_{x=0}^{x=L} \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

All of you should know how to solve that. So I leave that an exercise but the answer is $B^2 \times L/2 = 1$. The value of the integral is L/2. Therefore what is B? It is equal to √ 2/L.

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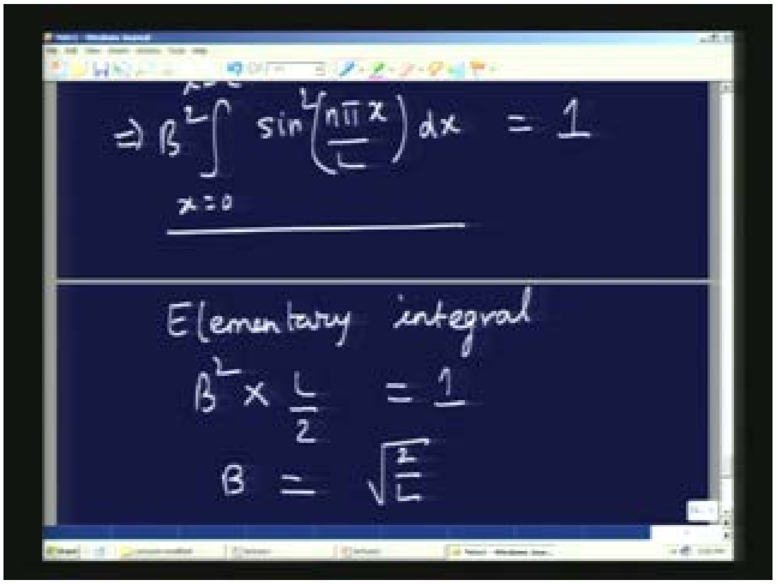

$$\Rightarrow B^2 \int_{x=0} \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

Elementary integral

$$B^2 \times \frac{L}{2} = \underline{1}$$

$$B = \sqrt{\frac{2}{L}}$$

So, simple particle in a one dimensional box model now what you have is these two ideas namely that the energy is quantized the energy of the particle if you measure it should be one of the values that we wrote down $h^2\ n^2/8mL^2$. The wave function is has the meaning that the absolute square of the wave function in a small region gives you the probability of finding the particle in that region.

Let me summarize that, therefore the solutions of the particle in a one dimensional box are solutions for the $H\psi = E\psi$, $\psi(x) = \sqrt{2/L}\,\sin(n\pi x/L)$ and E is $h^2 n^2/8mL^2$ where n = 1, 2, 3 etc. Therefore when you try to solve this Schrödinger equation $H\psi = E\psi$, you did not get one solution. You got an infinitely many solutions. So n can be any value from 1, 2, 3,….. ∞. Therefore the corresponding wave functions are also there are infinite numbers of such wave functions. Therefore the advantage in solving the Schrödinger equation is that you will obtain all the solutions you need to know.

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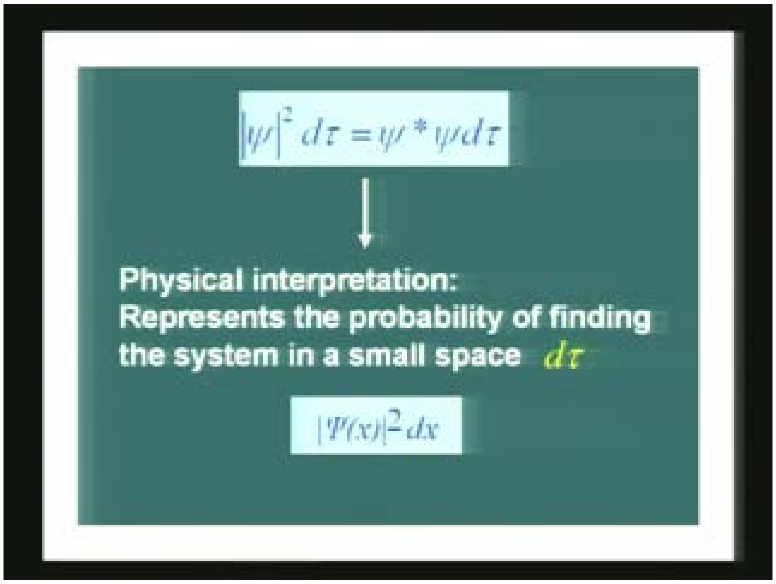

