Chemistry I – CY1001
Introductory Quantum Mechanics and Spectroscopy

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

Lecture - 05
Lecture 4: Part I - Probabilities-in-a-two-dimensional box (Infinite barriers)

Welcome back to the lecture, in the earlier lecture I talked about the particle in the one dimensional box and in the current one, let us discuss the particle in a two dimensional model or two degrees of freedom model. The particles, position coordinates are given by two x and y; two coordinates in a plane orthogonal to each other and then we discussed the quantum problem.

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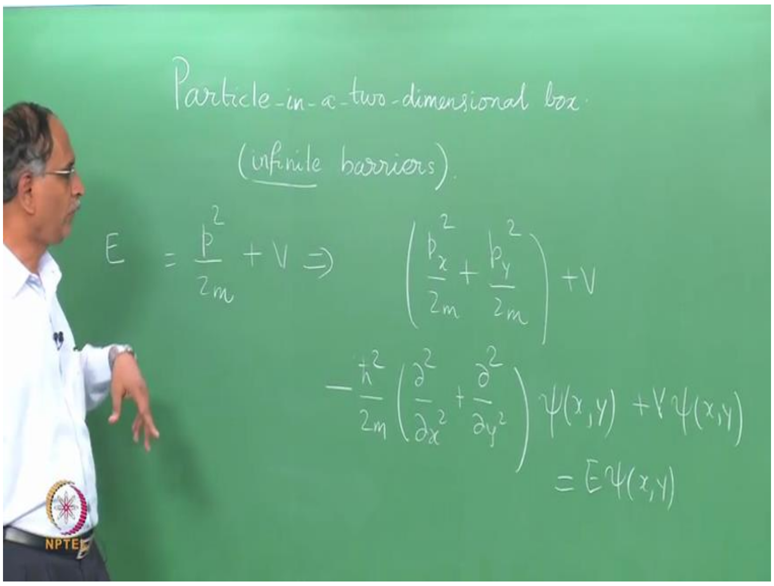

The barriers are infinite, therefore if you remember the problem p square by 2m plus V, which is the energy term gets changed to or it is rewritten as p x square by 2m plus p y squared by 2m plus V and the p x is replaced in quantum mechanics by the minus h bar square by the term; minus h bar square by 2m. The partial derivative now because we have the wave function as a function of two coordinates x and y and the momentum in the x direction is given by the partial derivative and this is the square of the moment, so you have minus h bar square; dou square by dou x square by 2m and correspondingly for p y square, you have dou square by dou y square.

This is the operator part for the kinetic energy of the Hamiltonian plus and the wave function is the function of x and y plus V; some potential times psi x comma y is equal to E psi x comma y. This is the two dimensional Schrodinger equation, in which you have got the h; this term plus the V h acting on the psi giving you E psi and for the current problem of particle in a two d box, we considered 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 L 1 or L 2; it does not matter; if it is a rectangular box.

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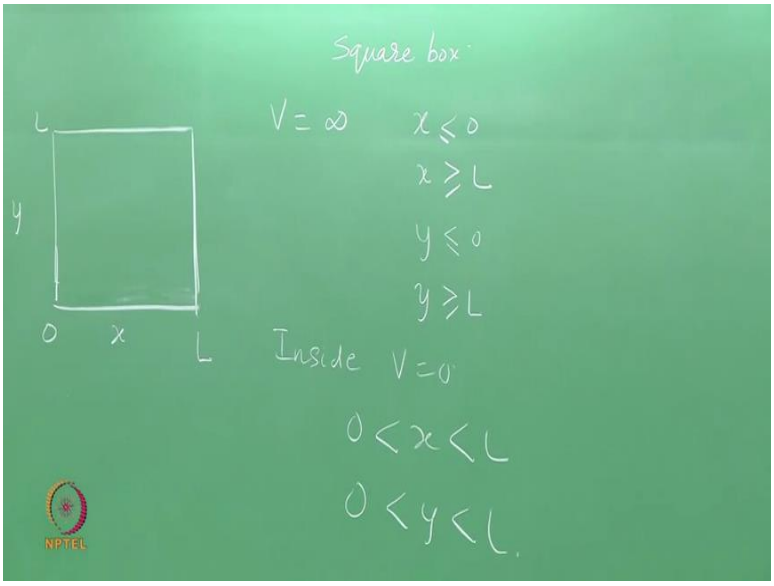

