Indian Institute of Technology Madras
Presents

NPTEL
NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

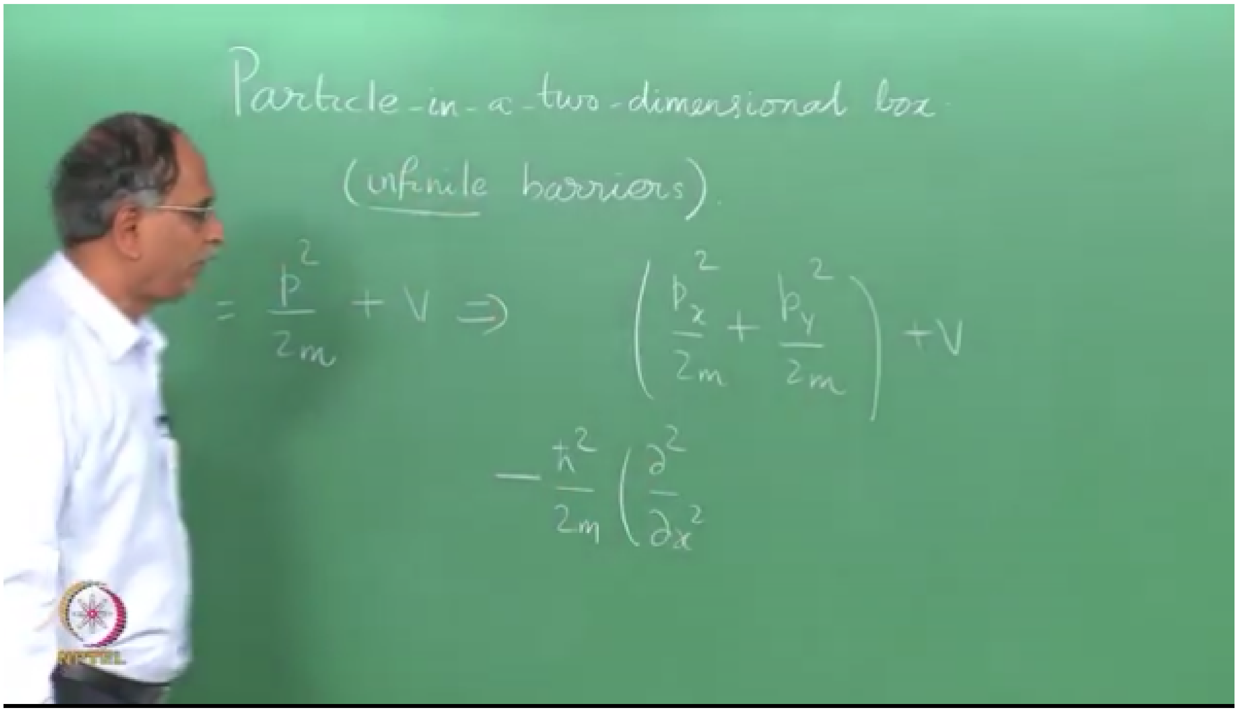
Chemistry I
Introduction to Quantum Chemistry And Molecular Spectroscopy

Lecture – 11
Particle in a One-dimensional Box : Part I
Schrodinger Equation

Prof. Mangala Sunder Krishnan
Department of Chemistry
Indian Institute of Technology Madras

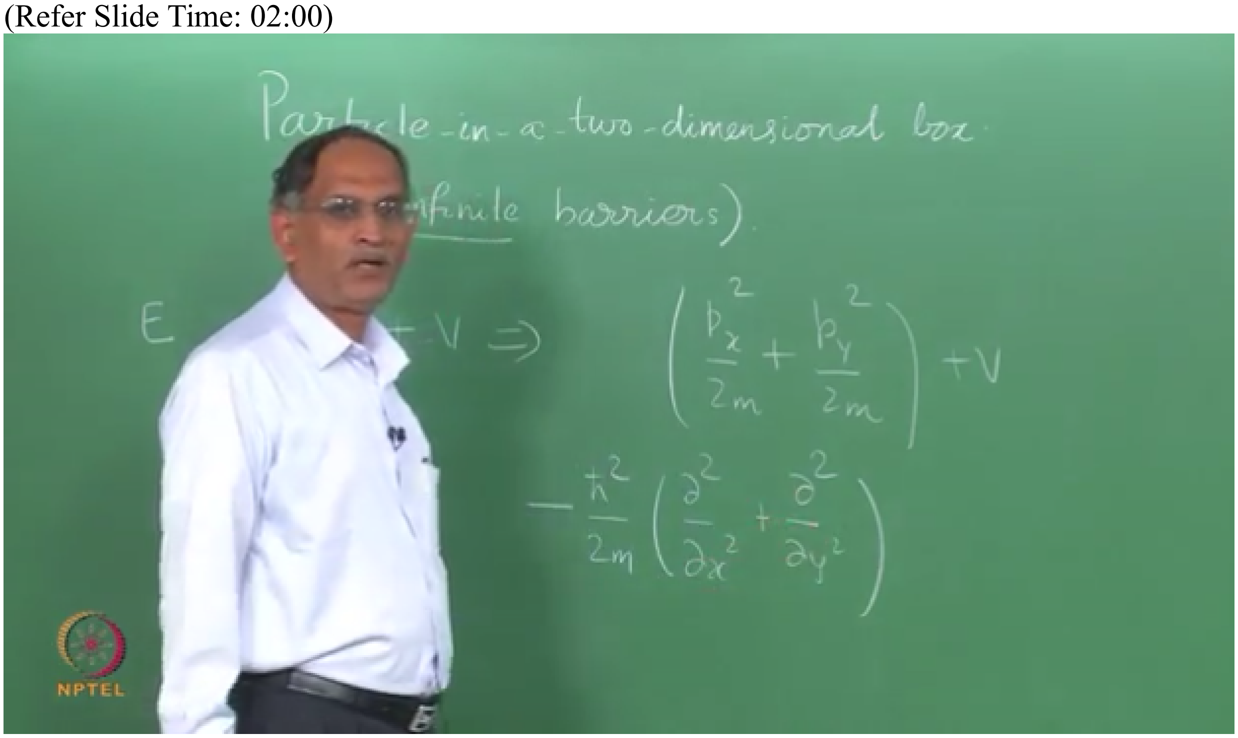
Welcome back to the lecture, the earlier lecture talked about, in the earlier lecture I talked about the particle in the one dimensional box. And in the current one let's discuss the particle in a 2 dimensional 2 dimensional model or 2 degrees of freedom model.

The particles position coordinates are given by 2, X and Y, 2 coordinates in a plane orthogonal to each other, and then we discussed the quantum problem. The barriers are infinite, therefore if you remember the problem P square/2M + V which is the energy term gets changed to, or it's rewritten as PX square/2M + PY square/2M, okay + V, and PX is replaced in quantum mechanics by the -H bar square by the term, -H bar square/2M, the partial derivative now because we have the wave function as a function of 2 coordinates X and Y,
(Refer Slide Time: 01:37)



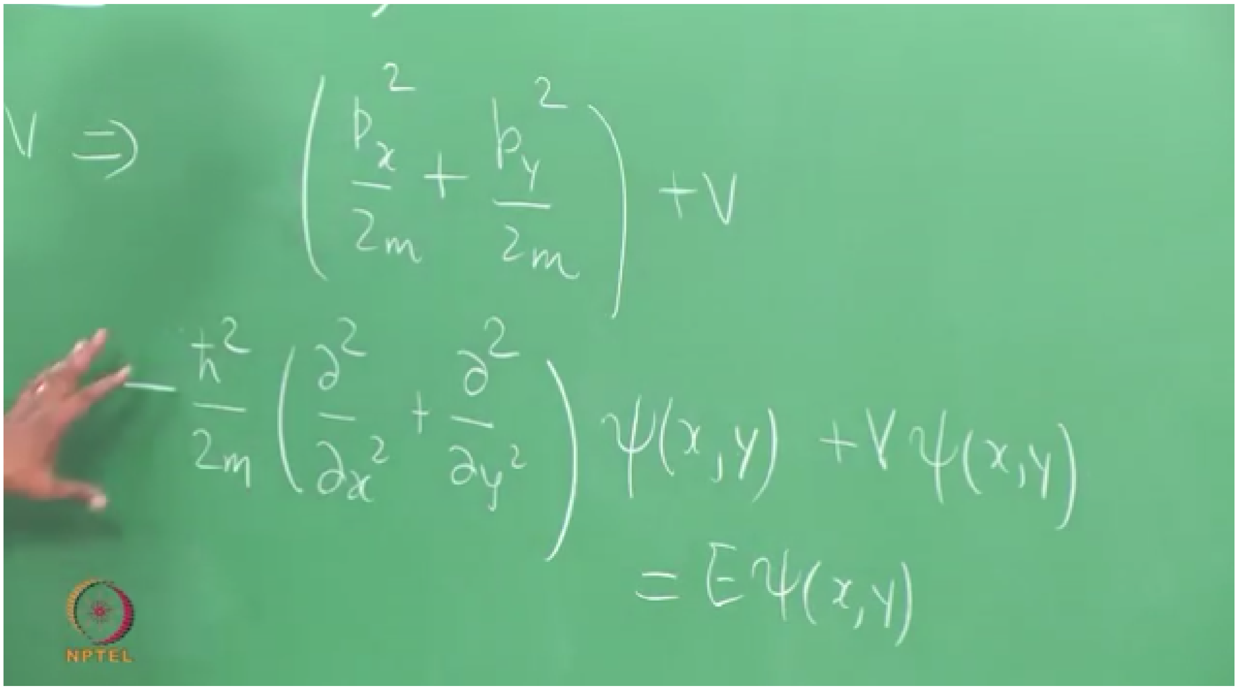
and the momentum in the X direction is given by the partial derivative, and this is the square of the momentum, so you have -H bar square dou square/dou X square/2M and correspondingly for PY square you have dou square/dou Y square, okay.

(Refer Slide Time: 02:00)



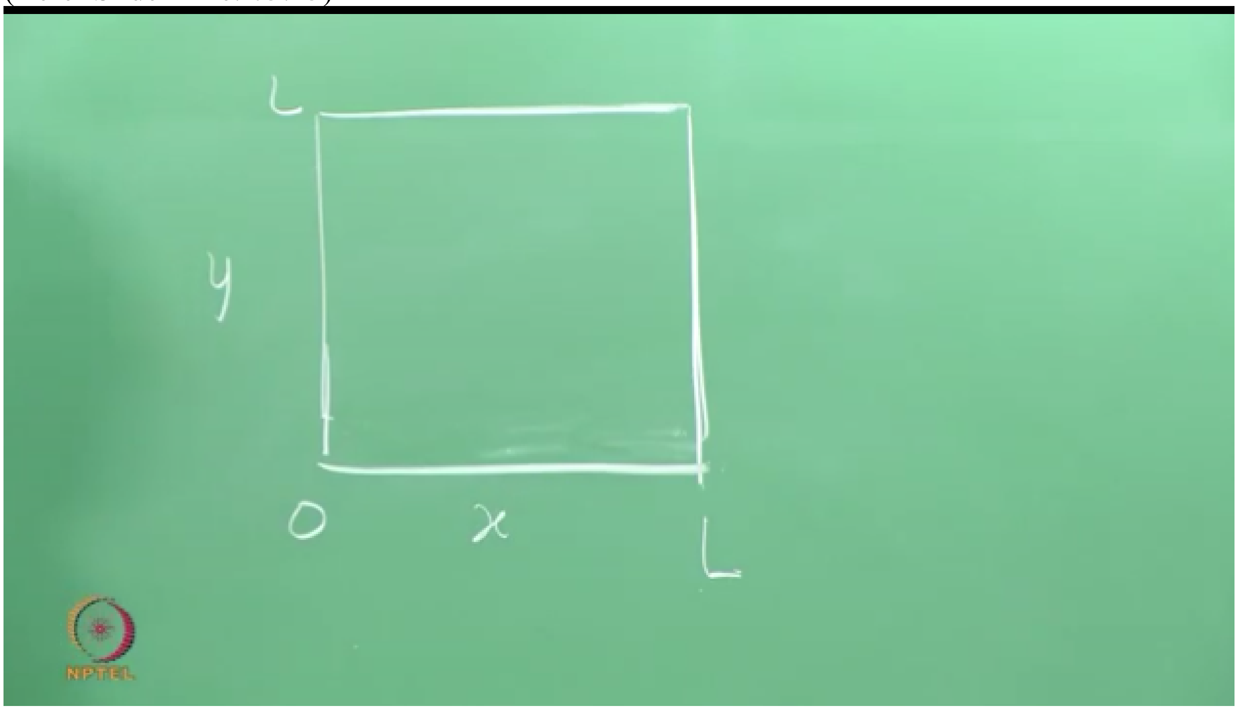
This is the operator part for the kinetic energy of the Hamiltonian + and the wave function is a function of X and Y + V some potential times sai X,Y = E sine X,Y,