$$|\psi|^2 d\tau = \psi^* \psi d\tau$$

$$\downarrow$$

Physical interpretation:
Represents the probability of finding the system in a small space $d\tau$

$$|\Psi(x)|^2 dx$$

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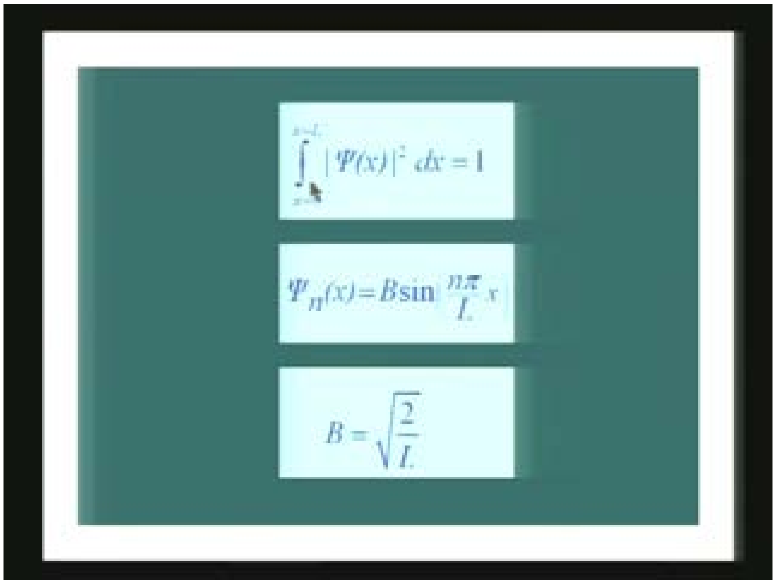

$$\int_{x=0}^{x=L} |\Psi(x)|^2\, dx = 1$$

$$\Psi_n(x) = B\sin\frac{n\pi}{L}x$$

$$B = \sqrt{\frac{2}{L}}$$

Therefore $\int|\psi(x)|^2dx= 1$in between the limits $x = 0$ to $x = L$ is nothing is often known in quantum mechanics as a normalization condition. The normalization condition merely refers to the fact that the total probability of finding the system with that wave function everywhere in that system should be unity. That is the normalization condition adding all the probabilities and that immediately gives you a value for the B in terms of the dimensions of the problem in the $1/\sqrt{L}$, the length.

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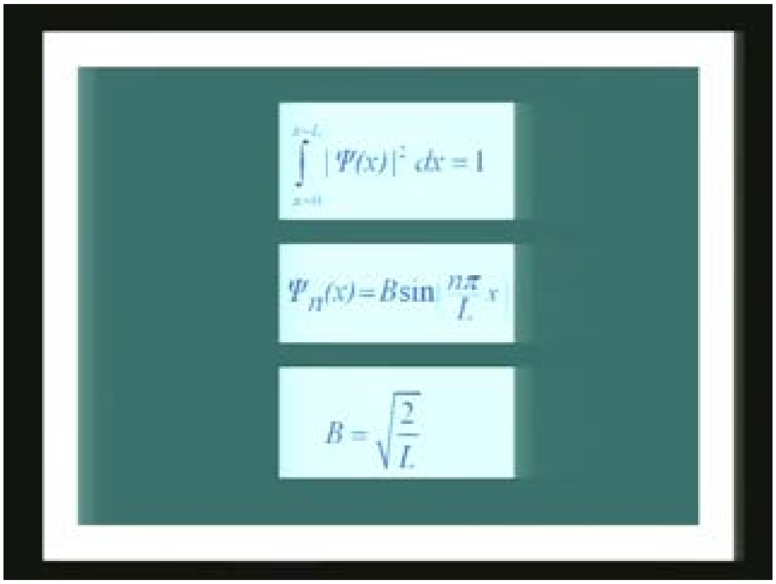