If it is a square box then essentially you are looking at the let us see you can have a square something like that. So, 0 to L and y is also 0 to L; only in this region, we are looking at the particle properties and the particles behaviour and for all others we have V is infinity. For all values of x 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 equal to l. So, this is the infinite boundaries that you have; it is not the single dimensional quantity, but it is a surface in a sense that we protect the particle from escaping this region and inside V is 0 between x and L, between y and L then this is a square box.

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 psi of x y.

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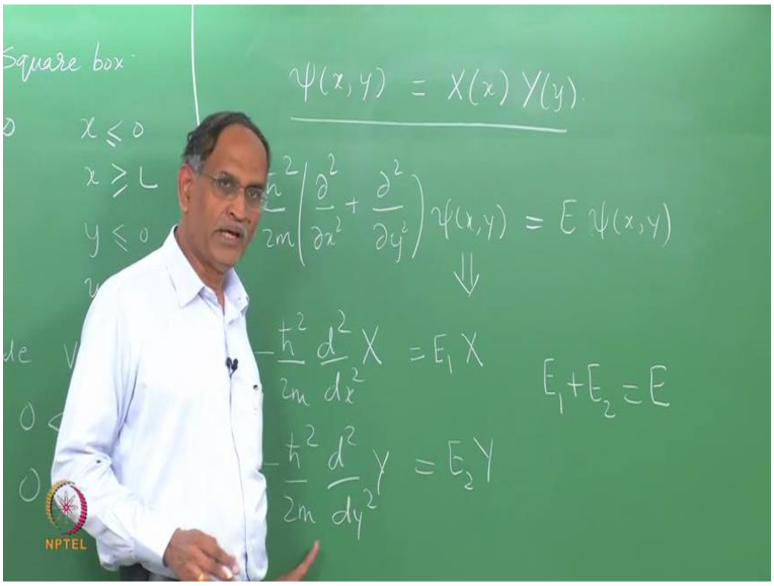

Such a problem is easily solved by (Refer Time: 04:54) written in terms of a product of a function of X alone and a function of Y alone. With this choice, it is possible to separate this equation minus h bar square by 2m dou squared by dou x square plus dou squared by dou y square psi of x comma y is equal to E times psi of x comma y into two equations namely minus h bar squared by 2m; d square by d x square x is equal to E 1 of x and minus h bar square by 2m; d square by d y square times y is equal to E 2 times y, but these two constants E 1 and E 2 are constrained by E 1 plus E 2 is equal to E.

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; one dimensional equation, one for x and one for y. With the constraint that the energies for the two one dimensional problems are related to the total energy has a sum E 1 plus E 2.

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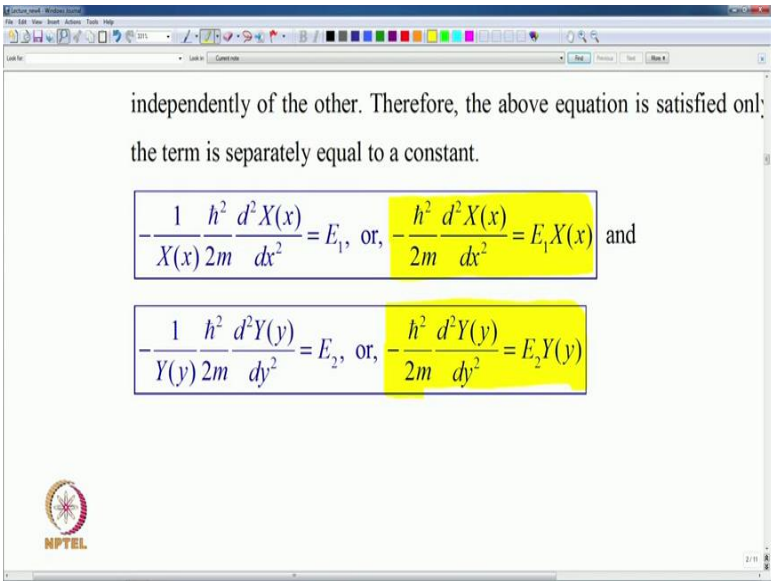