(Refer Slide Time: 02:25)



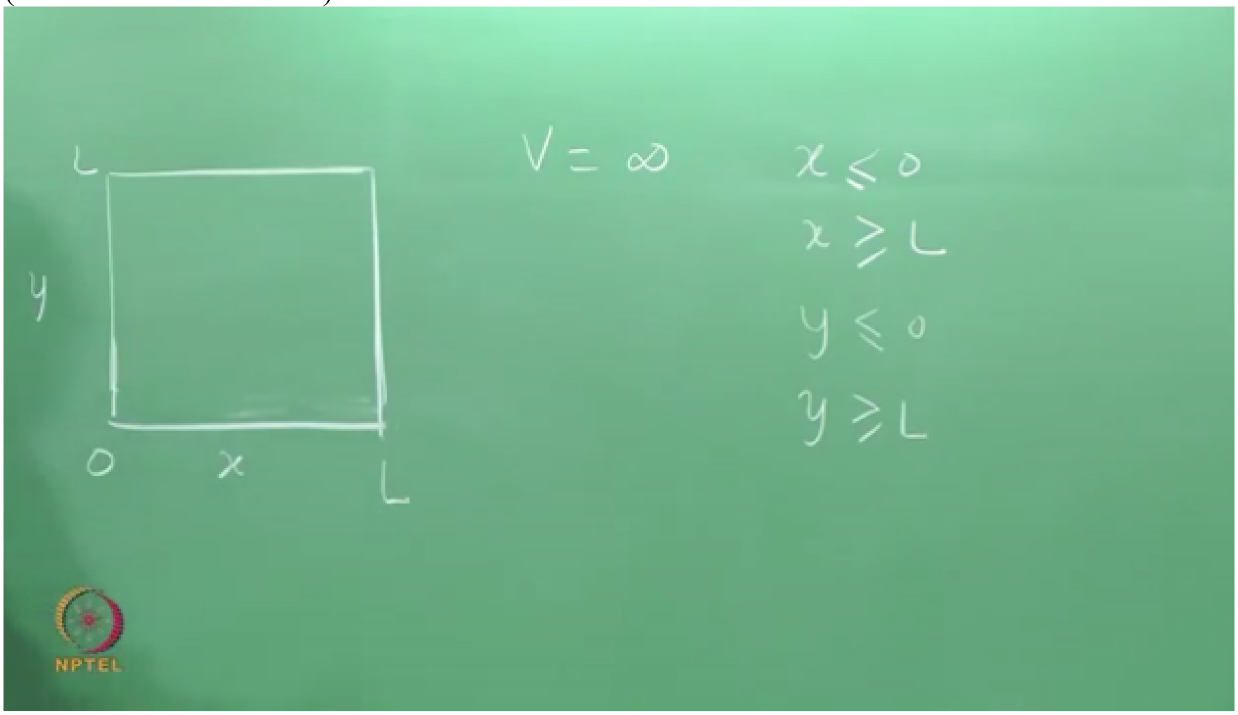
this is the two dimensional Schrodinger equation in which you have got the H, this term + the VH acting on the sai giving you E sai, and for the current problem of particle in the 2D box we consider V to be infinite for all values of X other than from 0 to L, and all values of Y from 0 to some other say A or L1 or L2 it doesn't matter if it's a rectangular box, if it's a square box then essentially you are looking at the, I'll see if we can have a square anything like that, so 0 to L and Y is also 0 to L only in this region,

(Refer Slide Time: 03:23)



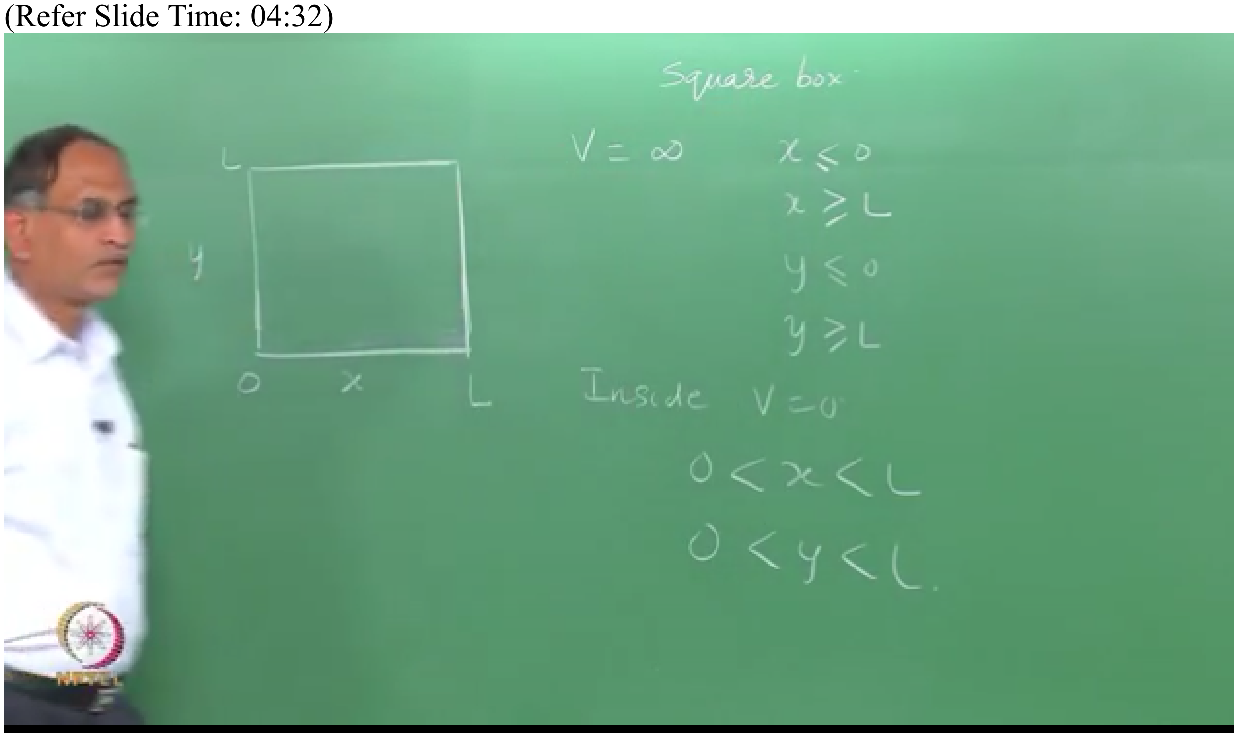
we are looking at the particle properties and the particles behavior, and for all others we have V is infinity for all values of X less than 0 or equal to, and for all values of X greater than or equal to L, and likewise for Y less than or equal to 0, Y greater than or equal to L, so this is the infinite boundaries that you have,

(Refer Slide Time: 03:58)



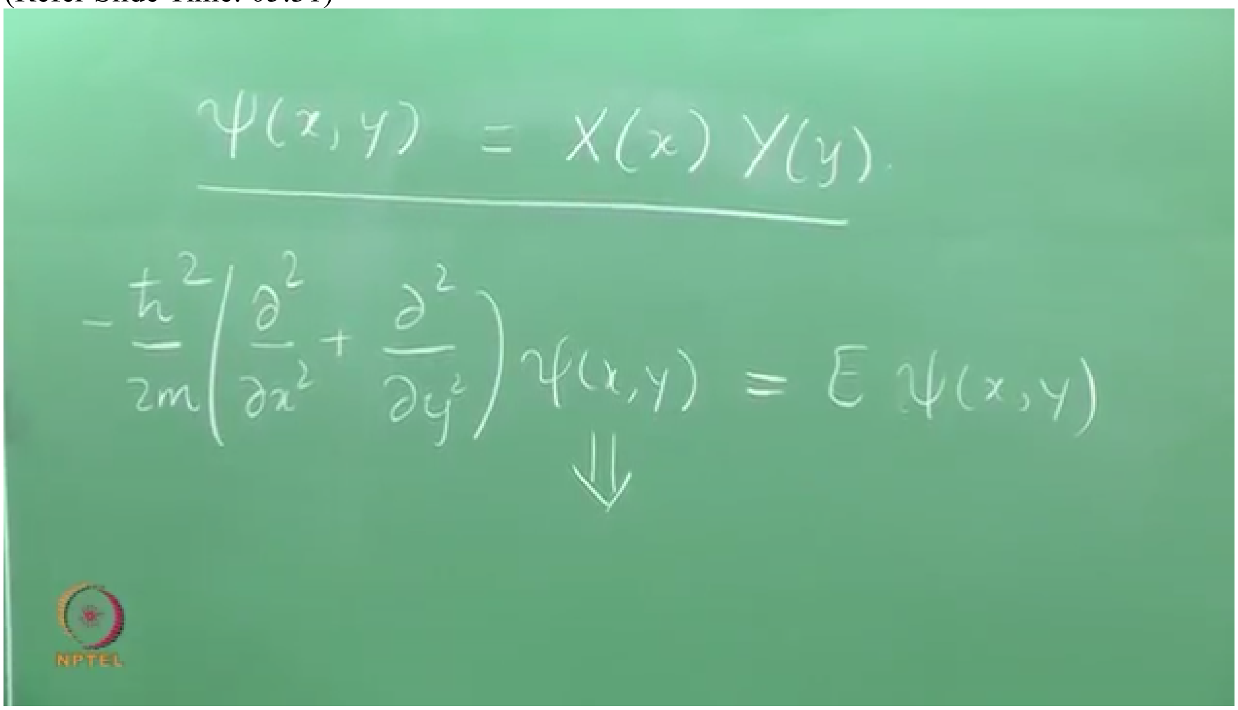
it's not the single dimensional quantity but it's the surface, in a sense that we protect the particle from escaping this region, and inside V is 0, okay, between X and L, between Y and L and this is a square box, okay.

(Refer Slide Time: 04:32)

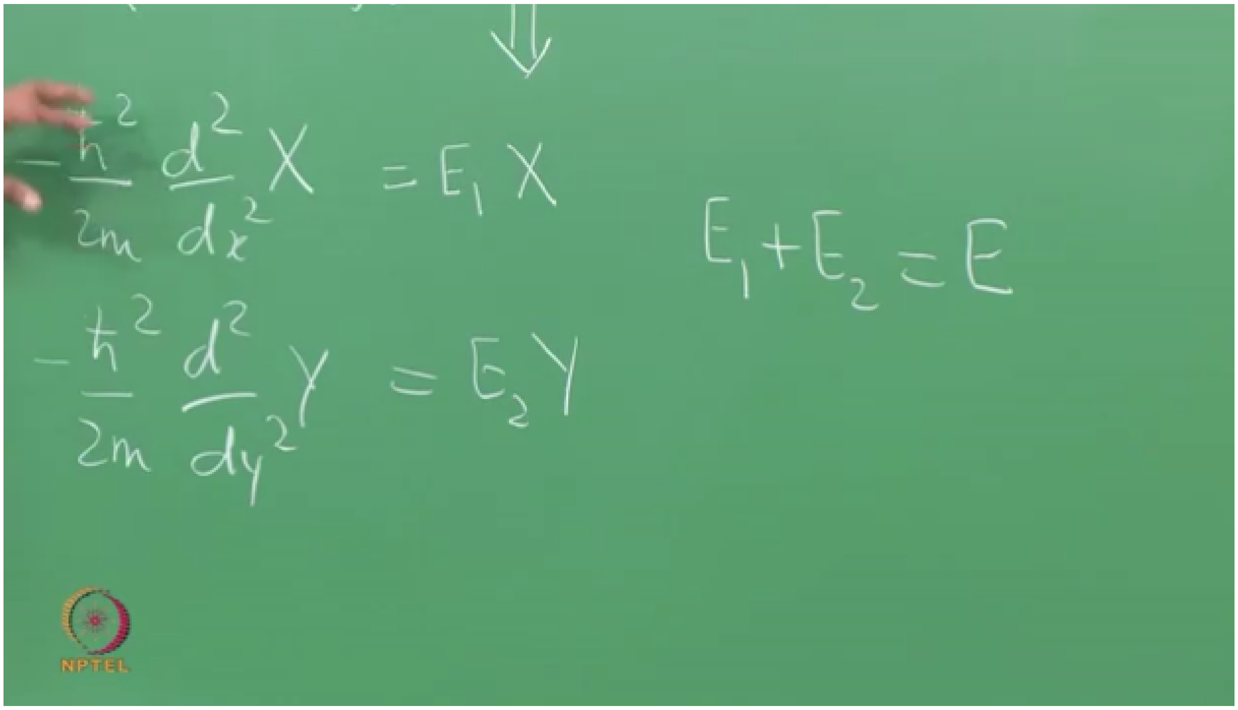


So if we do that obviously the differential equation simplifies without this term and you have a derivative square in one direction, a derivative square in another direction, and then you have the sai(XY), okay, such a problem is easily solved by is written in terms of a product of a function of X alone, and a function of Y alone, okay.