$$\int_{x=0}^{x=L} |\Psi(x)|^2\, dx = 1$$

$$\Psi_n(x) = B\sin\frac{n\pi}{L}x$$

$$B = \sqrt{\frac{2}{L}}$$

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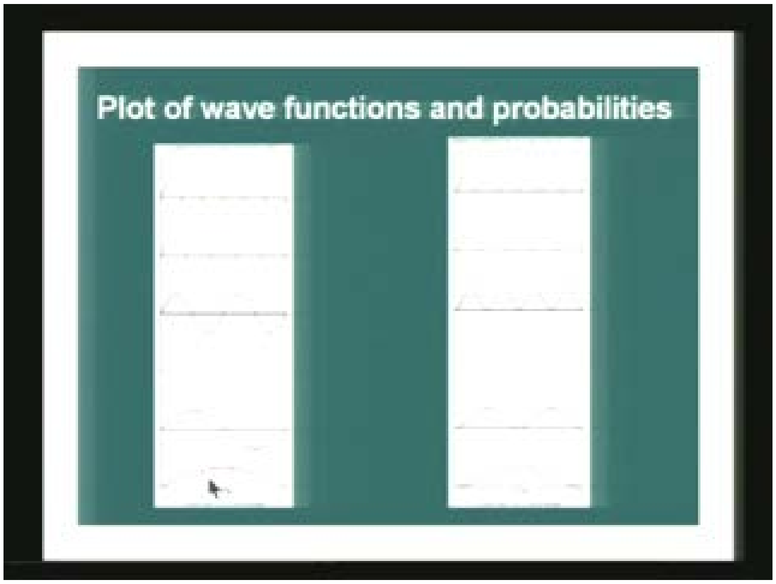

Plot of wave functions and probabilities

You can see here the wave functions plotted for various values. n = 1, already drew this as a half wave, sin wave. When n = 2 you see that wave function is a full wave function. Let us plot the wave functions, sin π x/L is a half sin wave, sin 2πx/L for n = 2 when x goes from 0 to L then sin 2πx/L goes from sin 0 to sin 2π therefore it is a full sin wave function. Therefore it goes 0 at half of the point. And the next one is sin 3πx/L which is a one and half sin wave. So what you have is a one and half sin wave.

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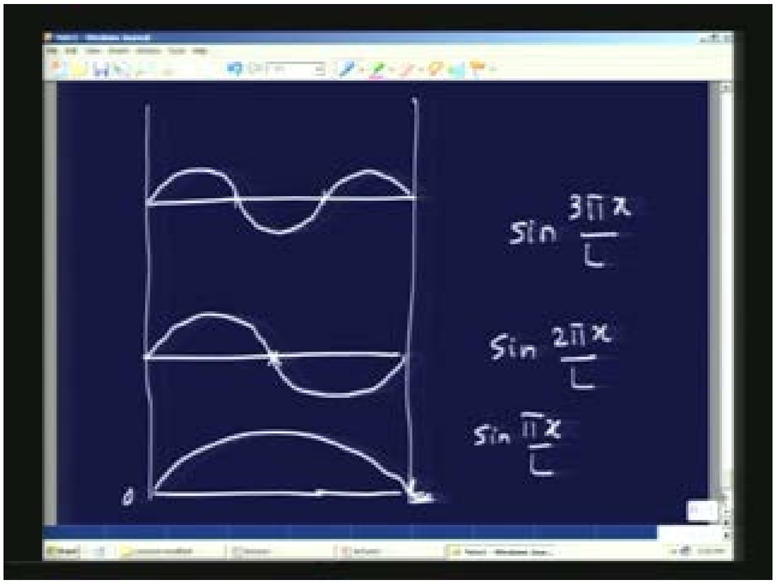

Now that is for the sin wave. What about the $\sin^2$ wave which represents the probability? Here there is no negative part. The sin square is looking like that, This is sin square pi x/L. The $\sin^2$

$(\pi x/L)$ is looking like $\sin \pi x/L$. Therefore $\sin^2(2\pi x/L)$ now has a node which is at the middle, no negative part with two equal halves and $\sin^2(3\pi x/L)$ has three such equal halves, one thirds and $\sin^2(4\pi x/L)$ has four one fourths and so on which is what you see in this slide.