Now, let us see the solutions that quantity which I have written on the board is namely this is the X equation and the corresponding Y equation is that; obviously, each one of them is like a one dimensional part particle in a box. Therefore, the solutions for each one of them will have a running quantum number for that particular equation. The X component of the wave function will be given by the solution, it is similar to the psi of x that we wrote except that now we call it X of x and now this will have a quantum number going from 1, 2, 3 to some value which we call as n 1.

In an exactly, in an identical manner, the y equation will also have a free quantum number n 2 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 E 1 plus E 2 is equal to E.

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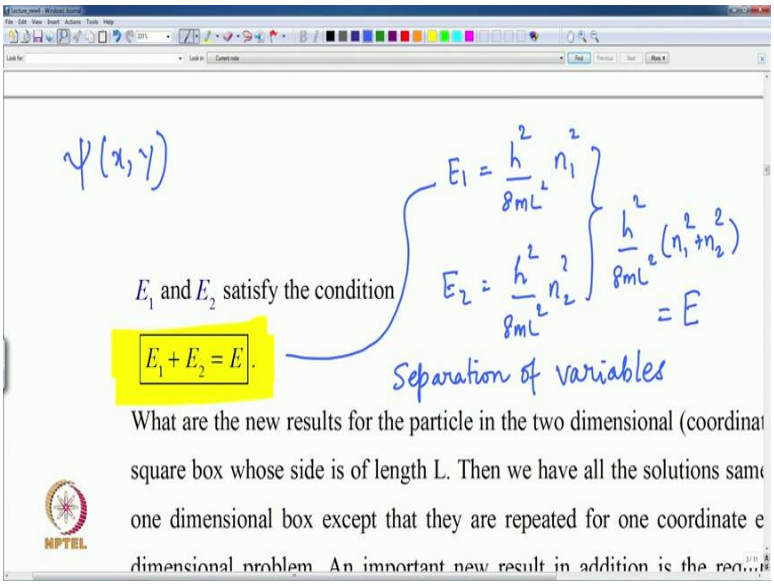

Now, remember the expression for E 1 from the particle the one dimensional box that is h square by 8mL square n 1 square; a free quantum number in the sense it takes 1, 2, 3 integer values and E 2 is also given by h square by 8mL square times n 2 square; such that this equation is satisfied. Therefore, you have h square by 8mL square times; n 1 square plus n 2 square is equal to the total E. So, this is the only constraint that comes out in the separation of the two dimensional Schrodinger equation that the total energy is the sum of the one dimensional energies and that is possible because we do not have a potential which couples the two dimensions we put V is equal to 0 and therefore the method of separation of variables.

We have separated the x and y; from the psi of x y if you recall the psi of x y; we have separated that into the x equation and the y equation, so that process is called the separation of variables.

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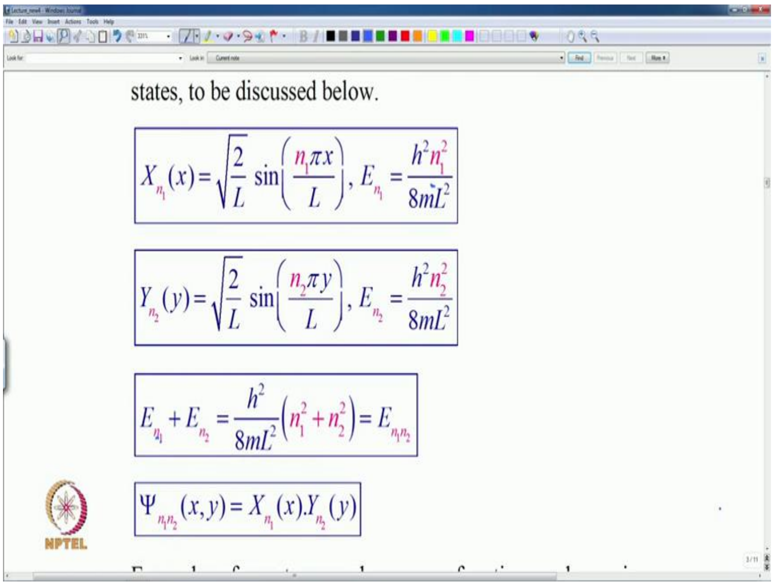

