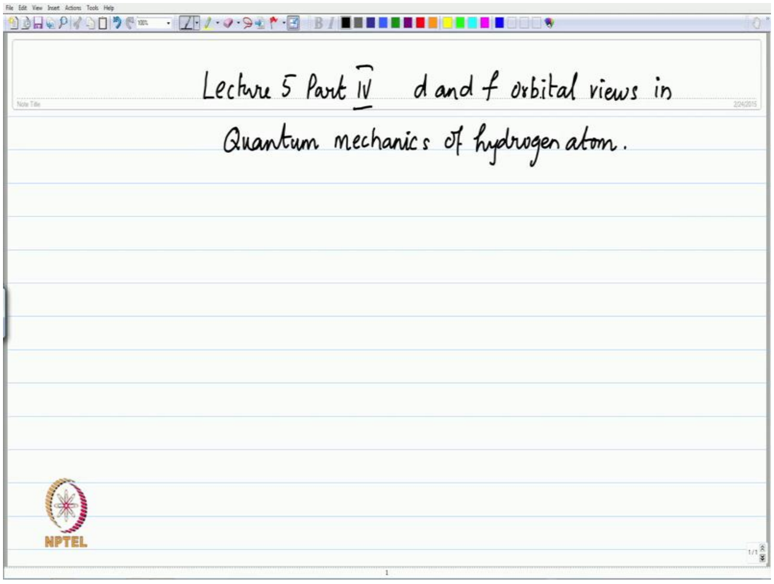
Introductory Quantum Mechanics and Spectroscopy
Prof. Mangala Sunder Krishnan
Department of Chemistry
Indian Institute of Technology, Madras

Lecture – 5
Part IV
The Quantum Mechanics of Hydrogen Atom

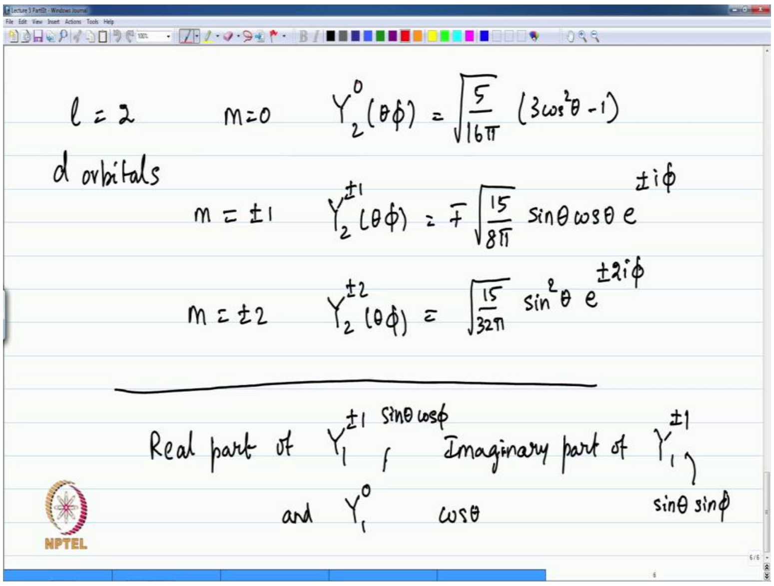
Welcome back to the lectures on the hydrogen atom. The lecture today is on the animated view and visualization of the d and the f orbitals. As I said in the last part of the last lecture, this is purely a visualization for some of the orbital or some of the angular parts of the orbital. d orbitals and f orbitals are quite interesting for the molecular systems particularly for the elements in the transition metal range and also the inner transition metals such as the lanthanides and actinides series. Therefore, a visualization of some of these f orbitals helps you to imagine – I mean in the case of say crystal field theory when you study the charge distribution of the legends and the energies of the orbitals. You can see why the conclusions are important. So, let me start by recalling what the d orbital angular part of the function is.

(Refer Slide Time: 01:34)



This is the part 4 of the fifth lecture on the d and the f orbital views in quantum mechanics.

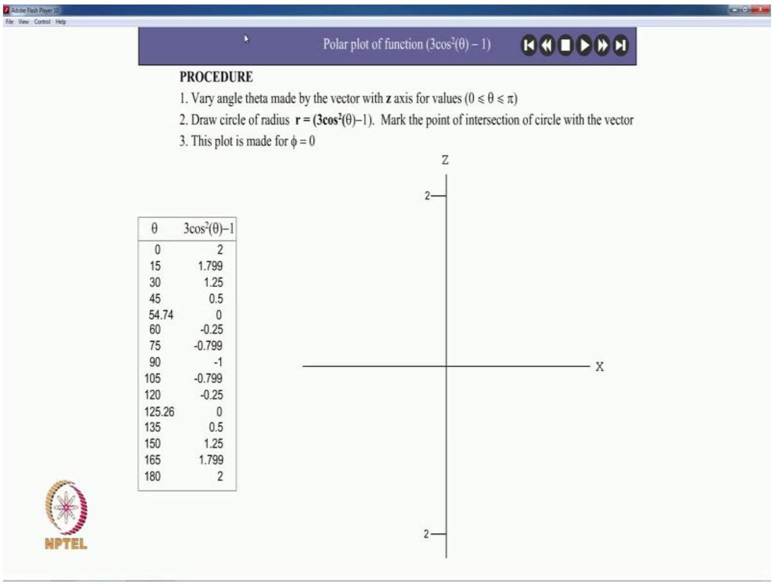
(Refer Slide Time: 01:43)



The d orbitals correspond to the quantum number l with a value 2. And there are five d orbitals with the quantum number m being 0 or plus minus 1 or plus minus 2; and the spherical harmonics second-rank tensor with the spherical component 0. I have not introduced this terminology until now; but keep this in mind; the spherical harmonics l and m are also referred to by the tensorial rank. We will have some of the mathematics lectures to determine what tensors are and understand them; but please take it from me that, these are second-rank tensors presentation in a spherical coordinate system with the component in the spherical coordinate system being 0 or plus minus 1 or plus minus 2. Now, that is the mathematics.

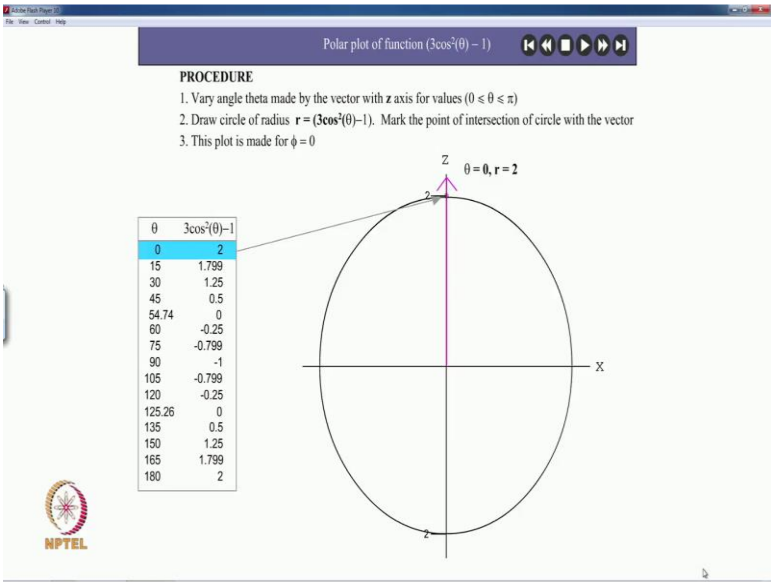
Now, the spherical harmonic Y 2 0 has the functional form 3 cos square theta minus 1; and m being 0, it does not have a phi dependent part; the exponential i m phi gives you 1 because m is 0. The Y 2 plus minus 1 theta phi is quadratic in the trigonometric functions sin theta, cos theta; and if you think of 3 cos square theta minus 1; 1 is nothing but sin square theta plus cos square theta. Therefore, this function is actually 2 cos square theta minus sin square theta. So, it is a homogeneous function – trigonometric function of order 2. And this is order 2 – sin theta, cos theta; but plus minus 1 means exponential i phi is plus minus i phi. And likewise, plus minus 2 for the Y 2 2 – tells you that, the angular part has trigonometric function, which sin square theta and a phi dependent function, which is an exponential plus minus 2 i phi. We shall plot one or two of these; and let us start with the picture part Y 2 0.

