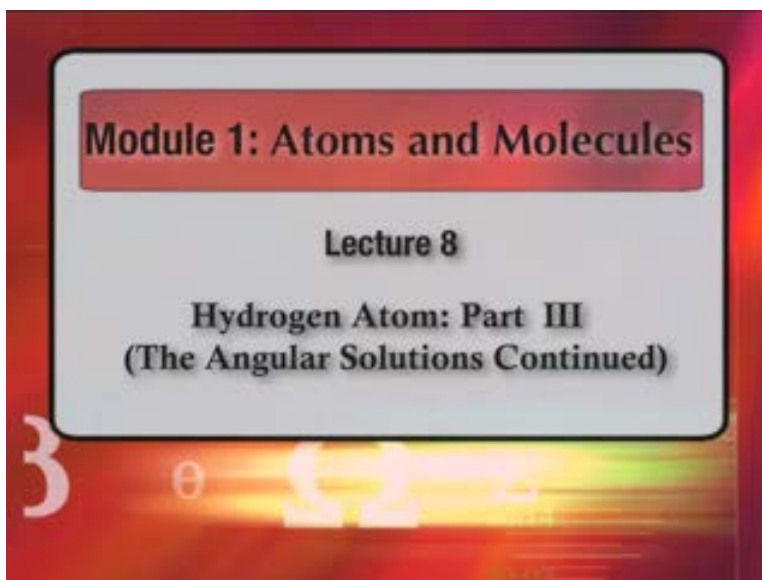**Engineering Chemistry - 1**
Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras
Module 1: Atoms and Molecules
Lecture 8
Hydrogen Atom: Part - III
**The Angular Solutions continued**

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Welcome to the lecture series in Chemistry under the auspicious of National Program on Technology Enhanced Learning. This is a series of lectures in Chemistry which we perceive as basic importance to all Engineering and Chemistry students who begin their academic career. This is a series of lecture on atomic and molecular aspects of Chemistry. It is a Quantum Chemistry of Atoms and Molecules. We have had several lectures already on the solution of the Schrödinger equation and also the last lecture and the previous one concentrated on the solutions of the Schrödinger equation for the hydrogen atom.

Today we continue with the solutions of hydrogen atom and we continue the pictorial demonstrations through the animations two dimensional and three dimensional of certain aspects of the solutions of the Schrödinger equation.

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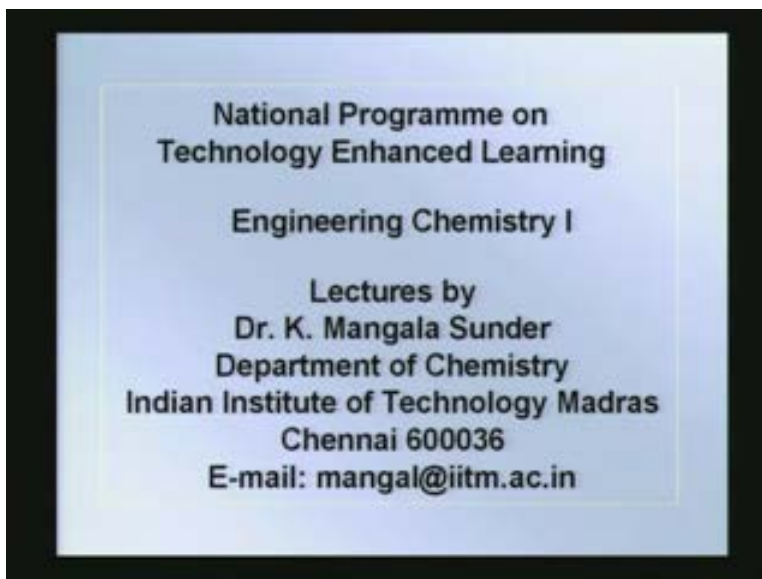
Let me start with the basic slides, I am Mangala Sunder from the Department of Chemistry and my email id is given as mangal@iitm.ac.in