With this choice it is possible to separate this equation -H bar square/2M, dou square/dou X square + dou square/dou Y square sai(x,y) = E times sai(x,y) into two equations,
(Refer Slide Time: 05:31)

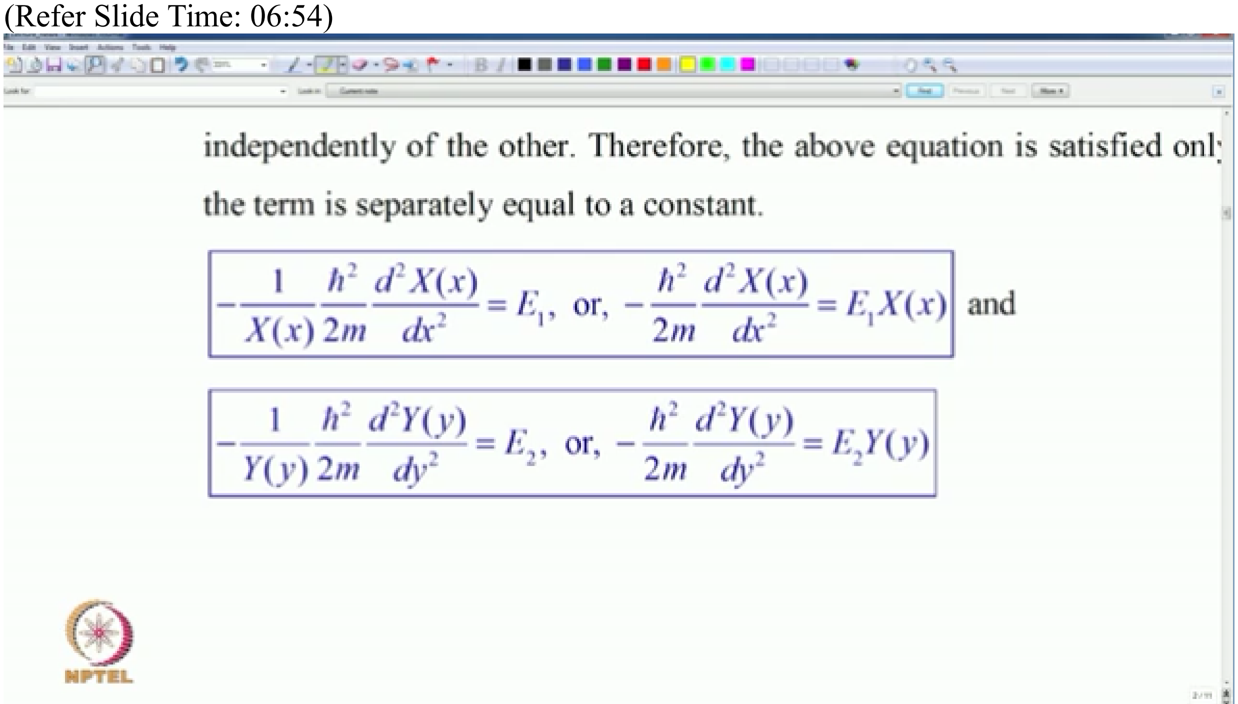


namely -H bar square/2M D square/DX square X = E1 of X and -H bar square/2M D square/DY square times Y = E 2 times Y, but these two constants E1 and E2 are constrained by E1 + E2 = E, okay.
(Refer Slide Time: 06:12)



The actual separation of, this is given in the notes that accompanies this video lecture therefore I would request you to look into that to see how this equation is separated into two 1 dimensional equation, 1 for X and 1 for Y with the constraint that the energies for the two 1-dimensional problems are related to the total energy as the sum E1 + E2.

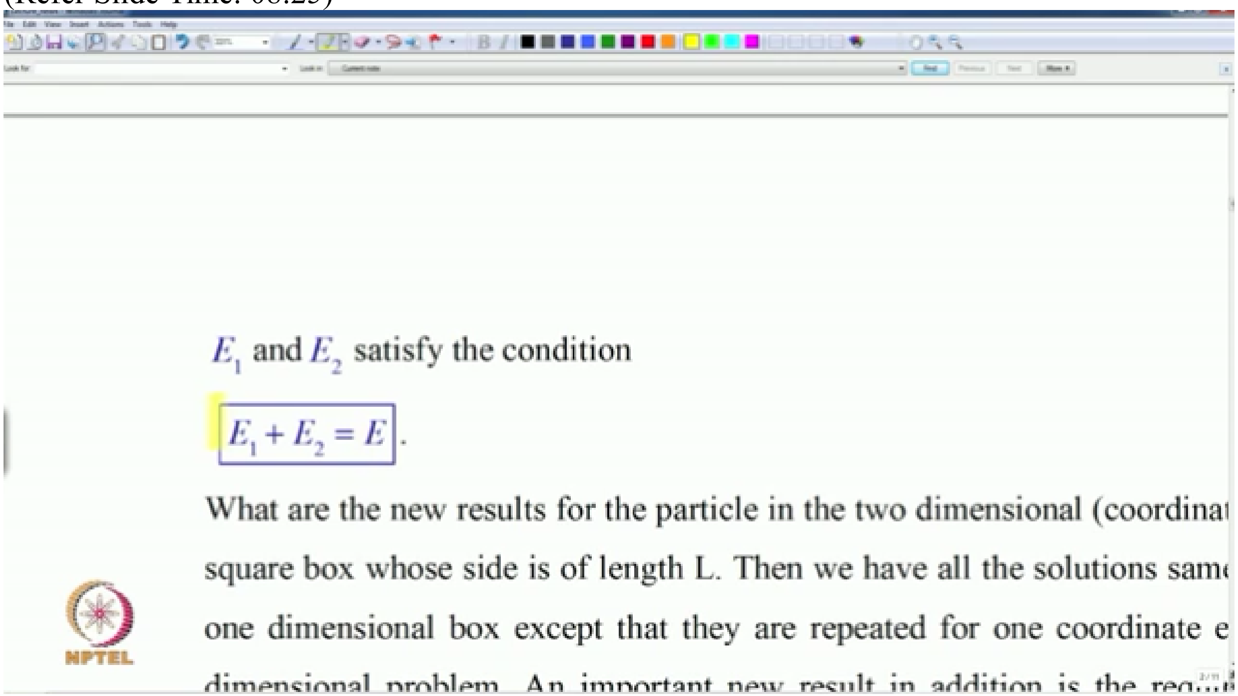
Now let us see the solutions that quantity which I have written on the board is namely,
(Refer Slide Time: 06:54)



this is the X equation, and the corresponding Y equation is that, okay. Obviously each one of them is like a 1-dimensional particle in the box, therefore the solutions for each one of them will have a running quantum number for that particular equation, the X component of the wave function will be given by the solution, similar to the sai(x) that be wrote except that now we call it X(x) and now this will have a quantum number going from 1, 2, 3 to some value which we call as N1.

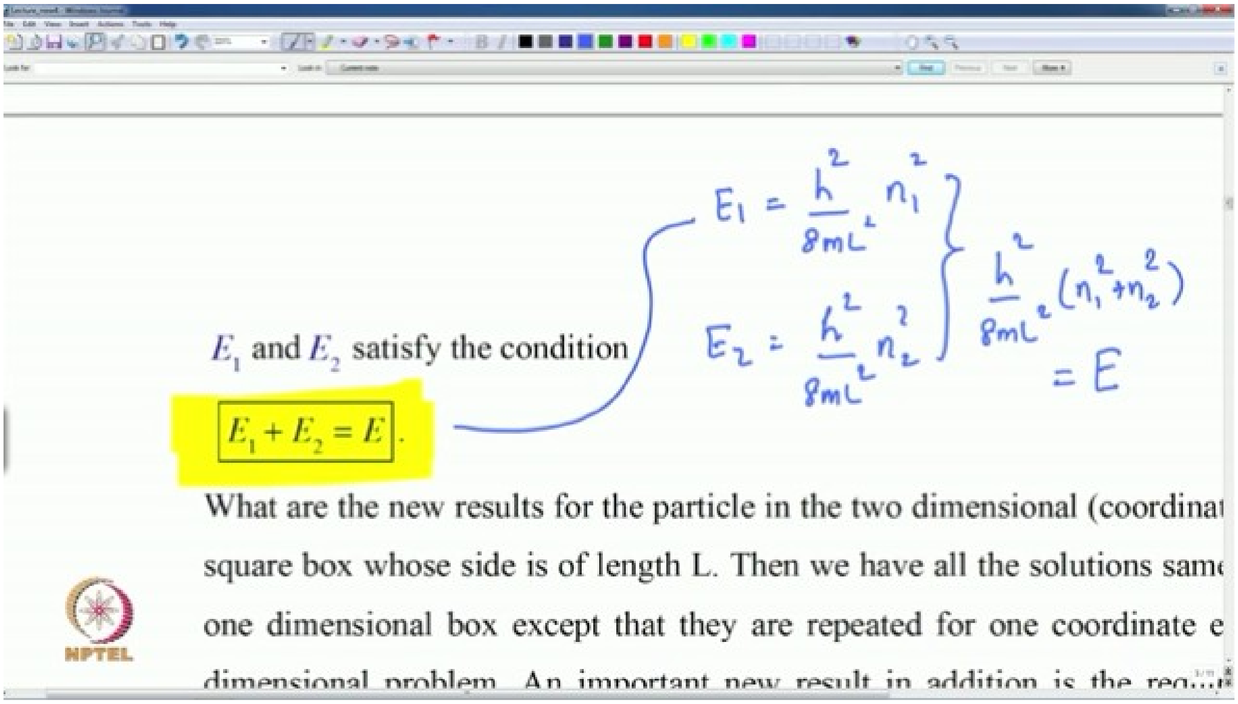
In an exactly, in an identical manner the Y equation will also have a free quantum number N2 which will run from 1, 2, 3 to whatever that we take, but please remember these two quantum numbers are not independent in the sense they are connected to the total energy, the requirement that E1 + E2 = E.