(Refer Slide Time: 03:56)

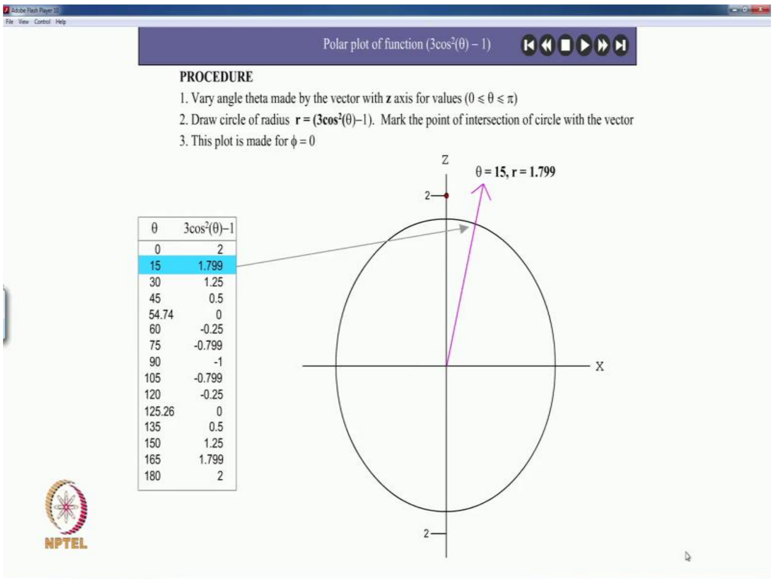


So, this is 3 cos square theta minus 1; I mean I am leaving out what is called the pre-factor – the normalization factor and all those things. They will only change the extension, but the shapes will remain the same. Therefore, we will keep 3 cos square theta minus 1 and we want plot this in the polar system with the theta axis going from 0 to 90 to pi to 180 degrees. The values of 3 cos square theta minus 1 for various values of theta are given here in this table; and you can see that, 3 cos square theta minus 1 goes to 0 at cos theta is equal to plus or minus 1 by root 3. Therefore, you see the plus 1 by root 3 corresponds to theta is equal to 54.74; and the minus 1 by root 3 corresponds to pi minus theta; and that is 180 minus 54.74, which is 125.26. In between 54 and 0.74 and 125.26, 3 cos square theta minus 1 is negative, because cos square theta is less than one-third. And at 90 degrees, this is 0. Therefore, this whole function is minus 1 maximally negative. So, from the magnitudes given here, the variation is between 2, 0, minus 1, 0, plus 2. Let us see the function plot.

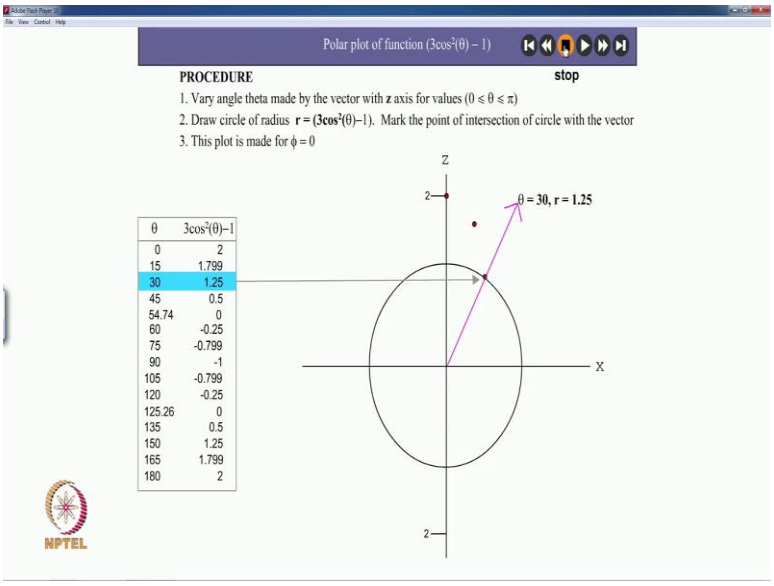
(Refer Slide Time: 05:37)



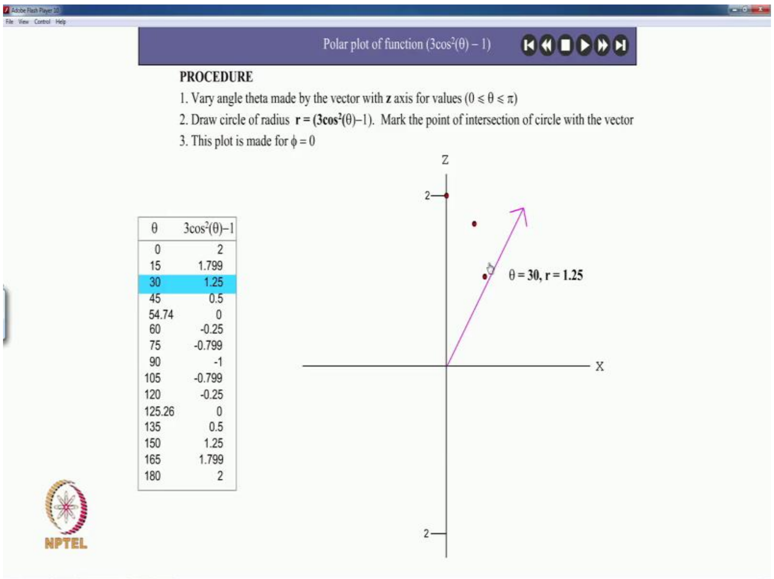
(Refer Slide Time: 05:41)



(Refer Slide Time: 05:46)

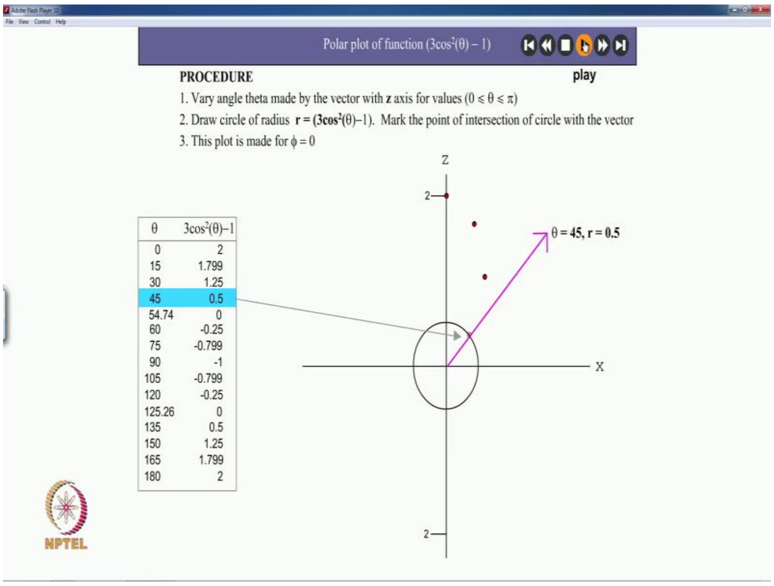


(Refer Slide Time: 05:48)