Now, how do these functions look like? Obviously, you have the solutions for the quantum number n 1. In terms of the one dimensional solution that you have seen in the previous lecture; root 2 by L sin n 1 pi x by L and the energy is given by n 1 square and likewise for the y with the n 2 square and with the constraint that the total energy E n 1 plus E n 2 is E n 1; n 2 we have seen that.

What about the wave function? The wave function now if you see this, the wave function psi of n 1, n 2 because it is obviously, specified by the two quantum numbers n 1 and n 2 has the independent function x with the quantum number n 1 and y with the quantum number n 2; each one is in an orthogonal direction.

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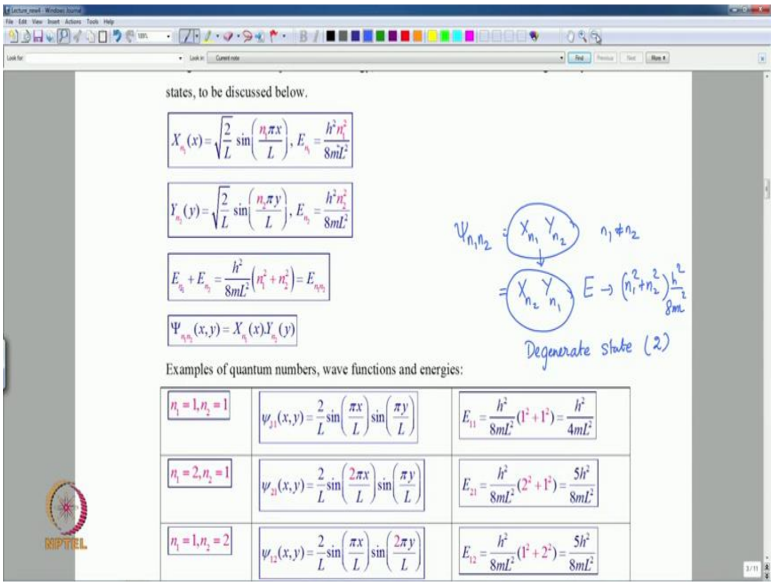

Therefore you see this interesting thing next line; when we have n 1 is 1 and n 2 is 1; when we have that case which is the starting point what is called the lowest energy for the particle in a two dimensional box. You can see that the wave function is given by psi 1 1; x comma y and is given by the product of the two functions that you saw the X of x and Y of y which gives you sin pi x by L and sin pi y by L.

Let me repeat this when the quantum number is 1 1; the wave function is given by psi 1 1 and it is given by the product of 2 by L sin pi x by L and sin pi y by L and the energy is of course, the sum of 1 square plus, 1 square times the whole thing, therefore the energy for this process E 11 is h square by 8mL square times 2. What is interesting is the next choice, you have psi n 1, n 2 as X of n 1, Y of n 2; it is possible if n 1 is not equal to n 2, it is possible to have the wave function given by X of n 2 and Y of n 1 because the energy is simply proportional to n 1 square plus n 2 square; times h square by of course, 8mL square which is the proportionality constant. Therefore, you see that you have the same energy, but you have two physically different states X of n 1, Y of n 2 and X of n 2, Y of n 1; both states have the same energy this is what is called degenerate state.

Degeneracy is 2; because there are two states which have the same energy, but have different quantum states.