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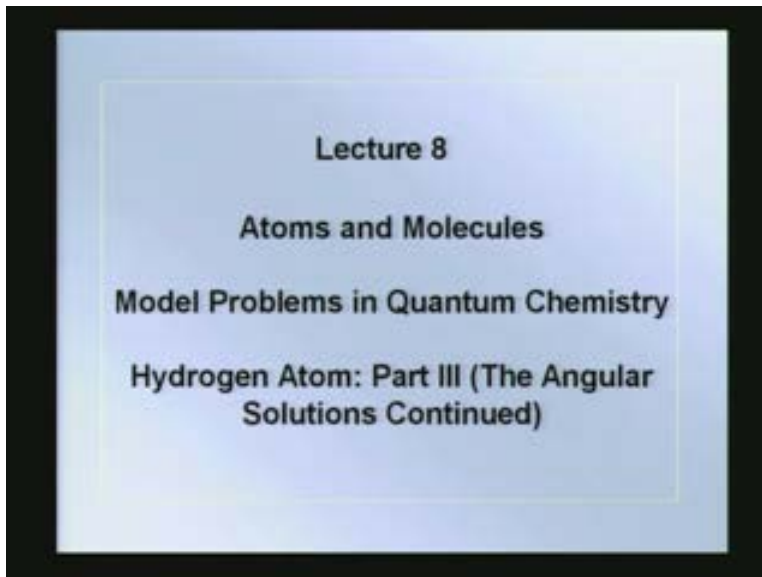
This is the 8th lecture on the model problem in Quantum Chemistry and we continue to visualize the angular solutions to the hydrogen atom problem as proposed by the Schrödinger equation and the solution.
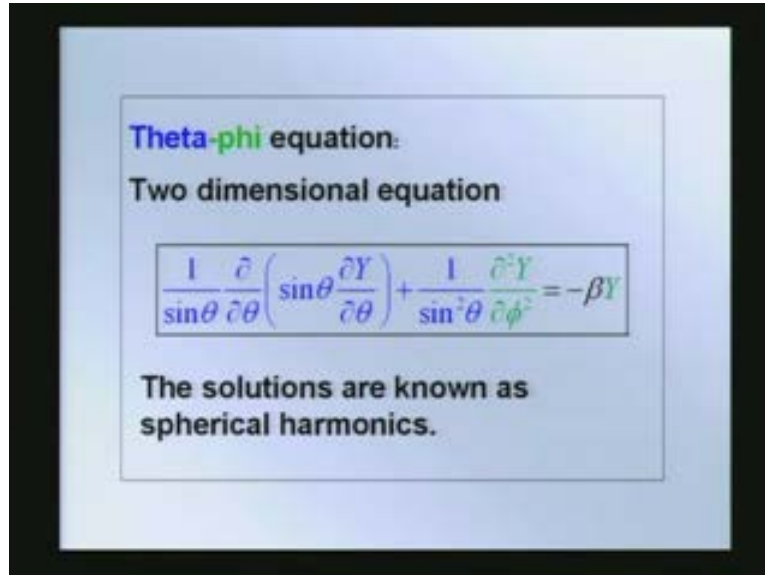
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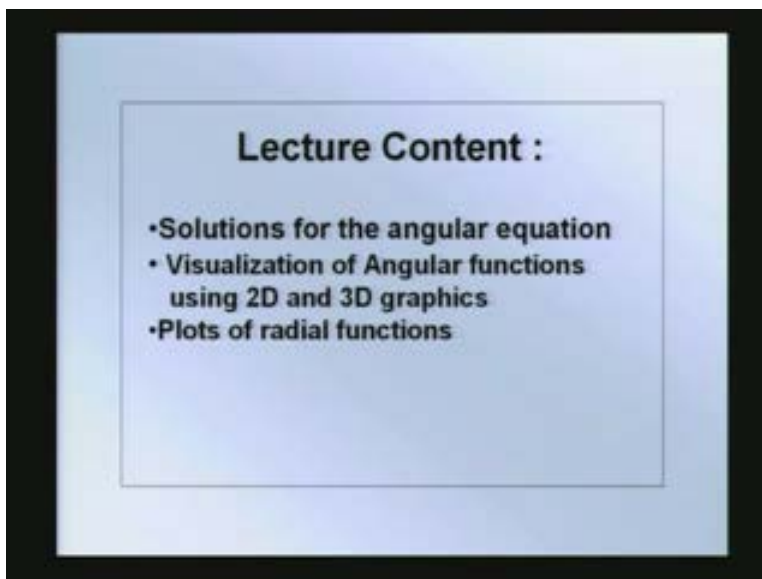
The contents for today's lecture are the essential solutions for the angular equation through visualization of the angular functions using both 2D and 3D graphics and if time permits we will also see the plots of radial functions.