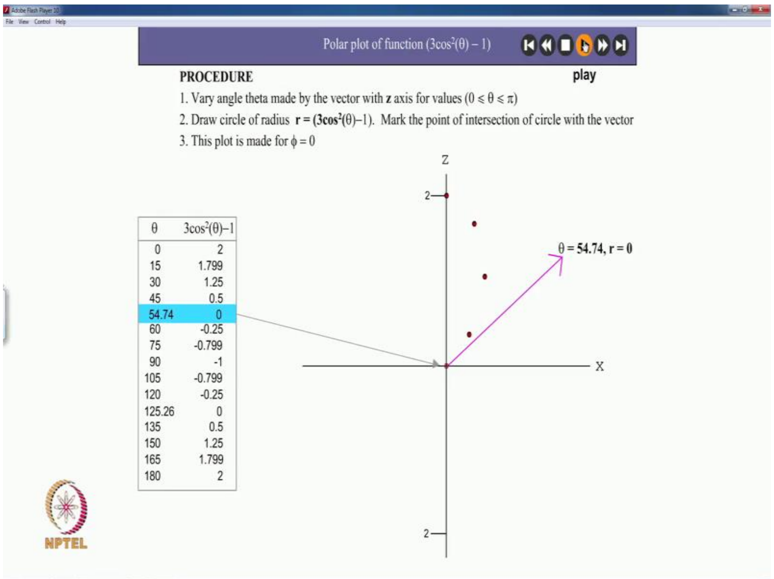


Remind yourself that, we are plotting the value of 3 cos square theta minus 1 on the radius that makes an angle theta with the z-axis. That is a plot; please recall that.

(Refer Slide Time: 06:06)

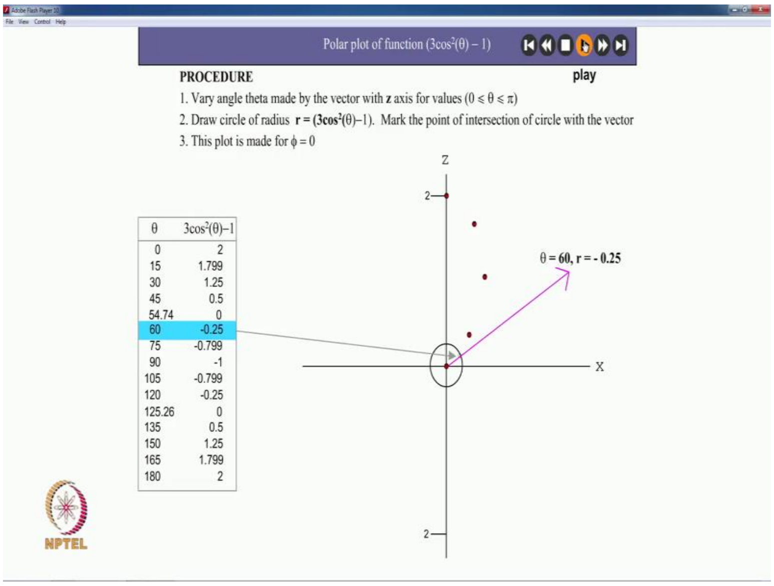


(Refer Slide Time: 06:10)



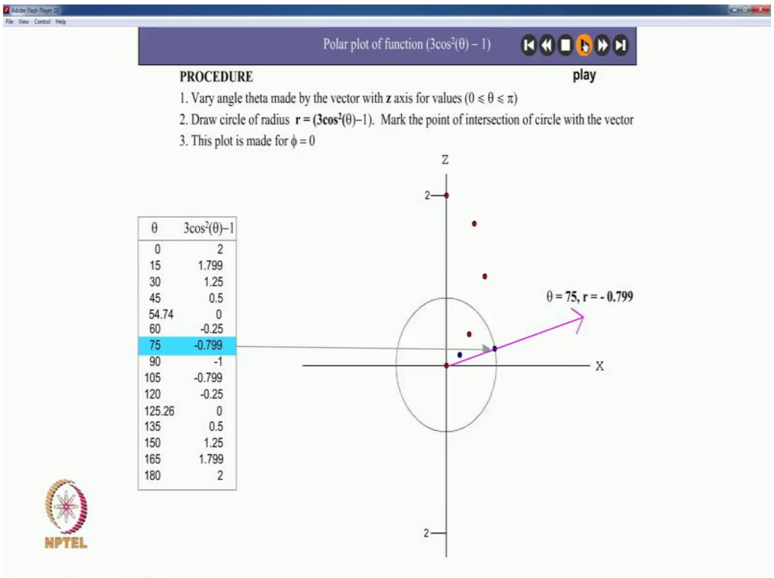
So, at 54.74, it goes to 0.

(Refer Slide Time: 06:13)



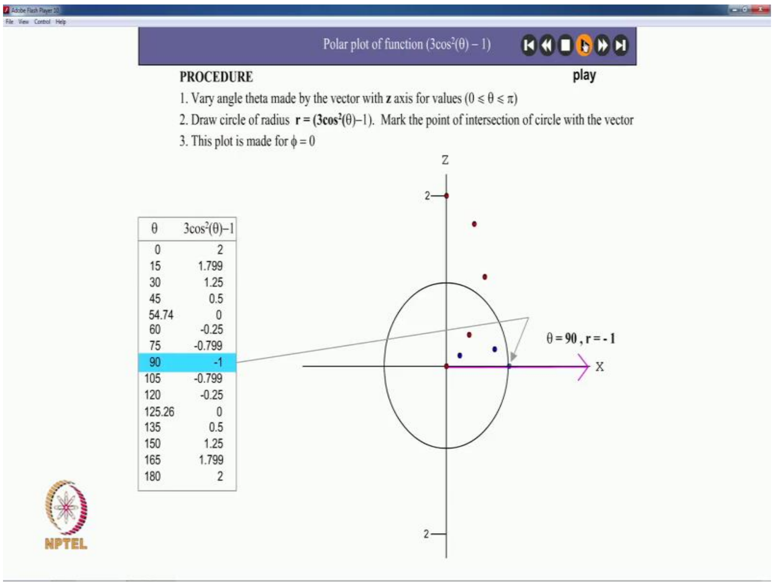
And then the function is negative.

(Refer Slide Time: 06:15)



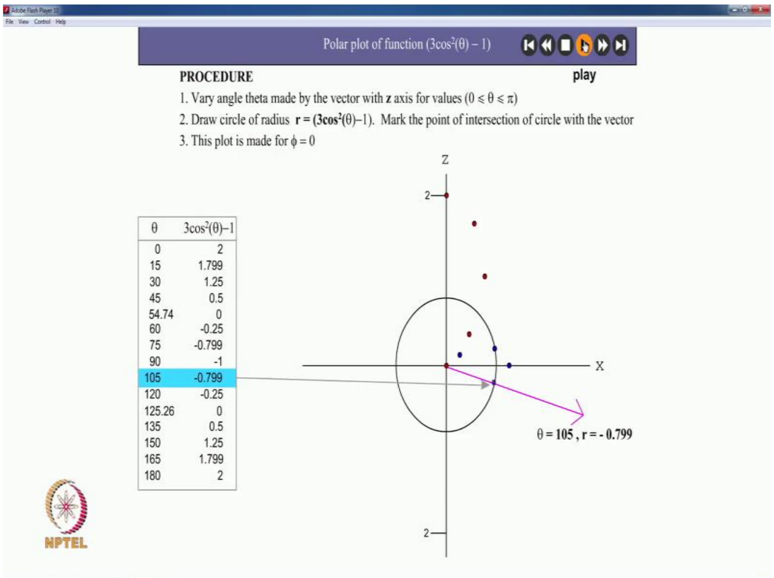
So, I have a different color for the points with the blue dots.