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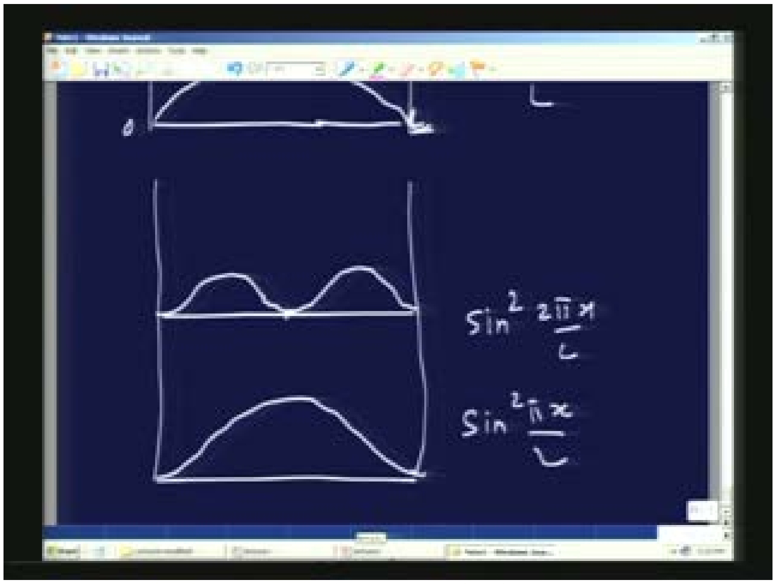

The above slide shows the $\sin^2$ wave, here the first one is $\sin^2 (\pi x/L)$ and second is $\sin^2(2\pi x/L)$ and then $\sin^2(3\pi x/L)$, $\sin^2(4\pi x/L)$ and so on. (Refer Slide Time: 45:16) sin pi x sin 2 pi x/L sin square pi x sin square 2 pi x/L 3 sin square 3 4 sin square 4 and so on. So this goes on and on as the n value increases to very large values. You will see that the graph has practically lots of oscillations but very tightly placed that when you try to measure the probability in any small region for particles with such large values of n you will get a uniform probability independent of the region which is the same as the classical ideas.

That is for large values of n we do not need to solve the quantum mechanical equations the classical mechanical equations and the concepts of classical mechanics makes sense. This you must have also recognized something as the Bohr's correspondence principle where quantum mechanics and classical mechanics meet. Anyway these are not important for us right now. We are looking at it from the point of view of the solutions of the chemical systems. The summary for the 1D box now is that the wave function is $\sqrt{2/L} \sin n\pi x/L$ and the energies are $(h^2/8mL^2)\ n^2$. Particle energies are discrete and particle position inside the box is given by a probability description.

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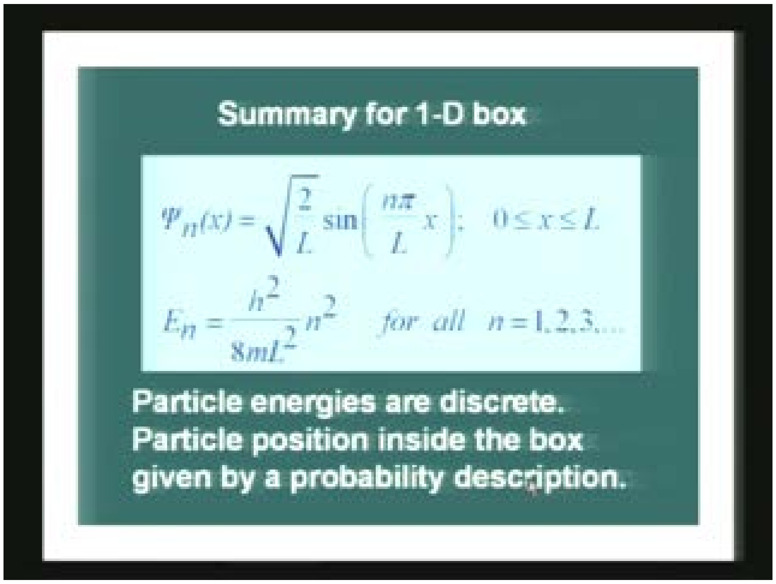

Summary for 1-D box

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

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

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

Let us digress for a minute the probability idea, let me play this movie for you and explain what this movie does. Let us assume that we are able to follow the motion of the particle by looking at a narrow window inside the box at any point of time. Assuming that all other things to be identical if the particle moving with a constant velocity inside the box as we would expect if there is no potential energy, Newton's first law tells you particles in motion will continue to be in motion, particles in rest will continue to be in rest, there is no potential there is no force therefore the particle will continue to move with its velocity constant.