What is extremely important in this set of lectures as given for the students is the enabling you to visualize these solutions rather than derive these solutions mathematically. The differential equations are hard and you need a certain amount of special functions, Mathematics to derive the solutions through the standard procedure. That is not of important to us from the Chemistry stand point but we want to see how quickly that the atomic orbitals can be visualized and how quickly we can keep a mental picture that we already started with in the high school days with the picture of the hydrogen atoms, orbitals in the textbooks.
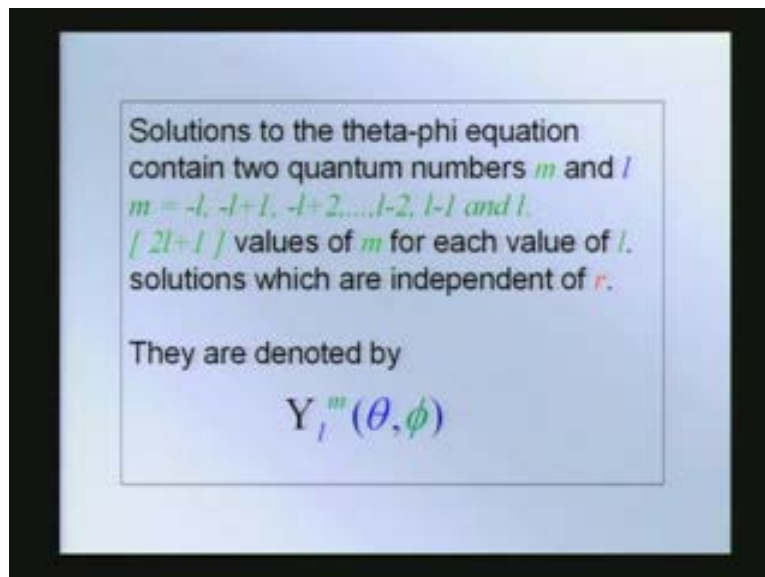
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Theta-phi equation.

Two dimensional equation

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}=-\beta Y$$

The solutions are known as spherical harmonics.

So let us see today in the lectures here. Let me recall the angular equation here. you remember from the previous lecture the angular variables for the hydrogen atoms satisfy the differential equation given by the equation here is $^{1}/(\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial Y/\partial\theta) + ^{1}/(r^2\sin^2\theta)\ \partial^2 Y/\partial\phi^2 = -\beta Y$, here these are the partial derivatives of the function Y which we are trying to obtain and β is a constant which is appied on the same function Y.

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Solutions to the theta-phi equation contain two quantum numbers m and l

$m = -l, -l+1, -l+2,....l-2, l-1$ and l.

$[\,2l+1\,]$ values of m for each value of l.

solutions which are independent of r.

They are denoted by

$$Y_l^m(\theta,\phi)$$

Y's were introduced to you earlier as spherical harmonics as a function of both θ and ϕ. And we started looking at the some of the functional forms of the spherical harmonics in the last lecture. And you also kindly recall that the solutions to the (θ, ϕ) equations contain two quantum

numbers m and l where the values of l are determined by the radial equation whose principle quantum number is n and the value of l is from 0 to $n - 1$. For any given value of l the values of m are known to be between $-l, (-l+1), (-l+2)$ and all the way up to l in integer steps. That is, there are two $l + 1$ values of m for each value of l and these are of course solutions for the angular parts only they are independent of the radial coordinate r. The Mathematical notation is that they are denoted by the spherical harmonics of spherical tensor of rank l and the spherical component m.

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Table of spherical harmonics of l and m.

$l = 2$	$m = 2$	$Y_2^2 = \sqrt{\dfrac{15}{32\pi}} \sin^2\theta\, e^{2i\varphi}$
$l = 2$	$m = 1$	$Y_2^1 = -\sqrt{\dfrac{15}{8\pi}} \sin\theta \cos\theta\, e^{i\varphi}$
$l = 2$	$m = 0$	$Y_2^0 = \sqrt{\dfrac{5}{16\pi}} \left(3\cos^2\theta - 1\right)$

In the previous lecture we looked at the $l = 1$ case and we looked at the 2D, 3D that is two dimensional and the three dimensional representations of these wave functions on a polar plot. We will continue that here for the $l = 2$ case. Obviously there are five such spherical harmonics and representing them in a polar coordinate is an exercise that is worth doing for anyone who solves the Schrödinger equation for the first time. Here we are not solving the equation here we are giving the solutions of the equation because the Mathematics is hard enough that we can postpone that to a later lecture. But what is important is of course to visualize these solutions.