(Refer Slide Time: 08:25)



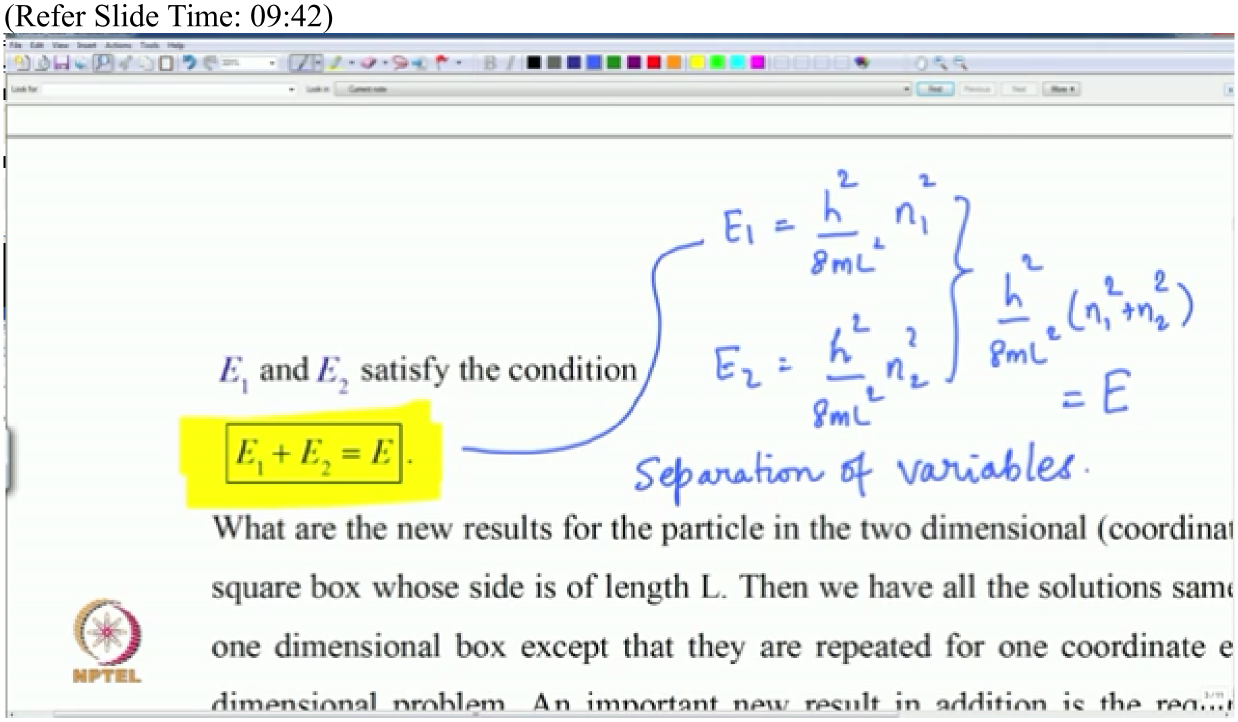
Now remember the expression for E1, from the particle in a one dimensional box it is H square/8ML square, N1 square a free quantum number in the sense it takes 1, 2, 3 integer values and E2 is also given by H square/8ML square times N2 square such that this equation is satisfied therefore you have H square/8ML square times N1 square + N2 square is equal to the total E,

(Refer Slide Time: 09:10)



so this is the only constraint that comes out in the separation of the 2 dimensional Schrodinger equation that the total energy is the sum of the two 1-dimensional energies and that's possible because we don't have a potential which couples the two dimensions we put V = 0, and therefore the method of separation of variables, separation of variables okay,

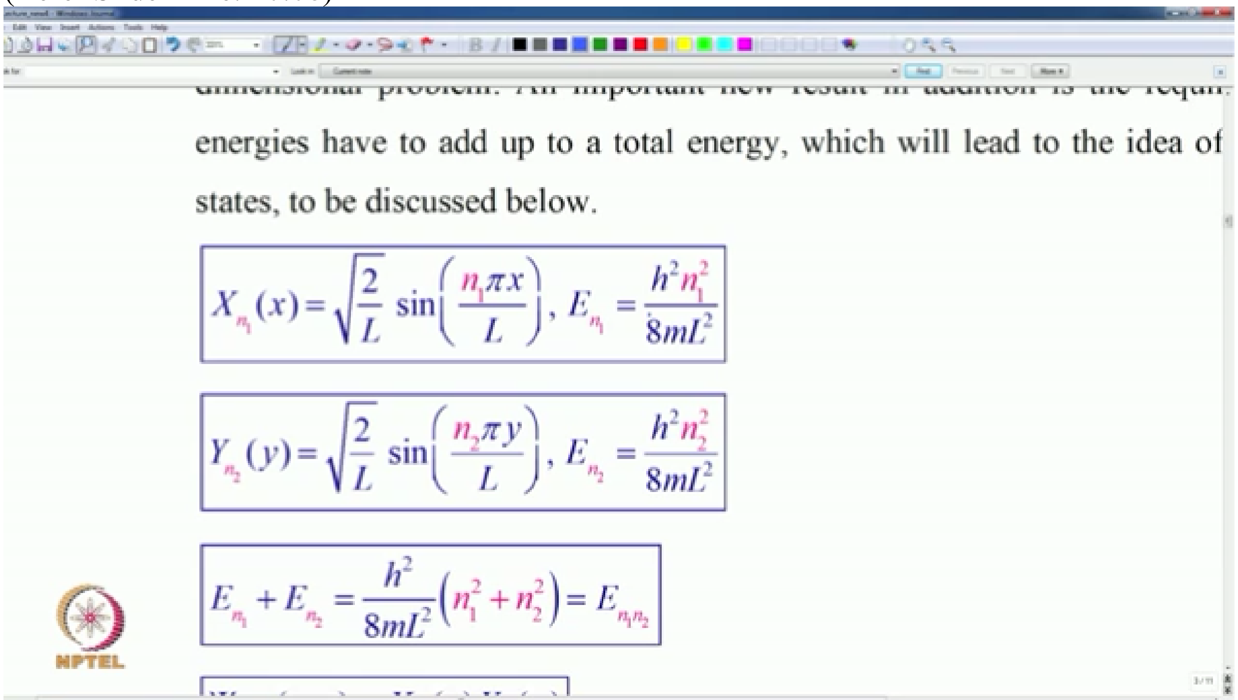
(Refer Slide Time: 09:42)



we have separated the X and Y from the sai (X,Y) if you recall, the sai(X,Y) we have separated that into the X equation and the Y equation so that process is called the separation of variables.

Now how do these functions look like?

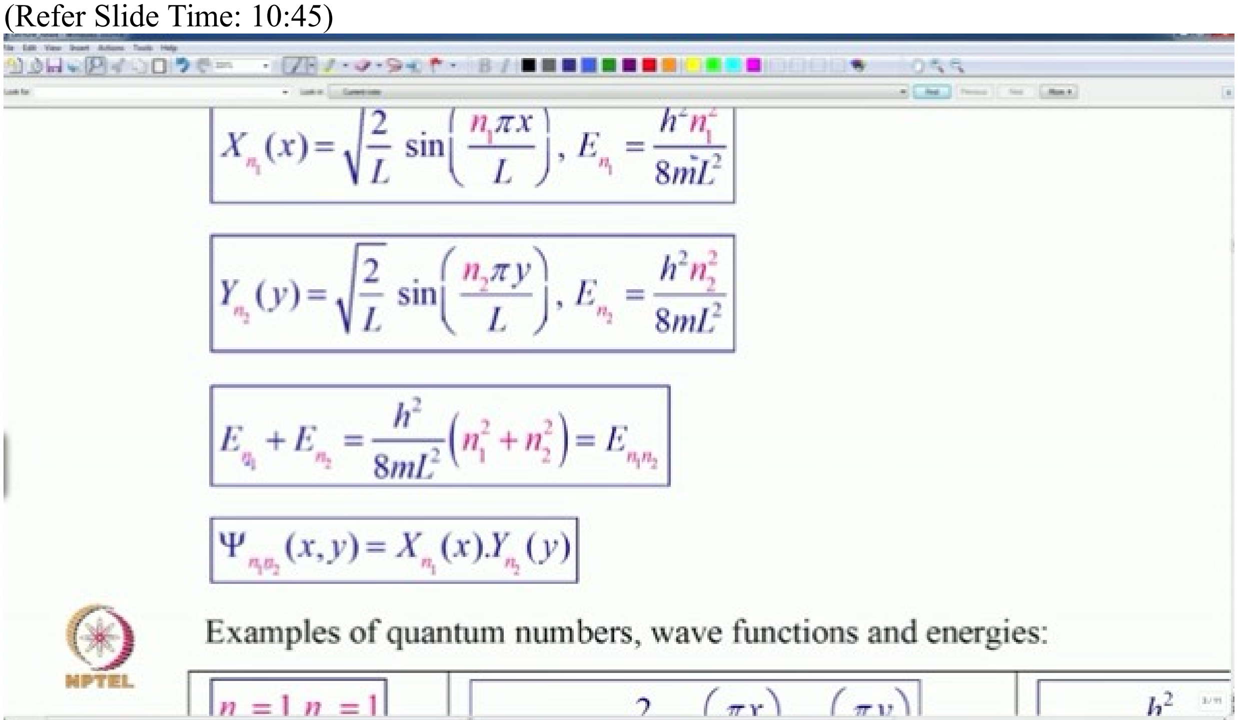
(Refer Slide Time: 10:08)



Obviously you have the solutions for the quantum number N1, in terms of the one-dimensional solution that you have seen in the previous lecture, root 2/L sine N1 pi X/L and the energy is given by N1 square, and likewise for the Y with the N2 square, and with the constraint that the total energy EN1 + EN2 is EN1 N2 you have seen that, okay.

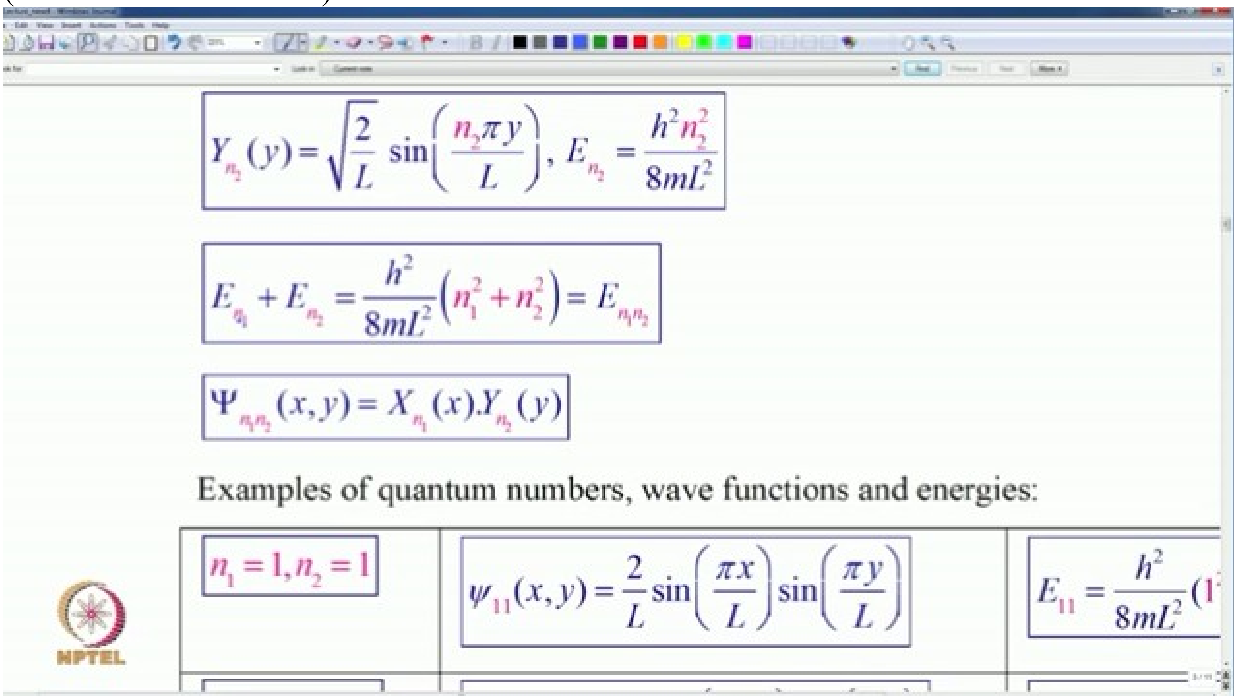
What about the wave function? The wave function now,

(Refer Slide Time: 10:45)