(Refer Slide Time: 06:19)

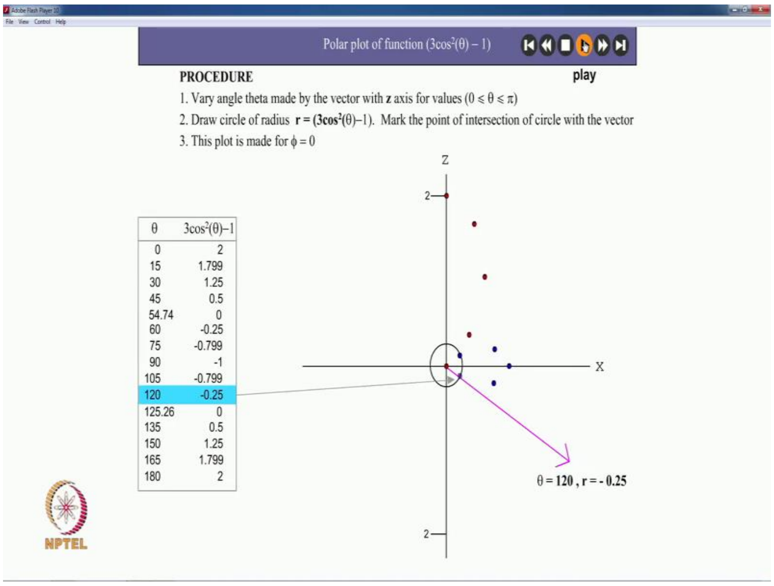


And that is minus 1; exactly half of the height.

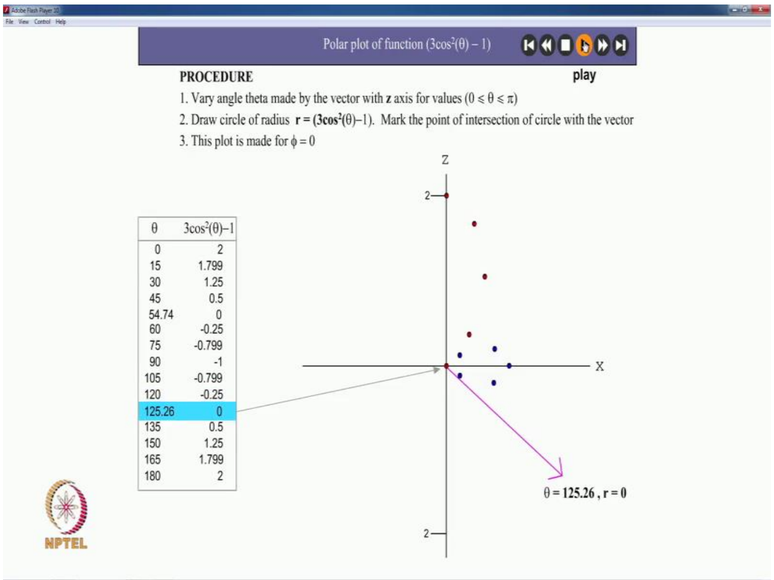
(Refer Slide Time: 06:22)



(Refer Slide Time: 06:26)

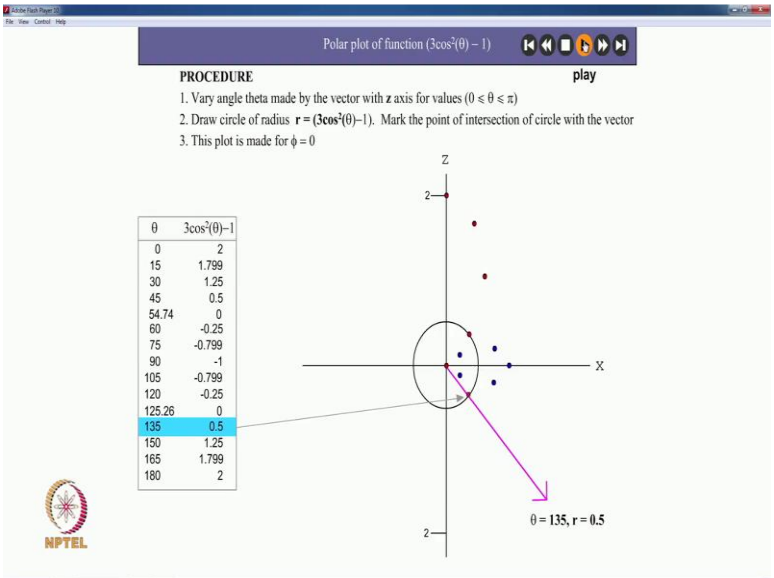


(Refer Slide Time: 06:29)



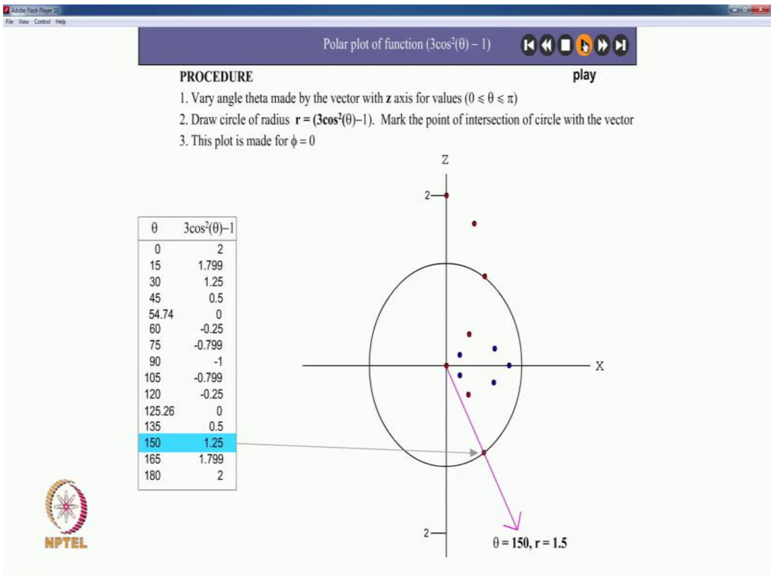
Again the function goes back to 0.