So what you see here are the three of the five spherical harmonic corresponding to $l = 2$. The m = 2 is given by the spherical harmonic Y_2^2 with some constant here. It is $\sin^2\theta\, e^{2i\varphi}$ that is important for m = 2 then the exponential are $e^{2i\varphi}$ where m corresponds to the variable φ and l corresponds to the variable θ. You see the colors more or less to indicate that kind of an association $\sin^2\theta\, e^{2i\varphi}$. Therefore $l = 2$, m = 1 the spherical harmonic is denoted by Y_2^1, again constants that do not appear all that random. Y_2^1 is $[-\sqrt{15/8\pi} \sin\theta \cos\theta\, e^{i\varphi}]$ here again for m = 1 the exponential is $e^{i\varphi}$. For $l = 2$, m = 0 you do not have any exponential φ part here but that is the equivalent of $e^{i0\varphi}$ where the value of m is 0 but the angular part is $(3\cos^2\theta - 1)$.

Table of spherical harmonics of *l* and *m*.

For l = 2 and m = –1 the spherical harmonics Y_2^{-1} is [$\sqrt{15/8\pi}\ \sin\theta\ \cos\theta\ e^{-i\phi}$] look at Y_2^1 is $\sqrt{15/8\pi}$ but with a – sign. And m = 1 has $\sin\theta\ \cos\theta\ e^{i\phi}$, but m = – 1 has $\sin\theta\ \cos\theta\ e^{-i\phi}$ which is again the corresponding m value. For l = 2, m = – 2 has $\sin^2\theta\ e^{-2i\phi}$.

So these are the five spherical harmonics we want to visualize in a polar plot. The Cartesian plots are something that you are very familiar with x, y, z. I have been telling that in the previous lecture what is the difference between a typical Cartesian plot and the polar plot and we try to plot the x, y and z orbitals for the p that is l = 1 case. The l = 2 case is known as the d orbitals and in the atomic spectroscopy parlance d is diffuse.

You recall sharp is for s, principle is for p, diffuse for d and fundamental is for f these are the four spectral series that were discussed by the atomic spectroscopies even before Quantum Mechanics came into existence the theory was put forth even before that. Now the l = 2 corresponds to the d orbitals and you know that l = 2 the principle quantum number has to be n = 3 or more because the maximum value of l is n–1. Therefore l cannot be 2 unless n is 3 or more. So let us take the lowest n value for which l = 2 is an allowed quantity, so 3d orbitals.

Let us look at the angular parts of the 3d orbitals. Then to complete this the next set is of course the f orbitals corresponding to the l value 3 and for l = 3 case there are seven spherical harmonics from + 3, +2, +1, 0, – 1, – 2, – 3 as you see in this table as well as in the last one.

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Table of spherical harmonics of l and m.

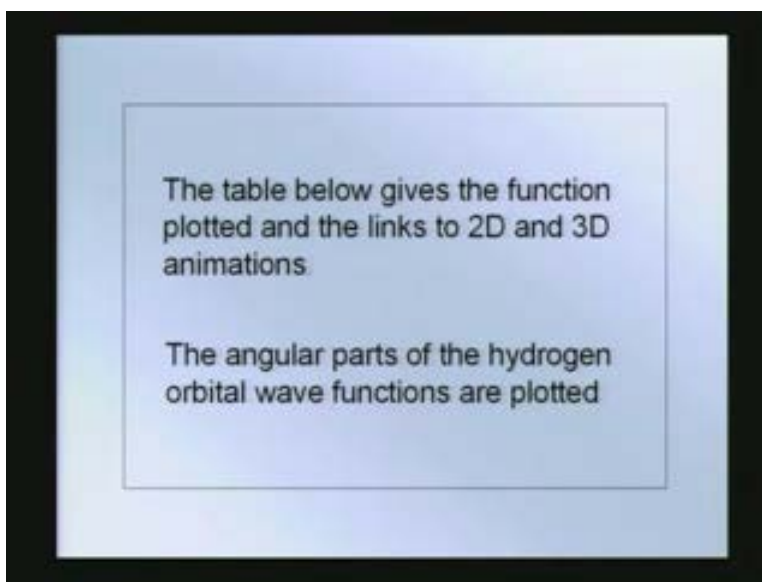| $l=3$	$m=0$	$Y_3^0 = \sqrt{\dfrac{7}{16\pi}}\left(5\cos^3\theta - 3\cos\theta\right)$
$l=3$	$m=-1$	$Y_3^{-1} = \sqrt{\dfrac{21}{64\pi}}\sin\theta\,(5\cos^2\theta - 1)e^{-i\phi}$
$l=3$	$m=-2$	$Y_3^{-2} = \sqrt{\dfrac{105}{32\pi}}\sin^2\theta\,\cos\theta\, e^{-2i\phi}$

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Table of spherical harmonics of l and m.