Therefore if we try to locate the particle by looking at any small region, Δx_1 which is given by this band the probability that we will find the particle in Δx_1 is given by this ratio Δx_1 the window divided by the total length of the window that is the box length itself. So, $P_1 = \Delta x_1/L$. This is the classical picture that we have in terms of locating the particle in terms of the finding where the particle is probably to be present. There is one more movie, and what is important is that this $P_1 = \Delta x_1/L$ (Refer Slide Time: 48:21) is independent of where the Δx_1 is and that is what the strip which is moving around will tell you whether the Δx_1 is centered at this point or it is centered here or it is centered here it does not matter as long as the Δx_1 is same the with the probability is the same value.

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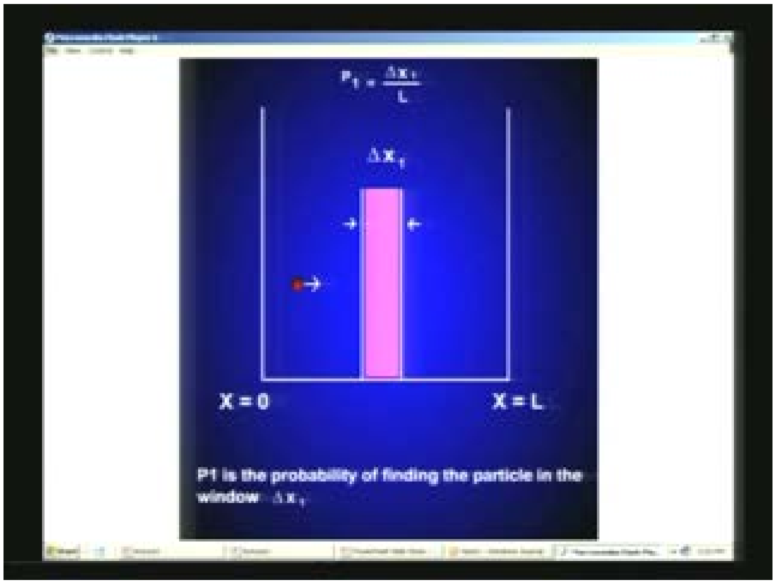

$P_1 = \frac{\Delta x_1}{L}$

P1 is the probability of finding the particle in the window Δx_1

If we increase that band obviously the probability is now much larger and if we can look at the whole box we will anyway locate the particle. But what is important in the classical idea is, that is independent of the particles velocity, independent of the location of the particle inside the box the probabilities are the same so long as you are looking at the narrow region of the same length in various elements, this is the classical idea.

Now, what you get out of the quantum mechanical picture? What you have here is on this side the right hand side of your picture where you see that this graph represents the particles the ψ^2. Therefore this is the probability density graph this is not the same everywhere meaning the likelihood of locating the particle in this small region is different from this region if the particles energy is E1 namely $h^2/8mL^2$, n is 1. If n is 2 the particles energies are now different and the probability density curve is also different. It is not only not the same in all regions it is also different for different energies of the particle. So you see that the quantum mechanical picture if the electron to be closely to be located from the hydrogen nucleus the likelihood of finding the electron in a region close to the nucleus the likelihood of finding the same electron in a region farther away from the nucleus they are not going to be one and the same if we have to follow this wave function picture.

Second, even if the electron has the same energy in one orbit for example the analog of boron, in different regions of the electrons domain with that same energy the electron is likely to be located with different probabilities. Therefore you see the quantum idea the Schrödinger equation introduces concepts which are foreign to us. Quantum mechanics itself is a sort of a strange idea and the derivations from that give us really strange results which we cannot comprehend.