(Refer Slide Time: 06:31)

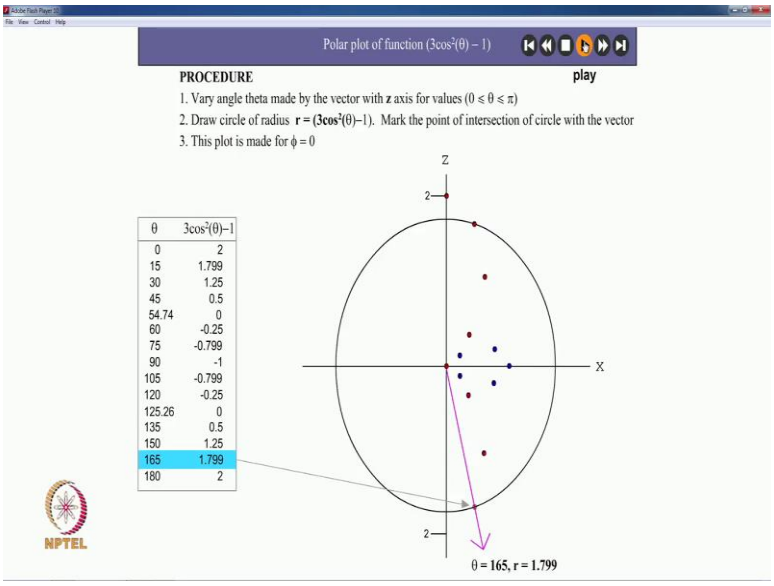


And starts increasing to larger values and reach 2.

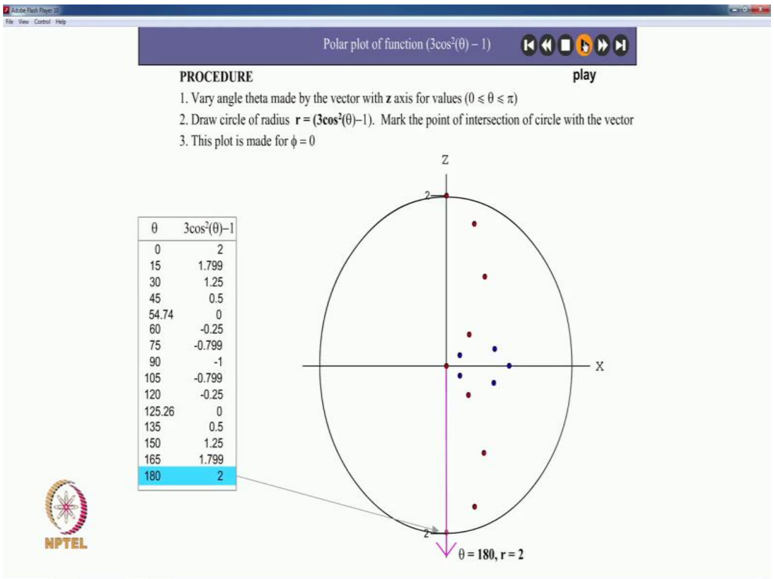
(Refer Slide Time: 06:34)



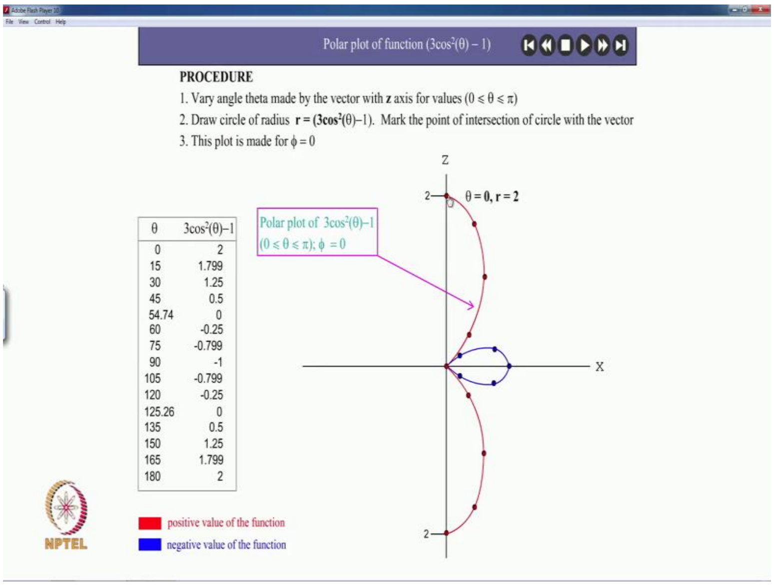
(Refer Slide Time: 06:37)



(Refer Slide Time: 06:41)

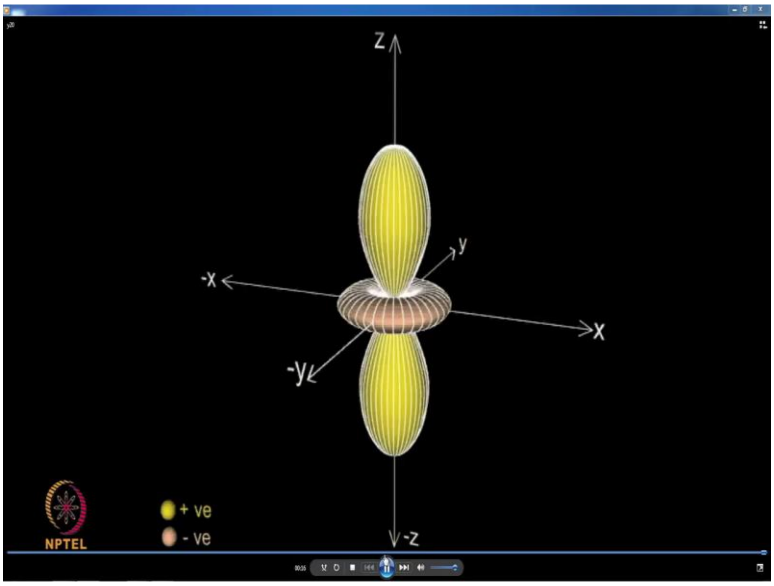


(Refer Slide Time: 06:44)



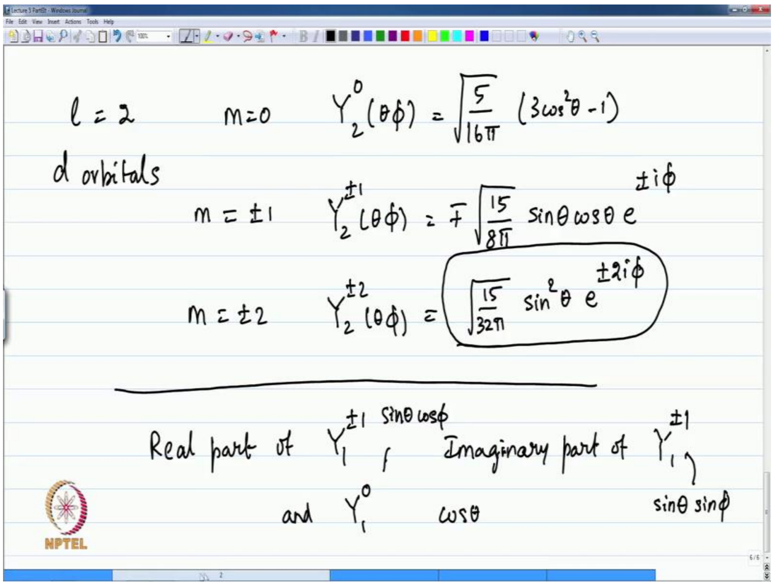
So, the graph is drawn by following the theta values namely, thetas equal to 0 up to 54.74; and then between 54.74 up to 125.26; and then for increased value of theta you have. So, this is a continuous plot. Now, this is phi independent.