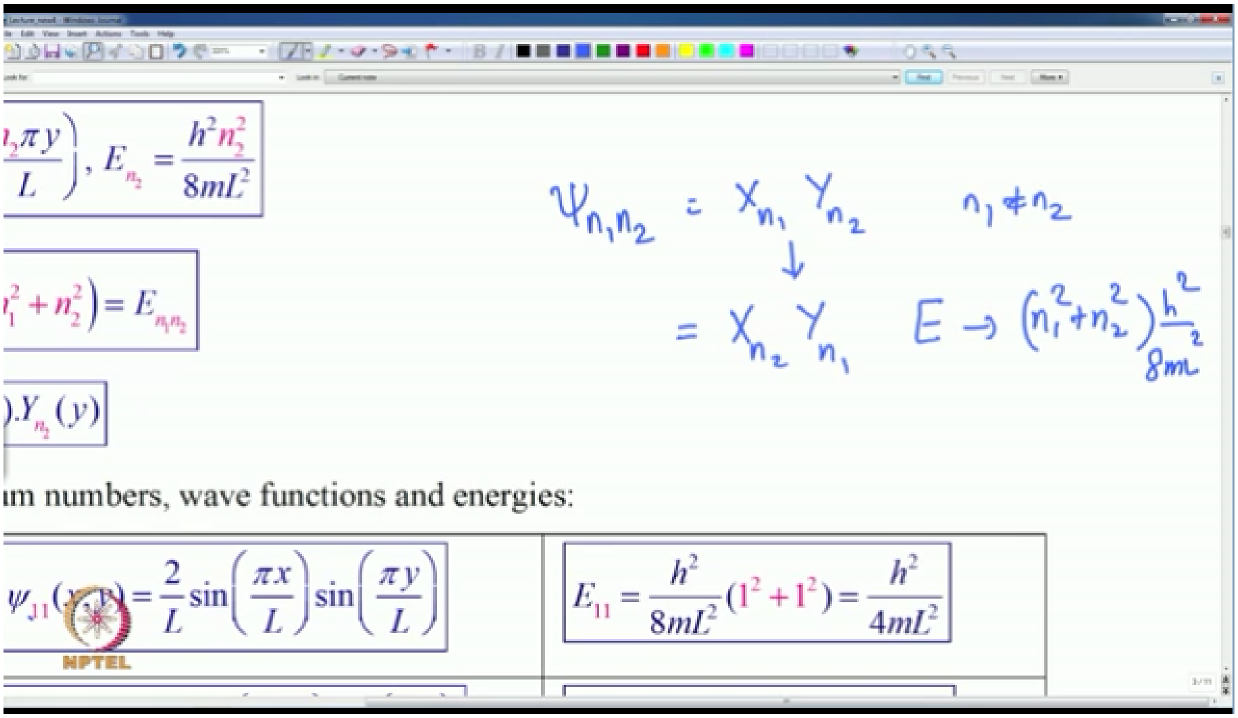
if you see this the wave function sai (N1, N2) because it's obviously specified by the two quantum numbers N1 and N2 has the independent function X with the quantum number N1, and Y with the quantum number N2, okay.

Each one is in an orthogonal direction, okay, therefore you see this interesting thing next line (Refer Slide Time: 11:15)



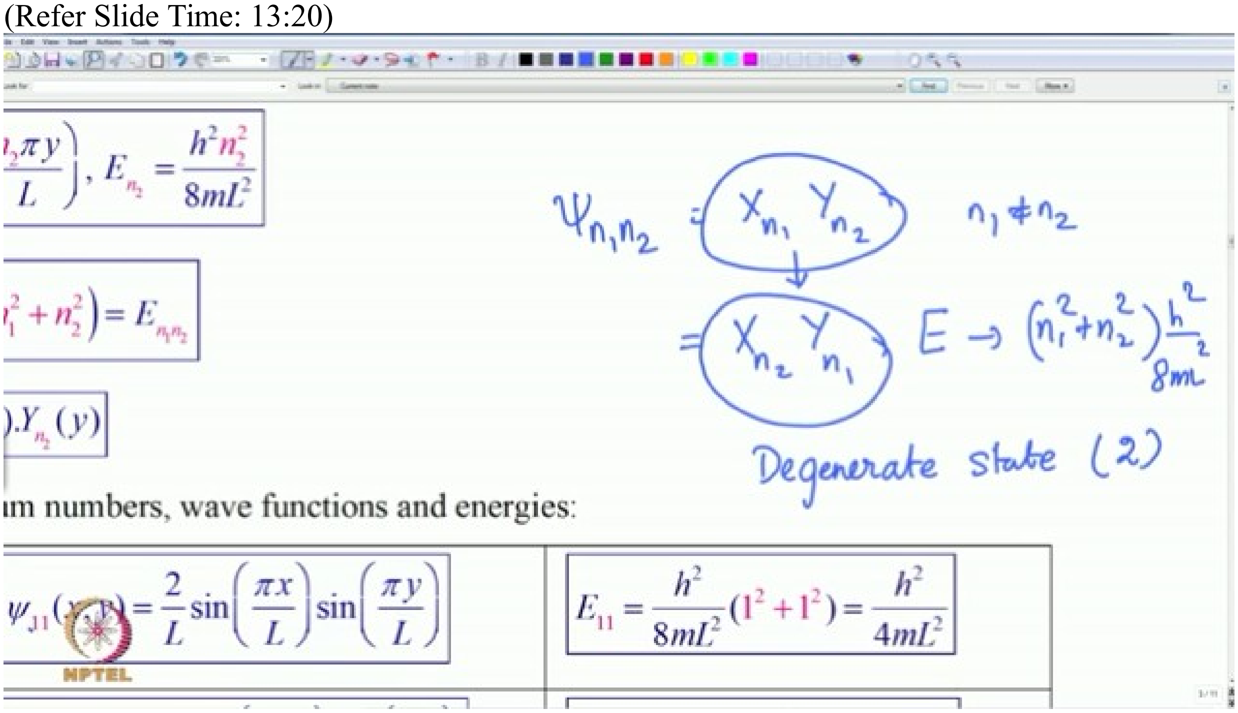
when we have N1 is 1, and N2 is 1, when we have that case which is the starting point what is called the lowest energy for the particular in the 2 dimensional box, you can see that the wave function is given by sai 1 1 (X,Y) and is given by the product of the two functions that you saw the X(x) and Y(y) which gives you sine pi X/L and sine pi Y/L, let me repeat this, when the quantum number is 1 1 the wave function is given by sai 1 1 and it's given by the product of 2/L sine pi X/L and sine pi Y/L and the energy is of course the sum of 1 square + 1 square times the whole thing therefore the energy for this process E 1 1 is H square/8ML square times 2.

What is interesting is the next choice, you have sai N1, N2 as X(n1) Y(n2), it's possible if N1 is not equal to N2, it's possible to have the wave function given by X(n2) and Y(n1) because the energy is simply proportional to N1 square + N2 square times H square by of course 8 ML square which is the proportionality constant, therefore you see that you have the same energy (Refer Slide Time: 12:55)



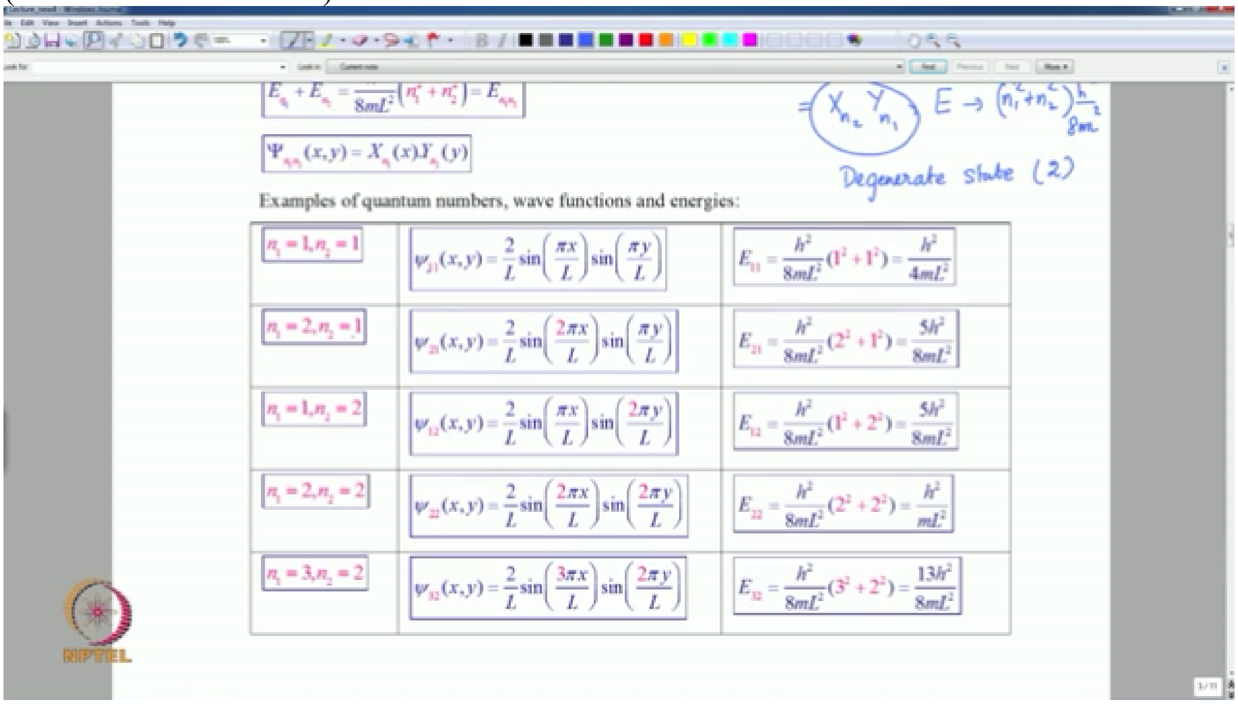
but you have 2 physically different states X(n1) Y(n2) and X(n2) Y(n1) both states have the same energy this is what is called a degenerate state.

Degeneracy is 2,
(Refer Slide Time: 13:20)



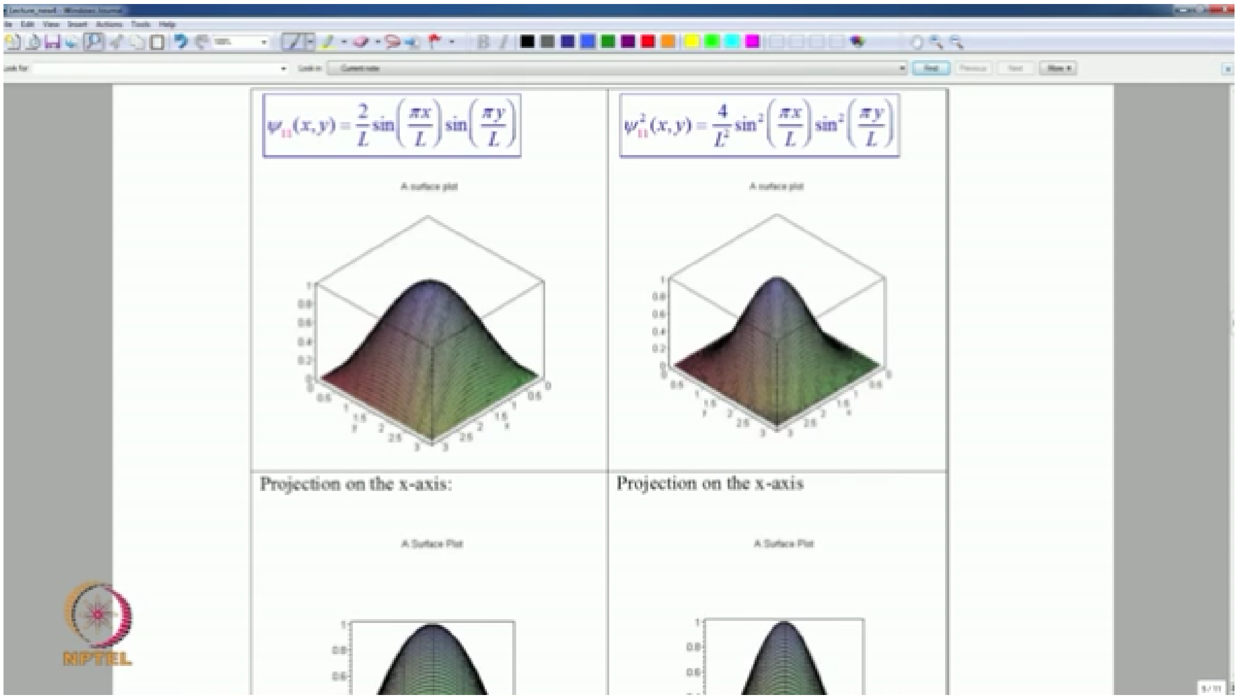
because there are 2 states which have the same energy but they have different quantum states, this is the introduction for the particle in a 2d box that the degeneracy is the additional factor.