This is the introduction for the particle in a two d 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 with which you can fill up any number of pages if you wish to see that n 1 is 2, n 2 equal to 1 corresponds to the wave functions psi 2, 1 with sin 2 pi x; sin pi y by L and n 1, 1; n 2, 2 gives you the other function namely sin pi x by L sin 2 pi y by 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 n 1 is not the same as the n 2. Then you can see that for 3 and 2, that you have here the wave function sin 3 pi x by L and sin 2 pi y by L and then 2 and 3 which is sin 2 pi x by L sin 3 pi y by L.

So the axis choice; the quantum number choice for a given axis determines the functions state.

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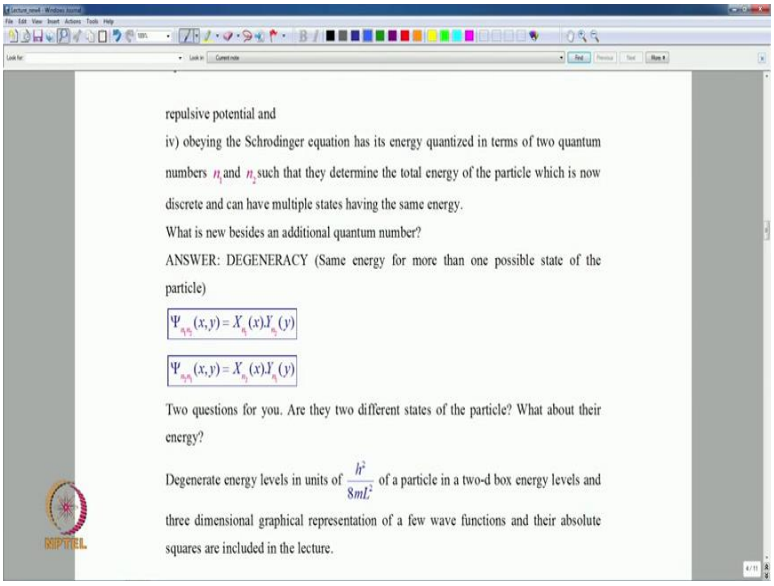

How do these things look like if we plot them? I mean this plot looks fancy, but actually it does not have much interpretation or meaning, but it is worth seeing the product wave function in two dimensions.

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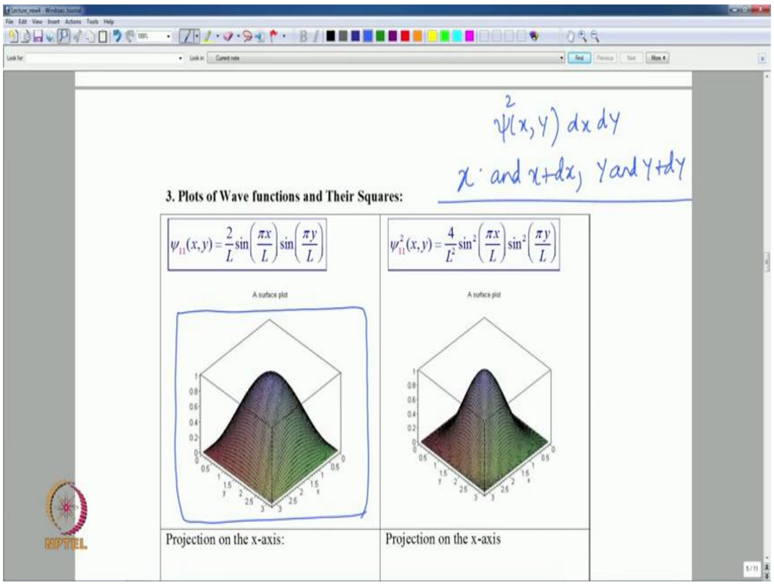

So, you see the wave function psi 1, 1 using this picture; it is a half wave similar to what you had in your particle in one dimensional box in the x direction and it is also a half wave in the y direction as you can see through the projection in the x direction here of this graph and on the y direction also you have the same thing; identical.