(Refer Slide Time: 07:10)



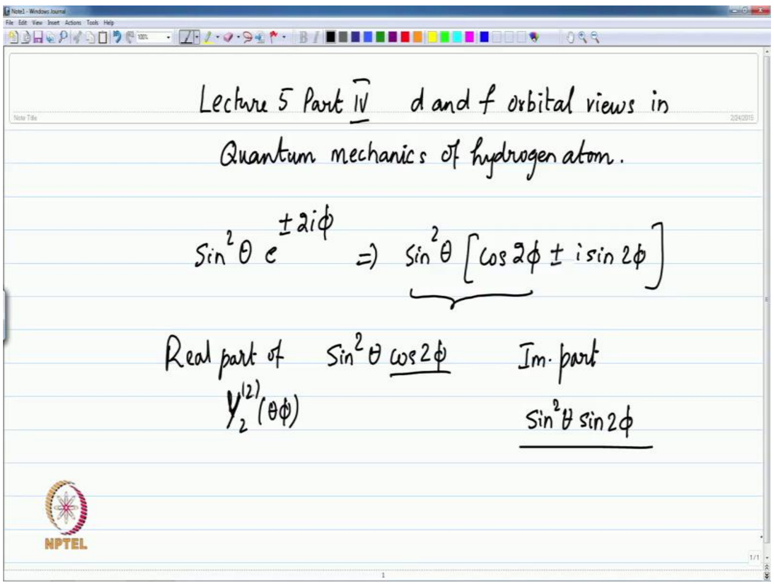
Therefore, it is a same plot for all values of phi, because the function is phi independent. Therefore, for 0 to 360 degrees, you get the familiar picture of the d orbitals with two balloons connected to each other by the torus – that the in between. And in some pictures you might see that the ring is standing out and the balloons are not touching the ring. But, that is wrong. This is the mathematical representation; the ring is tangential at 54.74 to the plus part; and also at the bottom 125.26, it is tangential. Therefore, you see that, this is the continuous surface. This is the d orbital, which you call as a dz square orbital sometimes as you might find in text books. But it is essentially 3 z square minus r square; and we have not considered the r; we had only worried about the fact that, three cos square theta minus 1. So, it is easy to visualize.

(Refer Slide Time: 08:26)



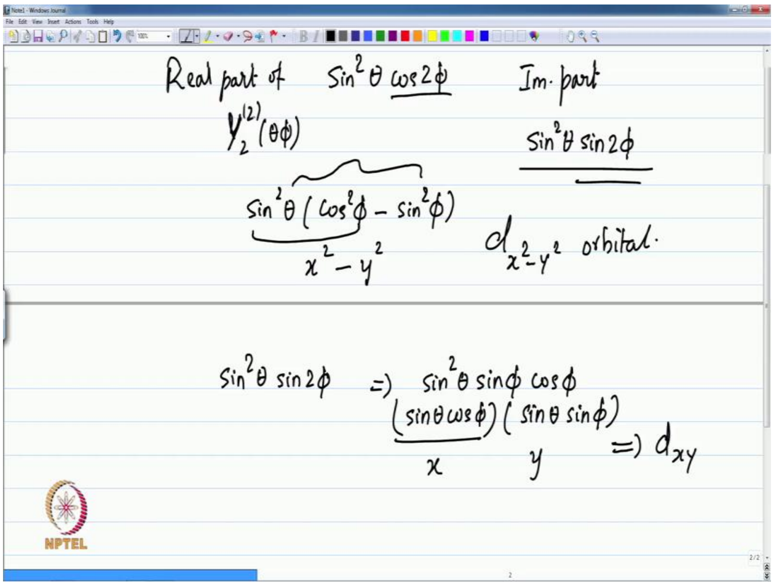
Let us take m is equal to plus minus 2 and find out what this picture is; plus minus 1 in a similar way, you can find out yourself. Plus minus 2 contains an imaginary, that is, a complex part. So, let me get the function into real and imaginary parts and let me leave the square root of 15 by 32 pi for the moment; we do not need to worry about that.

(Refer Slide Time: 09:08)



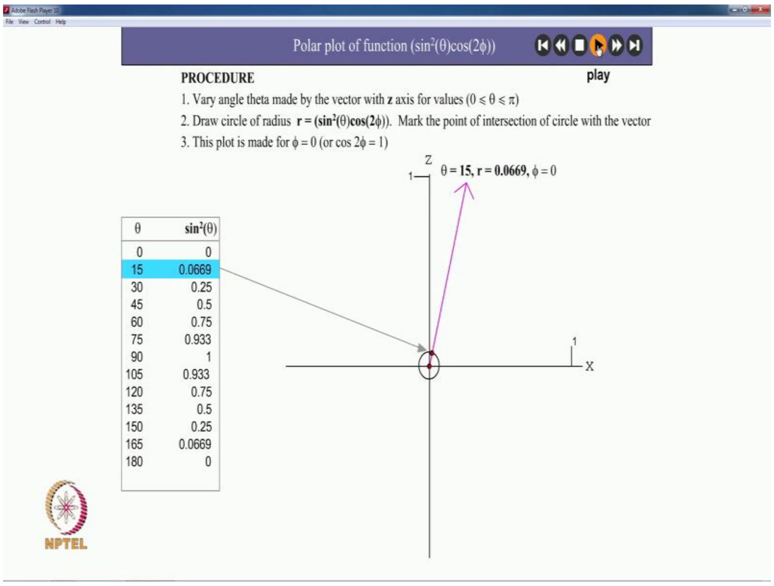
So, we have sin square theta e to the plus or minus 2 i phi, which is sin square theta cos 2 phi plus or minus i sin 2 phi. And the real part is sin square theta cos 2 phi. This is the real part of Y 2 2 theta phi. The imaginary part is leading the i out; obviously, the imaginary part is sin square theta sin 2 phi. Recall that cos 2 phi…

(Refer Slide Time: 10:13)



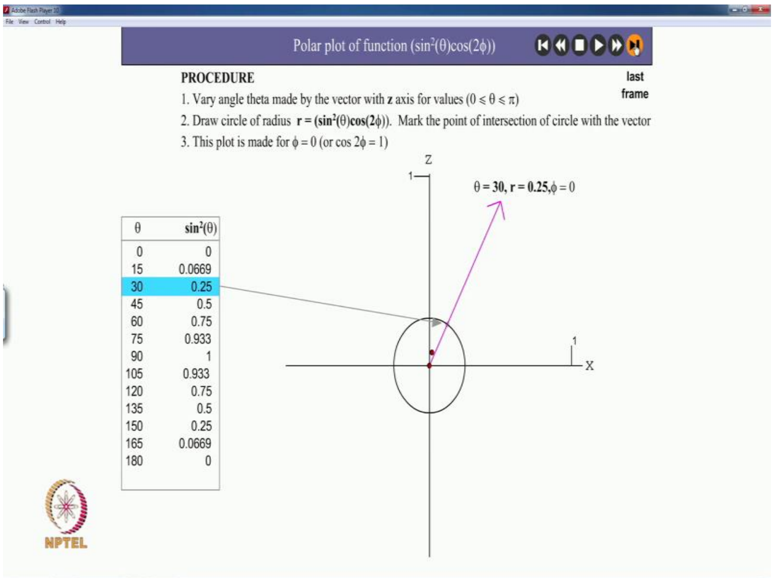
So, this function is sin square theta cos square phi minus sin square phi. And remember – sin theta cos phi is like x. Therefore, this is x square. And sin theta sin phi is like y; and therefore, this is minus y square. So, this part is often referred to in your text books as d x square minus y square orbital. And in the same way, if you look at sin square theta sin 2 phi; this is barring the numbers out – I mean the… that is a 2 here. But, what is important is it is sin square theta sin phi cos phi, which is sin theta cos phi and sin theta sin phi multiplied to each other. So, remember – this is x and this is y. So, this is often the d xy orbital that you see. And you see the difference between the two functions is essentially the difference between the cos 2 phi and sin 2 phi. Cos 2 phi and sin 2 phi differ by pi by 2 or pi by 4; if you change phi by pi by 4, cos 2 phi becomes a sin 2 pi. Therefore, you see that, whatever the shape that you will have for d x square minus y square, will be only rotated by 45 degrees to get the shape of the sin square theta sin 2 phi; that is a d xy; we will see that.