The only way to see that these results are no longer strange is by knowing more and more about similar systems by solving more difficult problems and interpreting our results along these lines and then finally coming to the agreement that even if I do not understand Quantum Mechanics I know how it works. Given a problem I know how to solve that problem and I would be able to obtain the solutions for electron densities in a molecule. Eventually that is what we want to do as Chemists is two map out the electron densities of the electrons in various atoms and molecules and show where are the electron depleting regions where are electron enriched regions where is the bonding is the bonding directly related to electron density present in that region or a depletion of electron density means no bonding, anti-bonding.

But how do we interpret them using the quantum mechanical ideas? Since we want to get to that point as quickly as possible we have to show the basic Mathematics. This is particle in the box model it gives you two important concepts namely discretization of the energy as a function as a result of boundary condition and that the probability densities being different for different regions.

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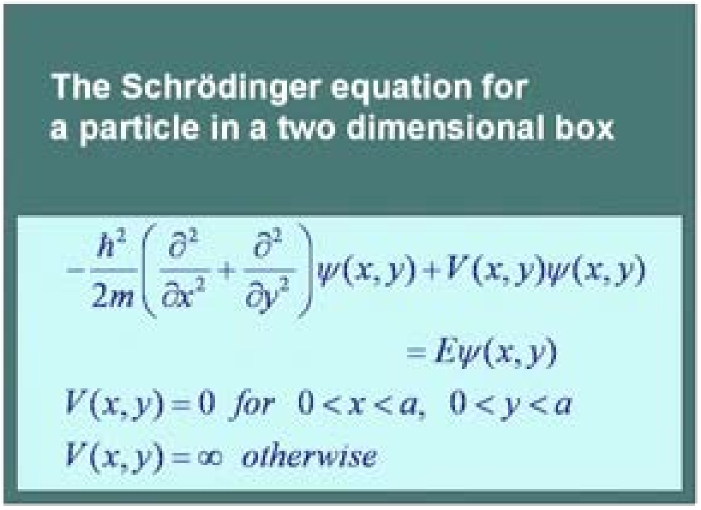

The Schrödinger equation for a particle in a two dimensional box

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

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

$$V(x,y)=0 \;\; for \;\; 0<x<a, \;\; 0<y<a$$

$$V(x,y)=\infty \;\; otherwise$$

If we have to extend this idea of the motion of the particle in a one dimension to the motion of the particle in a two dimensions namely in a plane not along a line but in a plane if you have to do that then corresponding expressions for the kinetic energy of the particle if you recall that $-\hbar^2/2m\ d^2/dx^2$ represented the momentum $(p_x)^2$. And in two dimensions what you have is the momentum of electron or the particle moving in a plane is not $(p_x)^2$ the momentum p^2 is $(p_x)^2 +(p_y)^2$. You recall the momentum p is a vector with p_x as the component along the x direction and p_y as the component along the y direction and the absolute square, p square is nothing but the p dotted p vector.

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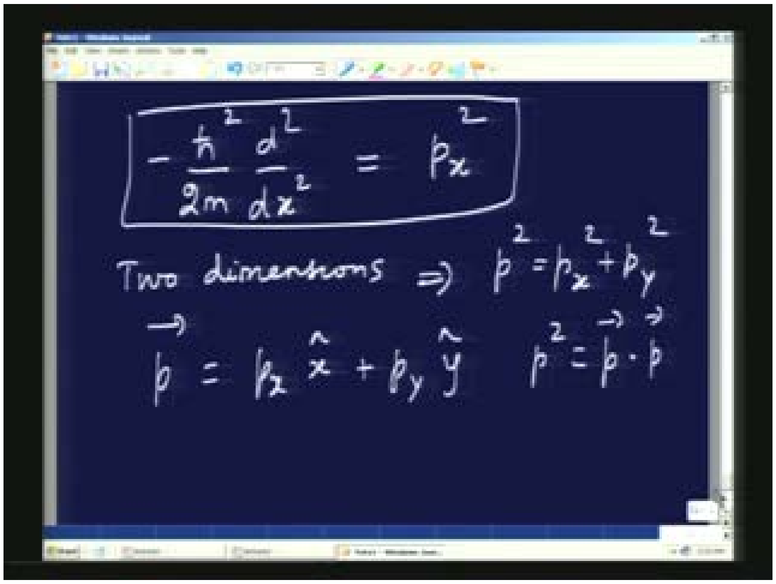