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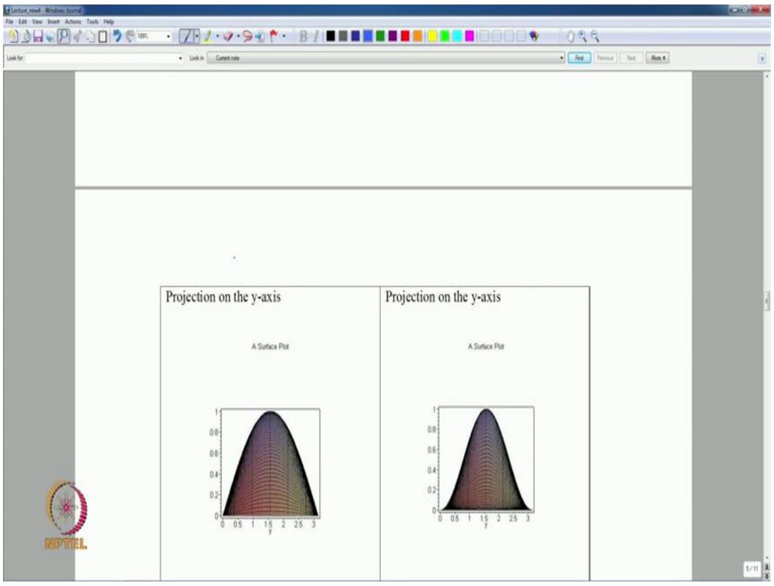

What about the psi square? The psi square which is associated with the probability that the particle be found; not in a small length region d x, but in a small area d x; d y; please remember psi x y, if you do that psi square d x; d y is the probability that the particle will be in the small rectangular region between x n; x plus d x and y and y plus d y, that is the small region and you can see that the psi square is given like this. Therefore, you can create I mean you can visualize what would be the probability exactly the same way that you have visualize the particle in one dimensional box except that now we have a motion on the plane.

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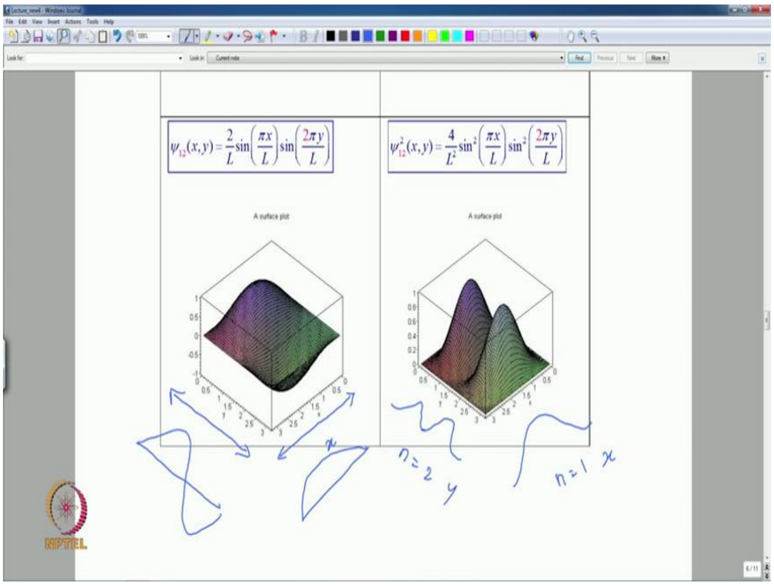

Now what is interesting is when you go to different quantum numbers where there is degeneracy psi 1, 2 if you look at this; psi 1, 2 is quantum number 1 for the x direction and quantum number 2 for the direction. Therefore, this is the quantum number for the x direction and you can see that it is the half wave which is either up or down; it is 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 a product of these two 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 is only for the wave function, we know the way function is not that important; it is a square of the wave function which is important for probability interpretation and you can see that psi square, which remove this negative character of the function gives you now very beautifully the 2 n equal to 1 case for the x axis and the n equal to 2, if you remember the graph that you had for n equal to 2 for the y axis and this is the x axis.