Now how do these things look like? Let us simplify this picture, now I have a whole series of functions here which you can fill up any number of pages if you wish, you see that N1 is 2,
(Refer Slide Time: 13:56)



N2 = 1 corresponds to the wave function sai 2 1 with sine 2 pi X sine pi Y/L, and N 1 1, N 2 2 gives you the other function namely sine pi X/L sine 2 pi Y/L and the energies are the same, so if the quantum numbers are identical there is no degeneracy, but if the quantum numbers are different for a square box because we have chosen the length L to be the same the square box gives you the solution that you have a minimum degeneracy of 2 if N1 is not the same as N2, and you can see that for 3 and 2 that you have here the wave function sine 3 pi X/L and sine 2 pi Y/L.

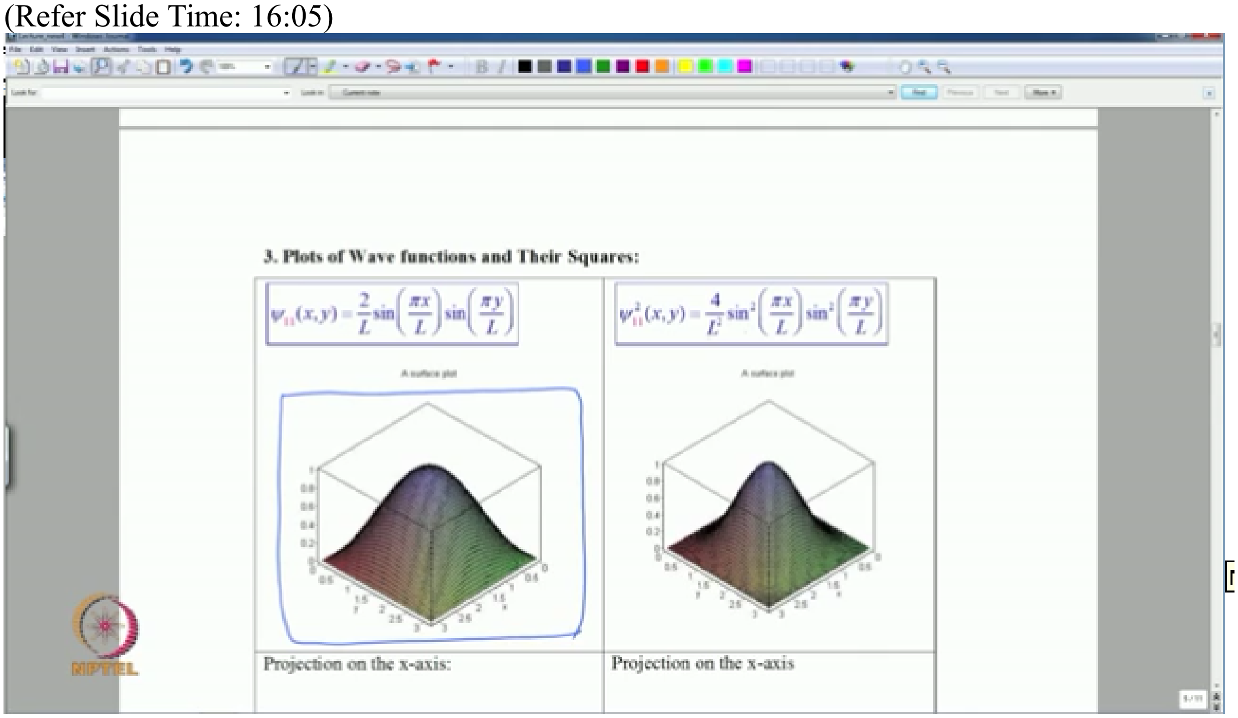
And then 2 and 3 which is sine 2 pi X/ L sine 3 pi Y/L, so the axis choice the quantum number choice for a given axis determines the functions state, how do these things look like if we plot them? I mean this plot looks fancy but actually doesn't have much interpretation or meaning but it's worth seeing the product wave function in 2 dimensions, okay, so you see the wave function,
(Refer Slide Time: 15:18)



you see the wave function sai 1 1 using this picture, it's a half-wave similar to what you had in your particle in a 1 dimensional box, in the X-direction and it's also a half wave in the Y-direction as you can see through the projection in the X direction here of this graph, and on the Y-direction also you have the same thing identical, okay.

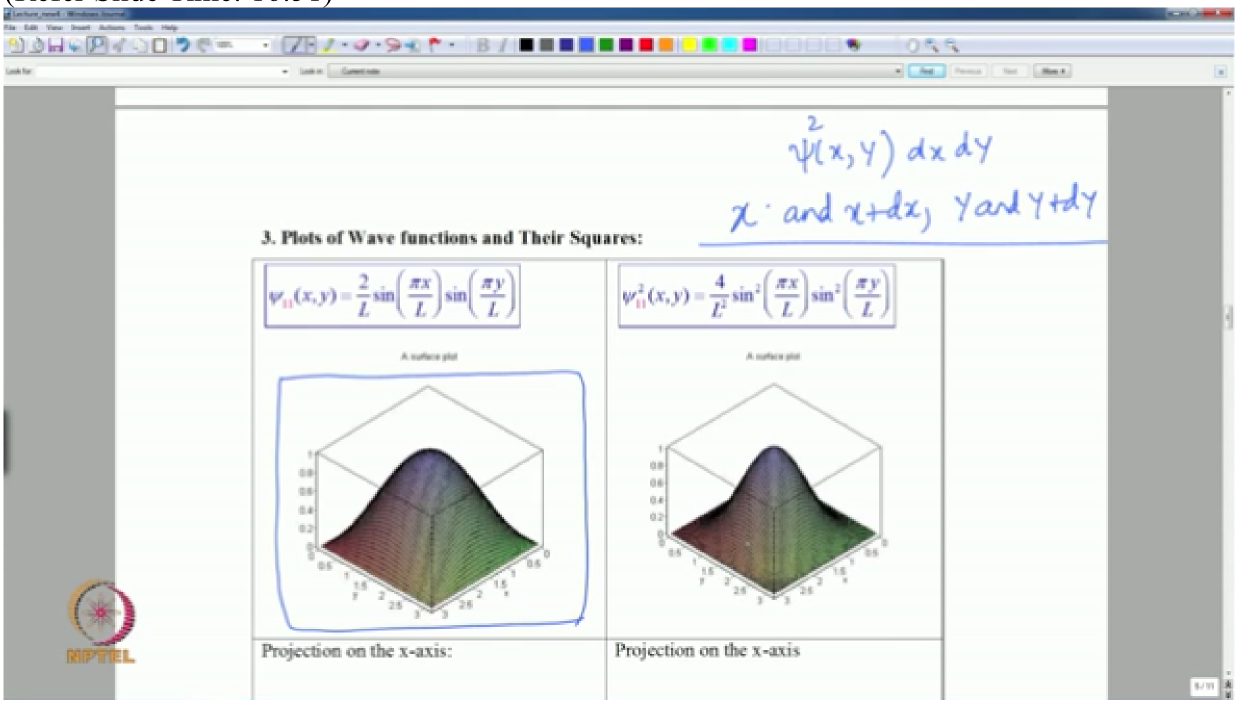
What about the sine square?

(Refer Slide Time: 16:05)



The sai square which is associated with the probability that the particle be found, not in a small length region DX but in a small area DX, DY please remember sai (x,y) if you do that sai square DX DY is the probability that the particle will be in the small rectangular region between X and X + DX, and Y and Y + DY, that's a small region, and you can see that the sai square is given like this therefore you can create,

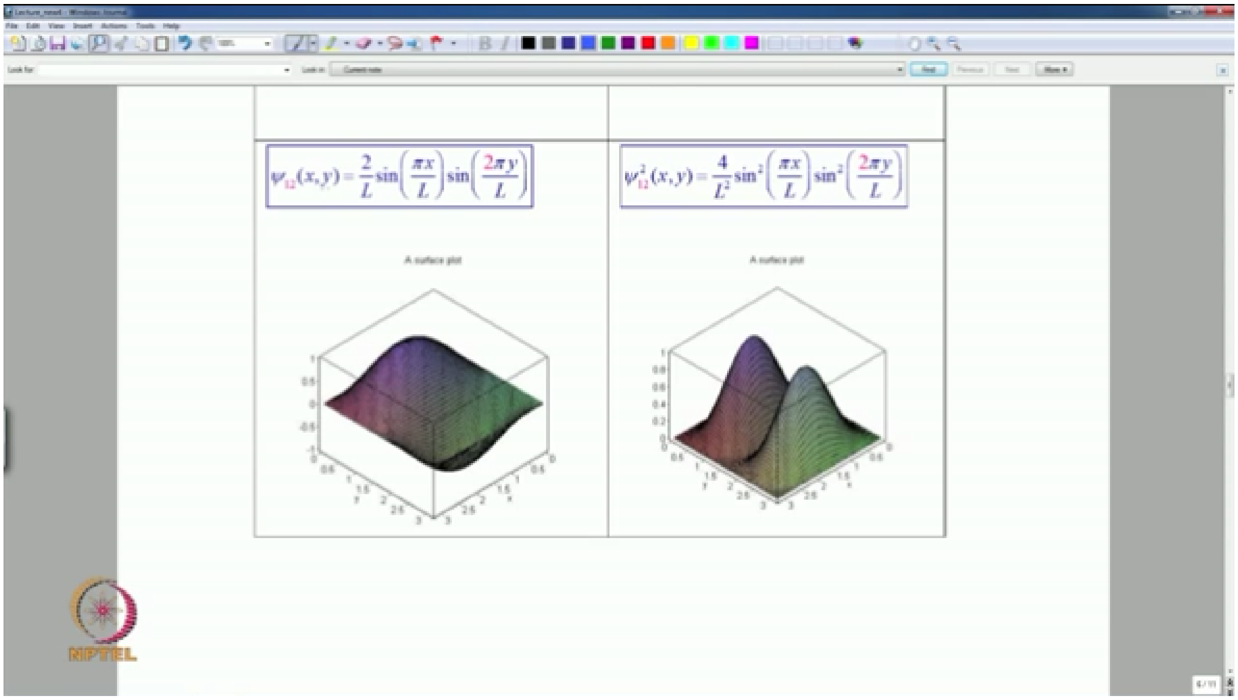
(Refer Slide Time: 16:51)



I mean you can visualize what would be the probability, exactly the same way that you have visualized the particle in a one dimensional box except that now we have a motion on the plane.

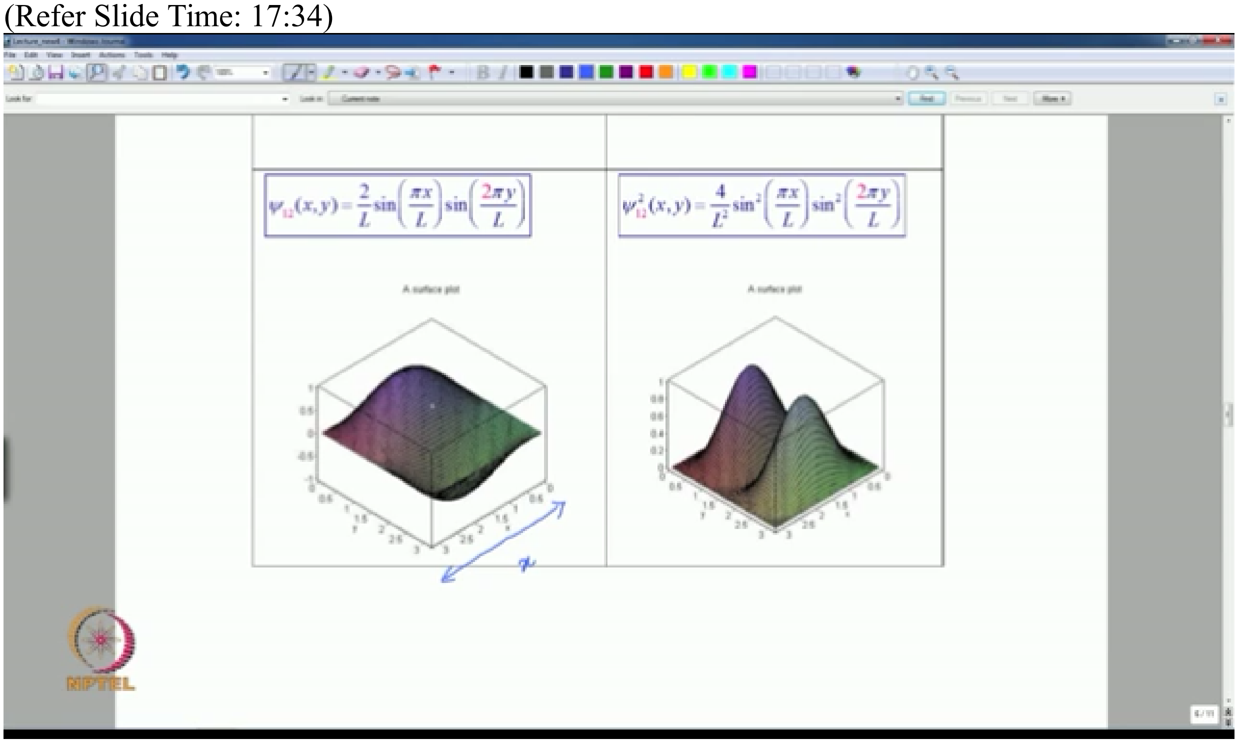
And now what is interesting is when you go to different quantum numbers where there is degeneracy sai 1 2 if you look at this,