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} = p_x^2}$$

Two dimensions $\Rightarrow p^2 = p_x^2 + p_y^2$

$\vec{p} = p_x\hat{x} + p_y\hat{y}$ $\quad p^2 = \vec{p}\cdot\vec{p}$

So now you have two components of momenta in two mutually orthogonal directions. Therefore this term which is unique for a particle in one dimension has to be modified to be written such that you have the two dimensional kinetic energy $-\hbar^2/2m\ (\partial^2/\partial x^2 + \partial^2/\partial y^2)$. This is the analog now of the classical mechanical p square for a two dimensional system. It is a partial derivative now meaning that whenever you evaluate the function under this derivative you keep the other variable constant. This is the kinetic energy operator for a particle in a two dimensional box. And obviously the particles potential energy is now a function of both the coordinates x and y because the position of a point in a plane is given by two coordinates. Therefore the potential that the particle experiences at that point is given by its value for both these coordinates. Therefore V is now a function of x and y. This $V(x ,y)$ is the potential energy.

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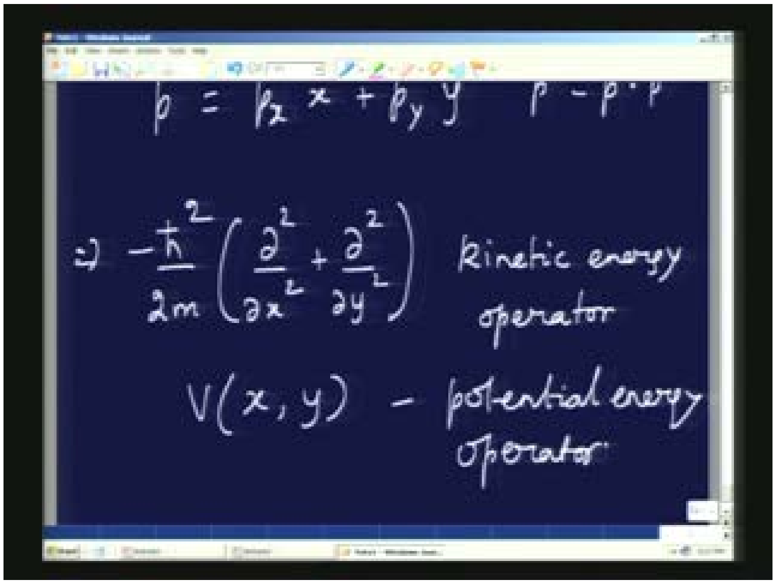

$$p = p_x x + p_y y \qquad p - p \cdot p$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$ kinetic energy operator

$V(x, y)$ - potential energy operator

Therefore the Schrödinger equation for this particle is now becomes for the solution $H\psi = E\psi$. To written explicitly the equation is $-\hbar^2/2m\ (\partial^2/\partial x^2 + \partial^2/\partial y^2)\psi(x ,y)$. The wave function is the function of both the variables x and y plus $V(x, y)$ times $\psi(x ,y)$ equals to $H\psi = E\ \psi(x, y)$. This is the equation that we have to solve, a motion in two dimensions. This is for a particle in a two dimensional box.