Therefore, the wave function features are captured when you doing a surface plot and you can see that the pictures can be created for a large number of them, but there is a limit two dimensions and in three dimension, we probably can use colour at the most to distinguish the function from the three axis but that is it, you cannot visualize this for n dimensions.

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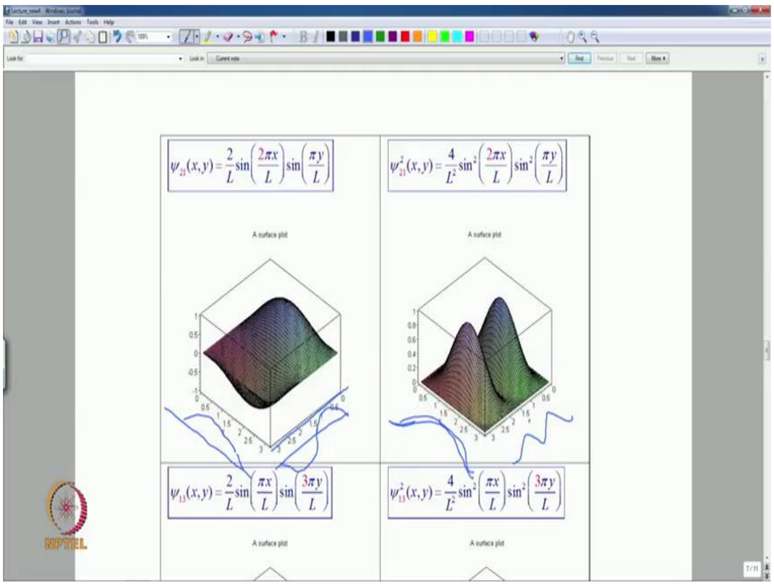

So, let us conclude this part of the particle in a two dimensional box with some examples of the wave functions and the squares of the way function for different quantum numbers. So, here is a 2, 1 as opposed to 1, 2 and you see all that happens is not for a 2, 1; the wave function along the x axis is like this and the wave function along the y axis is like that 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, have that and this is the y axis that is the reason why part 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 is a quantum number 1, so you have only 1 similar to the one dimensional y axis and let us see one or two more examples and let me stop with that.

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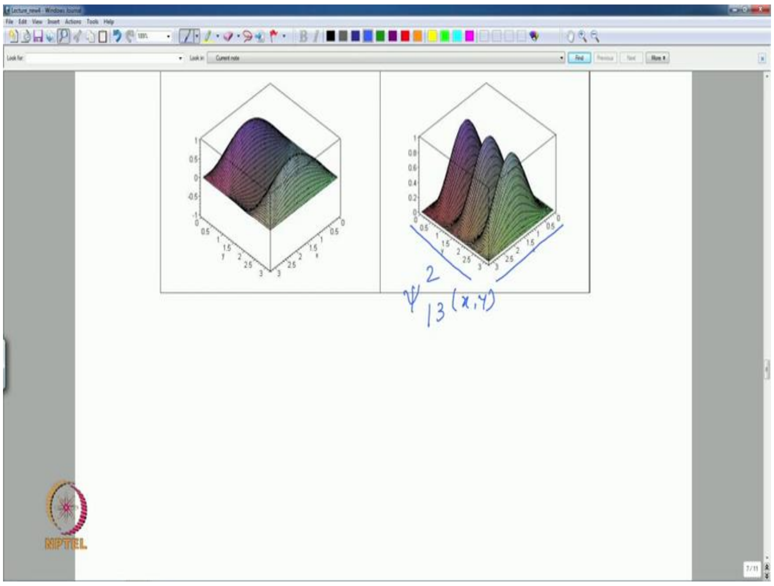

This is it; I mean the exercise here, what does this picture represent? There is one here along the x axis and there are three peaks therefore, you have this is a y is 3 and x is 1, so it is psi 1 3 square x y. So, the lecture notes give you many more such pictures, but in the next part of this lecture, 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 will stop here for this particular part of the lecture.

Thank you.