(Refer Slide Time: 17:15)



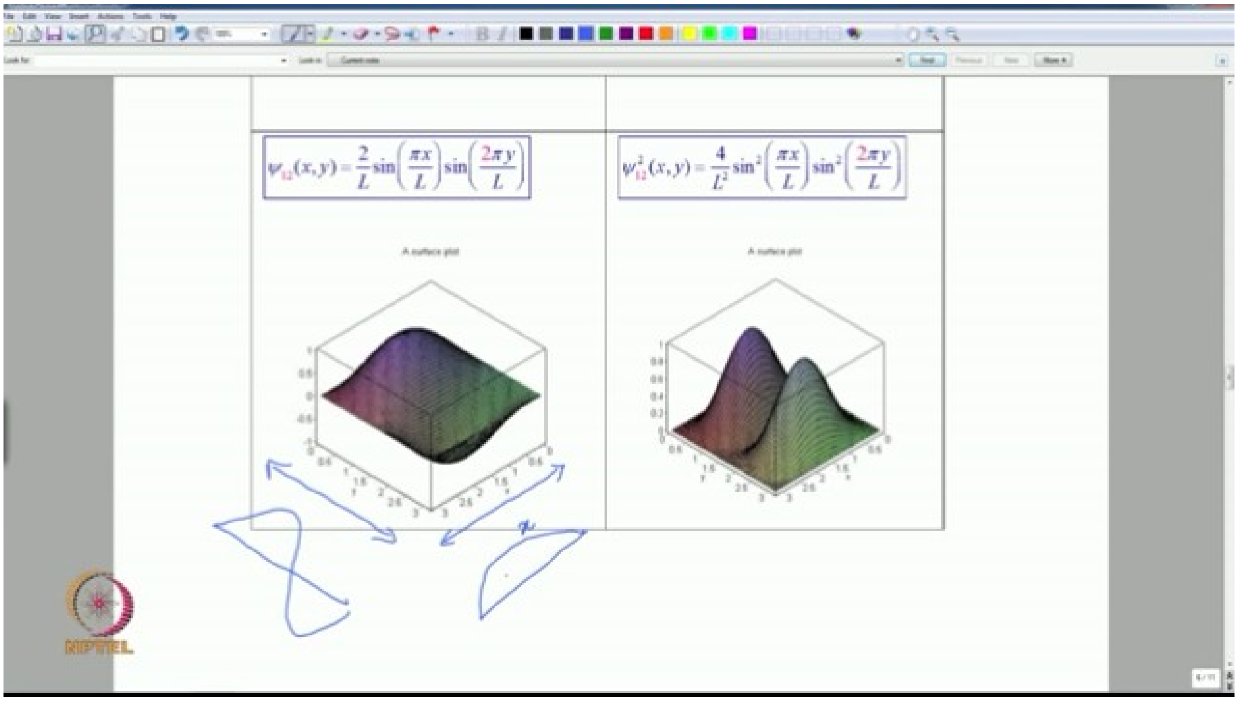
sai 1 2 is quantum number 1 for the X direction,

(Refer Slide Time: 17:34)



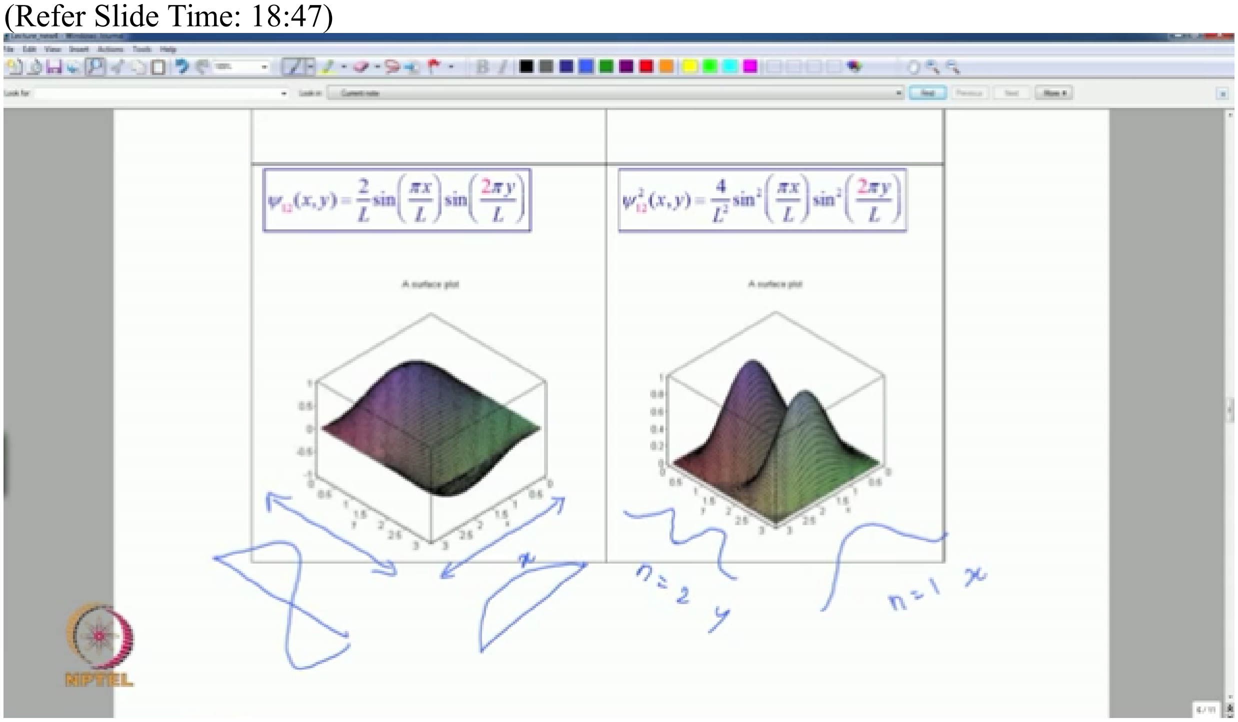
and quantum number 2 for the Y direction, therefore this is the quantum number, this is the quantum number for the X direction and you can see that it's a half wave which is either up or down, it's either positive or negative, the reason being the Y-direction wave is a full wave, so in this direction what you have is if I may draw this the wave function looks like that. In this direction the wave function looks like that, therefore when you take the product of these two

(Refer Slide Time: 18:04)



functions a negative side makes this wave function negative for half the length and therefore you see that for half the length you have either a positive wave function or you have a negative wave function, that's only for the wave function, we know that the wave function is not that important it's the square of the wave function which is important for probability interpretation, and you can see that sai square which removes this negative character of the function gives you now very beautifully the 2, N = 1 case for the X axis, and the N = 2 if you remember the graph that you had for N = 2 or the Y axis and this is the X axis, therefore the features are captured,

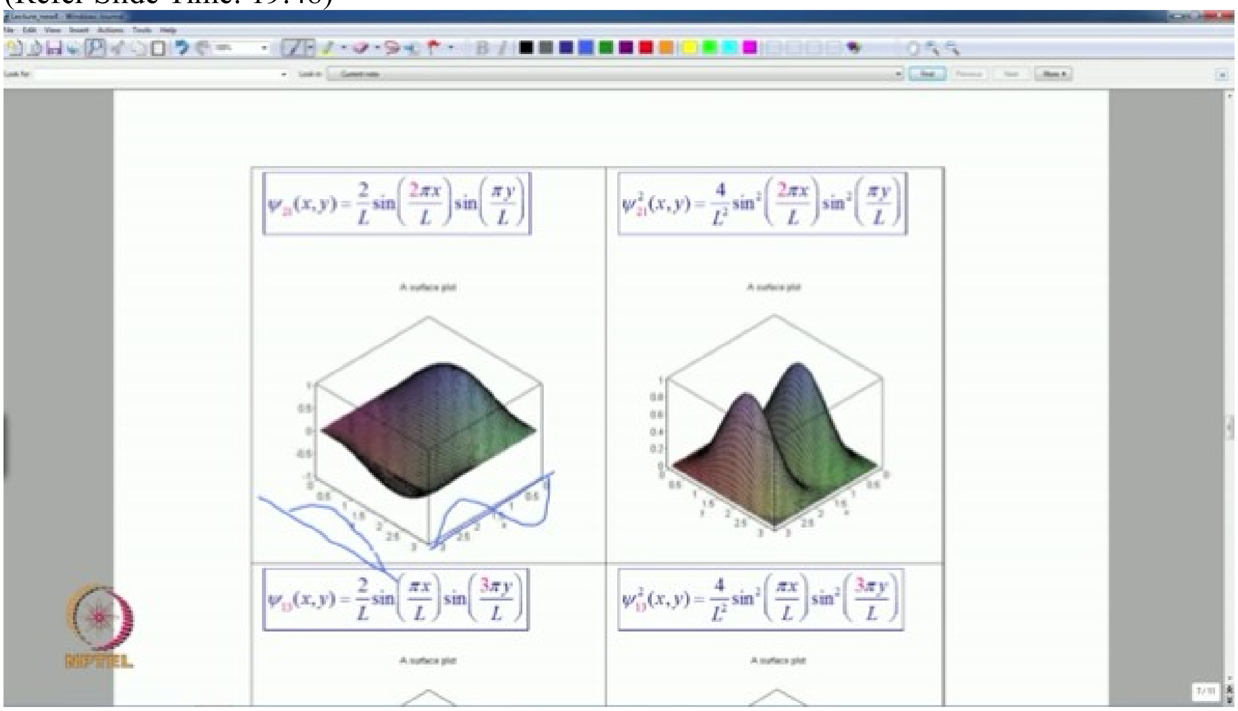
(Refer Slide Time: 18:47)



the wave function features are captured when you do your surface plot and you can see that the pictures can be created for a large number of them but there is a limit, 2 dimensions and in 3 dimension we probably can use color at the most to distinguish the function from the 3 axis, but that's it you cannot visualize this for N dimensions.

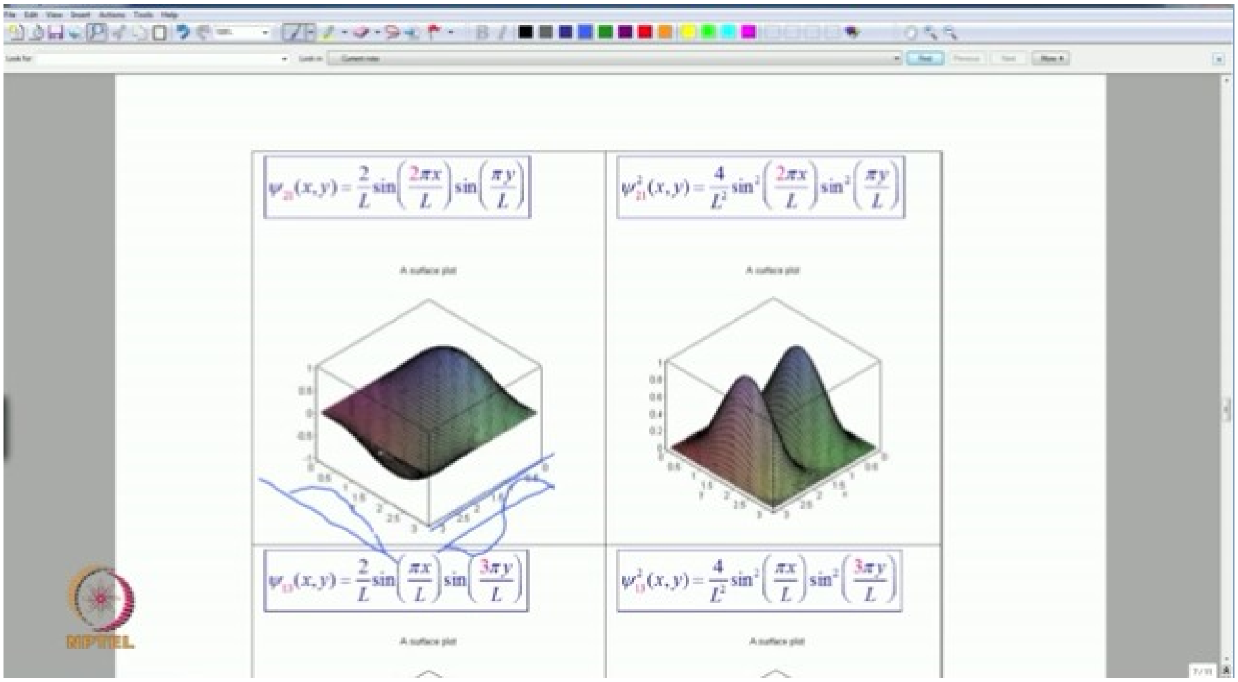
So let us conclude this part of the particle in a 2 dimensional box with some examples of the wave functions and the squares of the wave function for different quantum numbers, so here is a 2 1 as opposed to 1 2, and you see all that happens is that for a 2 1 the wave function along the X axis is like this, and the wave function along the Y axis it's like that, okay.