(Refer Slide Time: 12:03)



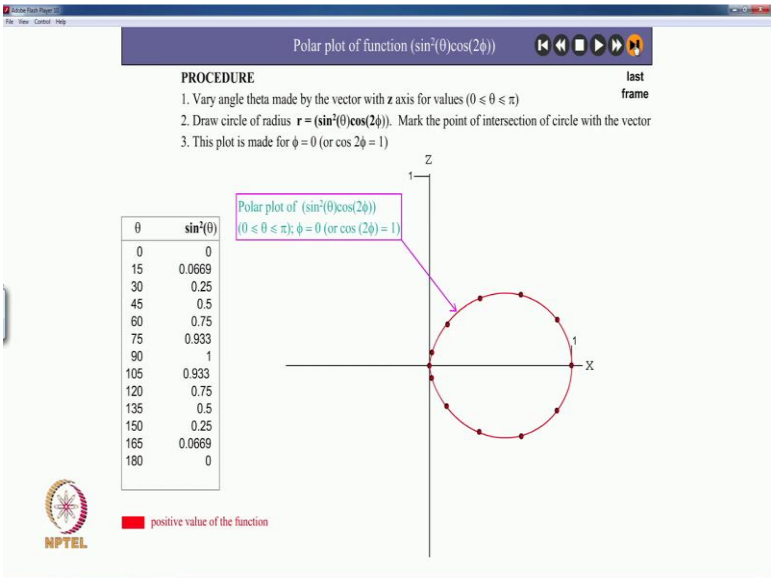
So, let us start with the real part for the d orbital – the sin square theta cos 2 phi. And since phi is equal to 0 gives you cos 2 phi is equal to 1; and therefore, you get the maximum value for sin square theta. Let us plot it along the x-axis and then plot it for various values of phi in going around, so that for each value of phi, the cos 2 phi multiplying sin square theta will change the shape to get you the full three-dimensional picture. This is sin square theta with cos 2 phi equal to 1.

(Refer Slide Time: 12:43)



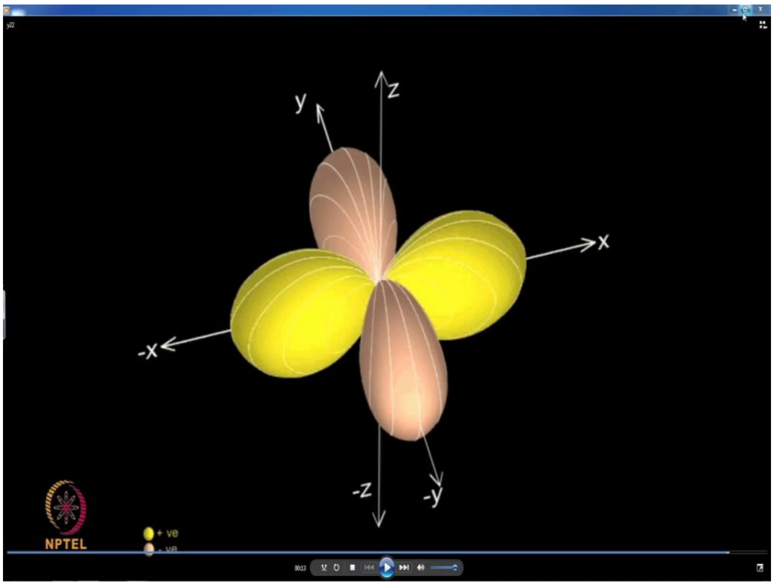
I do not have to go through this.

(Refer Slide Time: 12:46)



Let me go to the last frame; that is what you will get if you want to play around to see and stop and see that it plots the right thing. This is sin square theta.

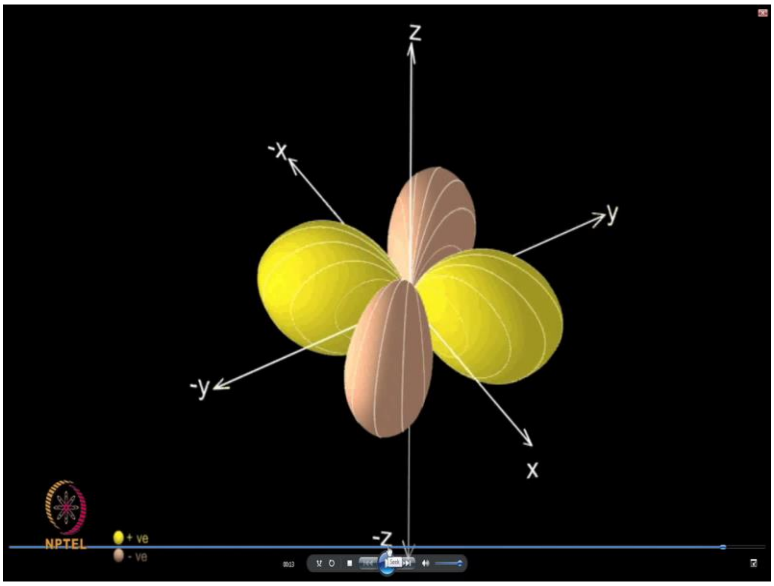
(Refer Slide Time: 13:01)



And then what you have is this is modulated by cos 2 phi; and is modulated by cos 2 phi with cos 2 phi being 1 at x; where, phi is 0; cos 2 phi being minus 1 at y, where phi is 90. So, in between, cos 2 phi goes to 0 namely, at phi is equal 45. Therefore, this graph goes to 0 at 45. And then it increases, but becomes negative, because cos 2 phi is negative in that quarter – in that part of the range – in that range of phi. And then when it comes to minus x-axis, this is 135 somewhere around. Again cos 2 phi goes to 0 at 135. But, when phi is greater than 135 and 180 and 225, cos 2 phi goes through positive values; see it for yourself. So, that is essentially how we picture. So, you see the picture of the d x square minus y square, which is a pair of ((Refer Time: 14:16)) along the x-axis as well as along the y-axis, but with the opposite signs because of the cos 2 phi modulation – 2 phi modulation. And this is an even function; you can see that, the plus x and minus x, plus y and minus y – they both have the same sign.