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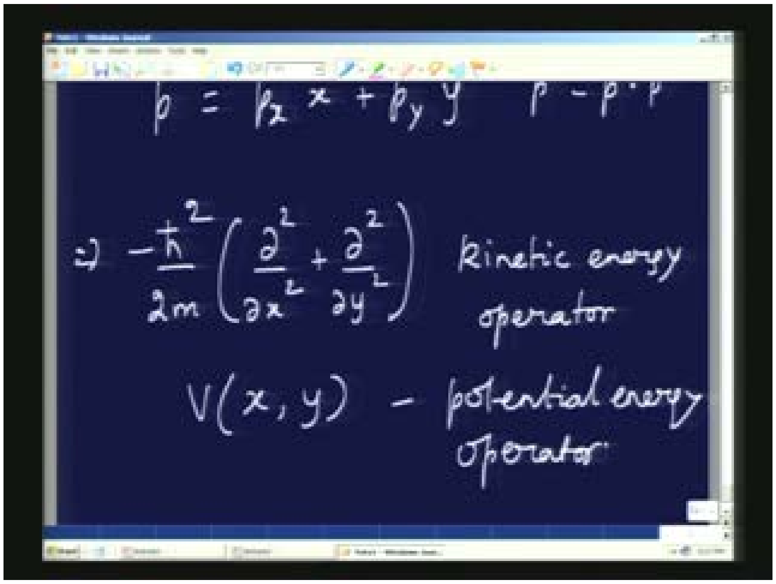

$$p = p_x x + p_y y \qquad p - p \cdot p$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$ kinetic energy operator

$V(x, y)$ - potential energy operator

Some of you might be worried about the fact I am drawing a two dimensional box and I call this as a one dimensional model and therefore if I have to draw a two dimensional box model it has to be a cubic what does this mean?

The one dimension here represents the variable with respect to which we are solving the Schrödinger equation. We are solving an equation in one variable that is what we call as the dimension.

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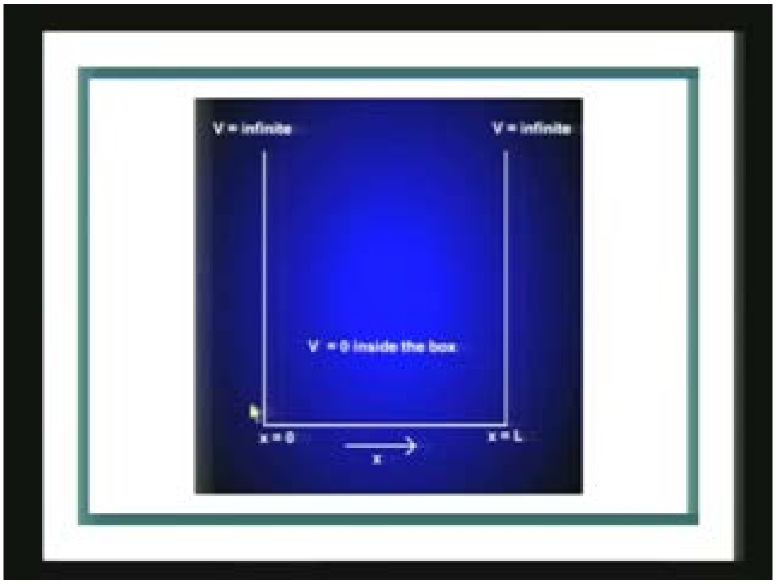

This is only a boundary to indicate that the particle cannot escape the box. Therefore, in a two dimensional motion likewise what you need to do is not to write a line but a box somewhat like that. And perhaps can just tell you that this is something like a box. So now you talking about the motion of the particle in two dimensions referring to the fact that one of them is the x variable the other is the y variable the position of the particle in this plane or any plane is what is meant by the model problem particle in a two dimensional box.

So let me summarize today's lecture. We introduced to the model problem of particle in a one dimensional box and its relevance to Chemistry in terms of following the electron energies in a specific example being that of a conjugated dyeing system. There are many other similar instances in Chemistry where this model has to be solved. But our purpose is having associated the solution with a corresponding chemical problem we went through the motion of the solution of the system and what is the meaning associated with the wave functions or its absolute square and the fact that the energy is a discrete quantity how do we arrive at that saying that the boundary conditions are important for the discretization of energy.

These are the things we have to remember as the consequences of solving the model problem and the results being different from our classical perception of the dynamical motion of the particle in the sense of classical methods. With these differences in the next lecture I would continue to illustrate the particle in a two dimensional box and there will be one surprise namely the concept of degeneracy that will arise when we solve the particle in two dimensional box in addition to everything that we had done now namely the quantization of energies, the probability description etc.

But in addition to that we will have what are called the degeneracy that will arise and therefore that is important to recognize as the next important step and till then thank you very much.