(Refer Slide Time: 19:48)



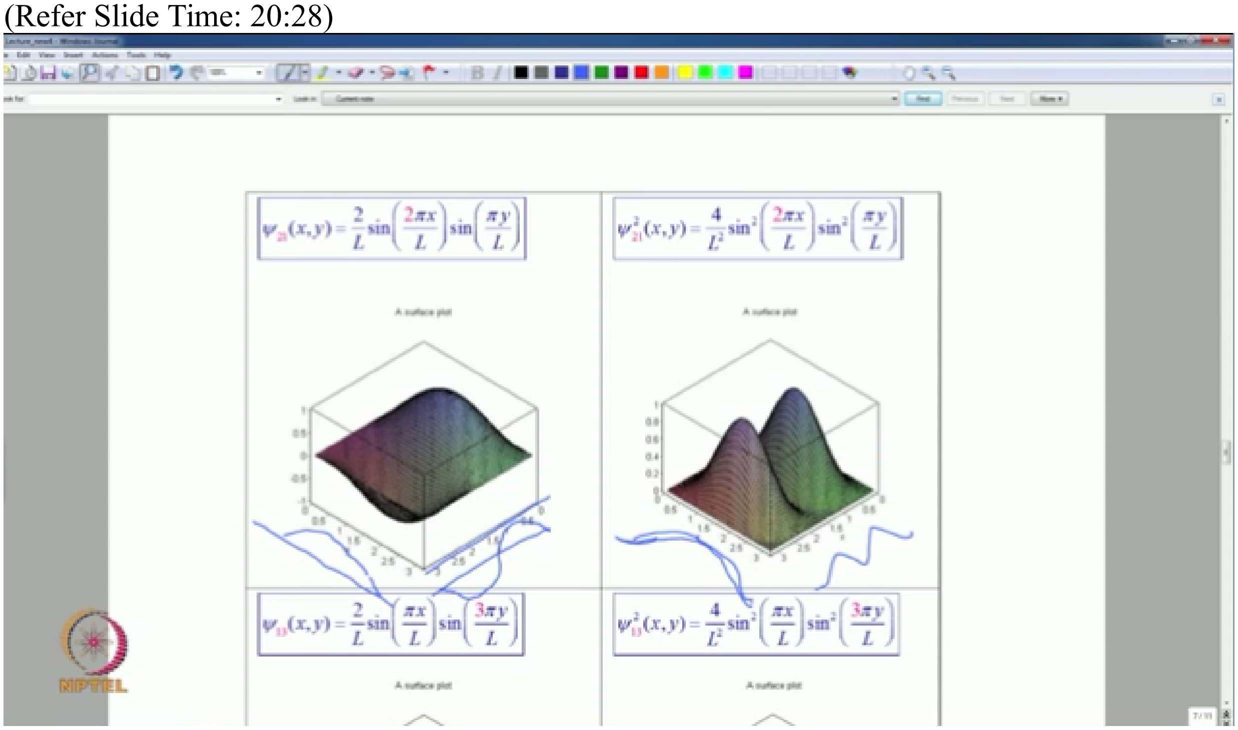
And you can see that actually, sorry this is in the wrong direction so let me erase that because your 0 starts from here, therefore you have that, and this is the Y-axis, that's the reason why part

(Refer Slide Time: 20:08)

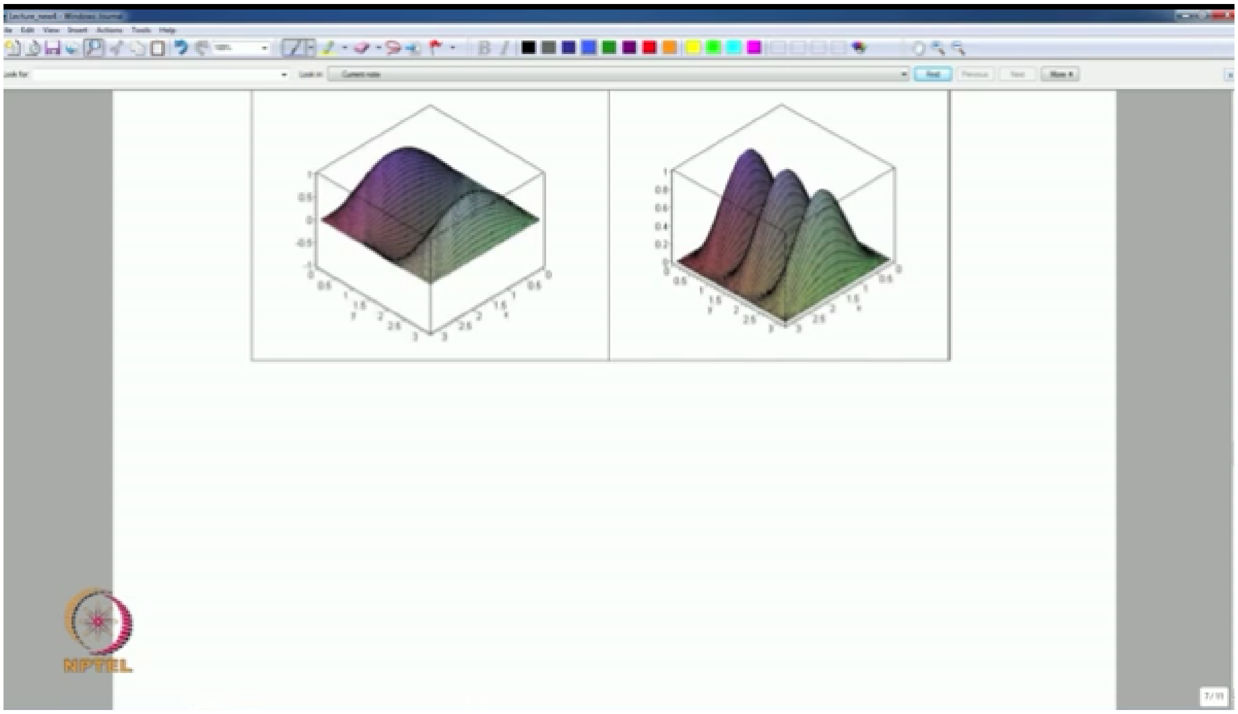


of it is negative and the other part is positive. And the square of the wave function you can see that there are two humps along the X axis, and along the Y axis it's a quantum number 1, so you have only 1.

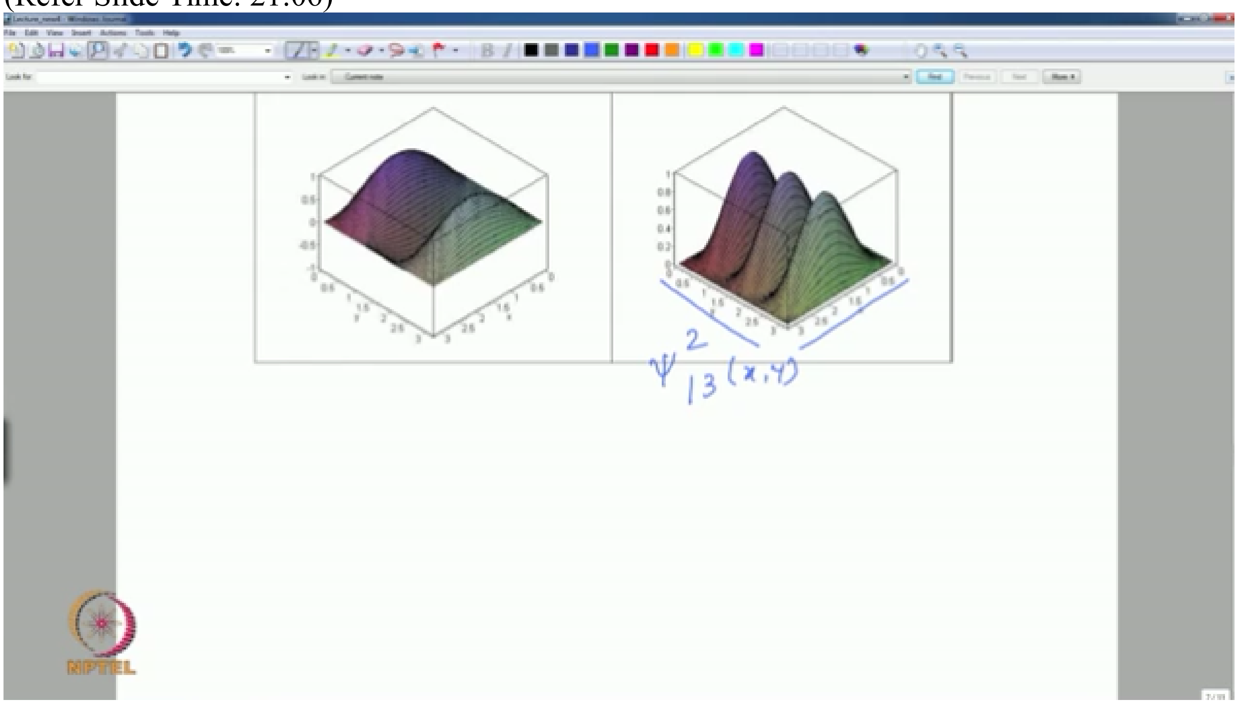
Similar to the 1 dimensional Y axis,
(Refer Slide Time: 20:28)



and let's see 1 or 2 more examples and let me stop with that, this is it,
(Refer Slide Time: 20:34)



I mean the exercise here. What does this picture represent? There is 1 here along the X axis, and there are 3 peaks therefore you have this is a, Y is 3 and X is 1 so it is sai 1 3 square (X,Y),
(Refer Slide Time: 21:06)



so the lecture notes give you many more such pictures, but in the next part of this lecture we will see what do all these things mean in terms of probability calculations and in terms of a new idea called the expectation values. We'll stop here for this particular part of the lecture. Thank you.

<u>Online Video Editing/Post Production</u>

K.R. Mahendra Babu
Soju Francis
S. Pradeepa
S. Subash

Camera

Selvam
Robert Joseph
Karthikeyan
Ramkumar
Ramganesh
Sathiaraj

Studio Assistants
Krishnakumar
Linuselvan
Saranraj

Animations

Anushree Santhosh
Pradeep Valan. S.L

NPTEL Web & Faculty Assistance Team

Allen Jacob Dinesh
Bharathi Balaji
Deepa Venkatraman
Dianis Bertin
Gayathri
Gurumoorthi
Jason Prasad
Jayanthi
Kamala Ramakrishanan
Lakshmi Priya
Malarvizhi
Manikandasivam
Mohana Sundari
Muthu Kumaran
Naveen Kumar
Palani
Salomi
Senthil
Sridharan

Suriyakumari

Administrative Assistant

Janakiraman. K.S

Video Producers

K.R Ravindranath
Kannan Krishnamurthy

IIT Madras Production
Funded by
Department of Higher Education
Ministry of Human Resource Development
Government of India
www.nptel.ac.in