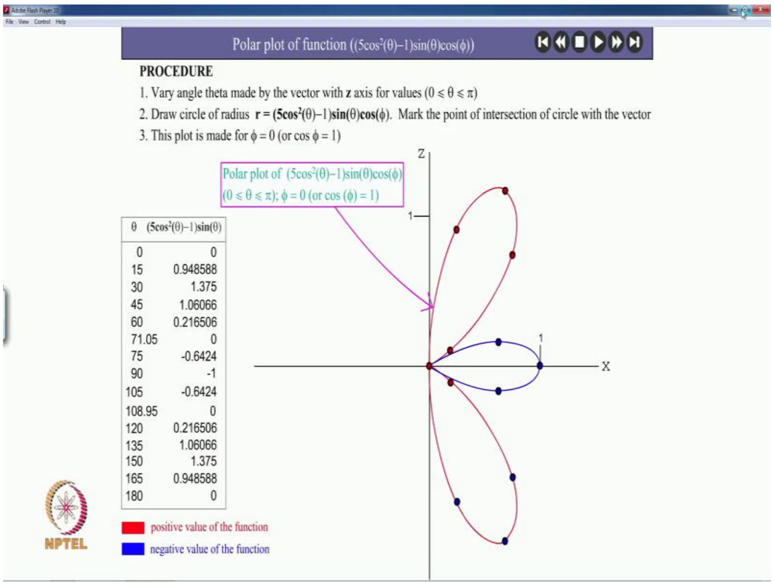
Now, what about the other function? The other function is sin theta cos phi sin phi – cos phi sin phi. Therefore, it is sin square theta. So, the plot of sin square theta is the same as what we had before. But, since it is cos phi sin phi, we do not want to plot it along the x-axis, because it is obviously 0 at phi is equal to 0. You can see that, it is a maximum at phi is equal to 45, not 90, because at phi is equal to 45, cos phi is 1 by root 2; sin phi is 1 by root 2 – they both have the same value. Therefore, you see this function actually is between the two axes; it is not split by the axis. At both the axes, the function is actually 0, because phi is 0, phi is 90, phi is 180, and then phi is 270. So, on all the axes, the function goes to 0; but between the axes, the function goes through a maximum from 0 to 45; and then it goes to 0 from 45 to 90 and so on.

(Refer Slide Time: 15:46)



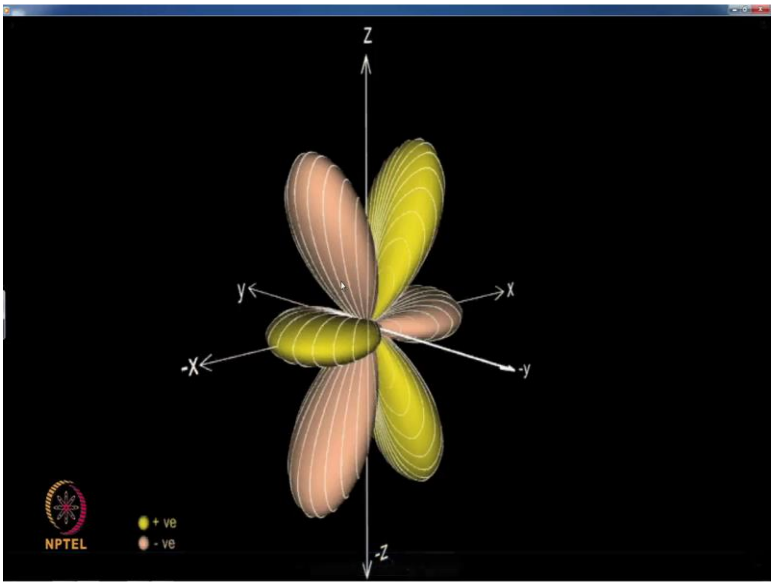
So, the picture – you can see that, the picture starts with the middle of the axis; at x, it is 0; and at y also, it is 0. So, the bulk of the picture – bulk of the shape is in between the axes; and it is only a 45 degree tilt, because the difference between the d xy and d x square minus y square is a 45 degree angle. So, the shapes are determined by the way we represent the mathematical functions. And then the way we plot them in a spherical axis system or in a spherical polar coordinate system. So, these are for the d orbitals. I will show one f orbital as I mentioned in the last lecture. And then we will leave the rest to be seen by you.

(Refer Slide Time: 16:40)



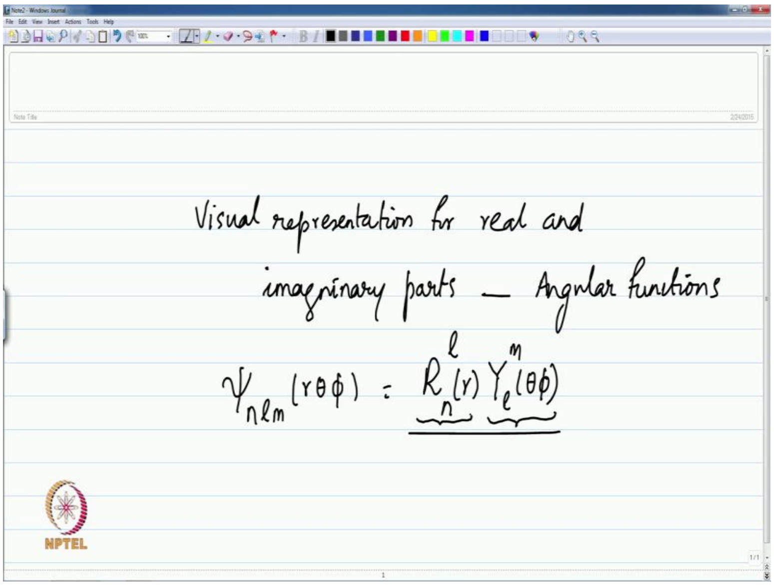
The function Y 3 1 is 5 cos square theta minus 1 times sin theta times cos phi. This is a trigonometric function – homogeneous function of order 3, because 1 is nothing but sin square theta and cos square theta. So, it is 4 cos square theta minus sin square theta times sin theta. So, everything is cubic times cos phi. And therefore, for phi, cos phi; and therefore, for phi, we have chosen the value 0 that, this is maximum. And so what you see is the plot of 5 cos square theta minus 1 times sin theta on the polar coordinates. You can see that, it goes to 0 at three places; phi cos square theta minus 1. This is minus 1 when cos theta is 0. And this is again phi cos square theta minus 1 at 0. And at 180 degree, it is 0, because there is a function sin theta. Therefore, the plot looks like the shape. You start from 0; as the theta value goes this way, the function increases to this point; and then as the theta becomes more and more, the function comes to 0; then the functions goes through this value and it comes back to this. And this is multiplied by cos phi. And therefore, the actual representation; and again, you can see that, there is a plus part, there is a minus part, and there is a plus part multiplied by cos phi.

(Refer Slide Time: 18:42)



So, if we look at to the cos phi part together, the modulation that you see is followed by that – followed by that. But now, in the whole phi-axis system, therefore, you see the plus minus, plus minus, plus minus; and this is an odd function. The f orbitals are odd functions in the three-dimensional coordinate systems. And you can see that, whatever is here, it is opposite on the side is negative; whatever is here, its opposite part is negative here and so on. So, this is the shape of one of the f orbitals; it has the value phi; it has the equation phi cos square theta minus 1 times the sin theta cos phi. The cos phi comes from the real part of exponential i phi. Therefore, what you see is this is Y 3 plus or… This is plus 1; and if it is multiplied by sin phi, that is, Y 3 minus 1.

(Refer Slide Time: 20:08)



So, what we have is a visual representation for real and imaginary parts. But, this is only angular function. We have not seen the angular function multiplied by the radial function, because you remember – psi n l m r theta phi is the radial function R n l of r multiplied by Y l m theta phi. So, what you have seen is only the visual presentation for these, but the radial functions bring in their own nodes along the radii r – the sphere. And therefore, the radial function multiplied by the angular function, the three-dimensional visual representation is quite complex. In the next part, we will see the radial function and the square of the radial function; we will discuss the probabilities – the radial probability distribution; we will discuss the angular probability distribution and do a small bit of calculations involving the spherical coordinate system for the hydrogen atom. And with that the mathematical as well as the physical picture of the hydrogen atom that, I wanted to give for this course is complete. So, we will do that in the next part.

Thank you very much.