$l=3$	$m=-3$	$Y_3^{-3} = \sqrt{\dfrac{35}{64\pi}}\sin^3\theta e^{-3i\phi}$

So, for m = 3 you have $\sin^3\theta e^{3i\phi}$ and for m = 2, it is $\sin^2\theta\cos\theta\, e^{2i\phi}$. So the m's are reflected by the exponents in the exponential of iø, 2iø, 3iø and so on. For the number of such sine functions the degree here is 3, the degree here is 3, the degree here is 3 and 1 where 3 is higher $\sin\theta\cos^2\theta$. (Refer Slide Time: 11:20 min). So if you look at that degree $(5\cos^3\theta - 3\cos\theta)$, $\sin\theta\,(\cos^2\theta - 1)$ and $\sin^2\theta\cos\theta$ all of these correspond to l = 3. The trigonometric functions have a degree of 3 and the exponential ø functions have the m as the running index for the corresponding exponential functions. This is a way of identifying a pattern in these wave functions. The first thing when you look at Mathematics is all us would like to derive if you want to understand the equations themselves. Now, if you cannot derive the equations because of the Mathematical skills required

or because of the details involved. Let us at least quantify these functions by looking at them somewhat closely and see how we identify these patterns.

Spherical harmonics give you beautiful patterns. By the way spherical harmonics is not of interest only to Quantum Chemistry but even to those who study electromagnetics, those who study aeronautics all kinds of Engineering comes with the spherical harmonics pattern in every one of them. Therefore aside from looking at it as orbitals you can also see these as visualizations of spherical harmonics as applicable to your respective Engineering branches.

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The table below gives the function plotted and the links to 2D and 3D animations

The angular parts of the hydrogen orbital wave functions are plotted

Now, let us look at the visualization part of the 2D and 3D animations and the orbitals that we are plotting are the 3d angular functions. But before let me give you a little bit about the notation. In the last lecture when we wrote p_x orbital we took this as a linear combination of the spherical harmonic of Y_1^1 and Y_1^{-1}. This was fairly simple because you looked at this formula Y_1^1 was $-\sin\theta e^{i\phi}$ and other one had a $-\sin\theta e^{-i\phi}$ and this is a linear combination. We needed to take that because this $e^{i\phi}$ is a complex function $e^{-i\phi}$ is also a complex function we cannot plot the complex functions as they are but we have to plot the real and the imaginary parts of the complex functions separately.

And if you want to do that you have to actually take the real part of the function the imaginary part of the function which means you have to take the linear combination of real and imaginary part by taking the function and its complex conjugates. You see that Y_1^1 and Y_1^{-1} are related to each other through complex conjugation, $e^{i\phi}$ and $e^{-i\phi}$ but with a – sign in front. So this gave you the quantity $\sin\theta\cos\phi$ leaving aside all the other things.

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You know that polar coordinate is like x that is the definition of the spherical polar coordinate representation for x and for y it is $\sin\theta$ $\sin\phi$ and obviously you got $\sin\theta$ $\sin\phi$ from linear combination of $\sin\theta e^{i\phi}$ – $\sin\theta e^{-i\phi}$ and this gave you $\sin\theta$ $\sin\phi$. Now this was p_y orbital and with respect to p_z there was no problem it was simply $\cos\theta$ which is proportional to the spherical harmonic Y_1^0.

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So the orbital notations as the real and imaginary parts of the spherical harmonic were implied by these labels p_x, p_y and p_z. Now let us do the same thing for the d orbital. (Refer Slide Time: 15:12 min)

You have to recall from your elementary Chemistry that the five d orbitals from your high school textbooks and also any other Quantum Chemistry book is that the notations are $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz} and d_z^2 but which is typically $d_{3z^2-r^2}$ in order to write this we will usually call this as d_z^2 but the correct notation is $d_{3z^2-r^2}$. Now where do these things come from? You have look at these spherical harmonic closely, so here are the functional forms.

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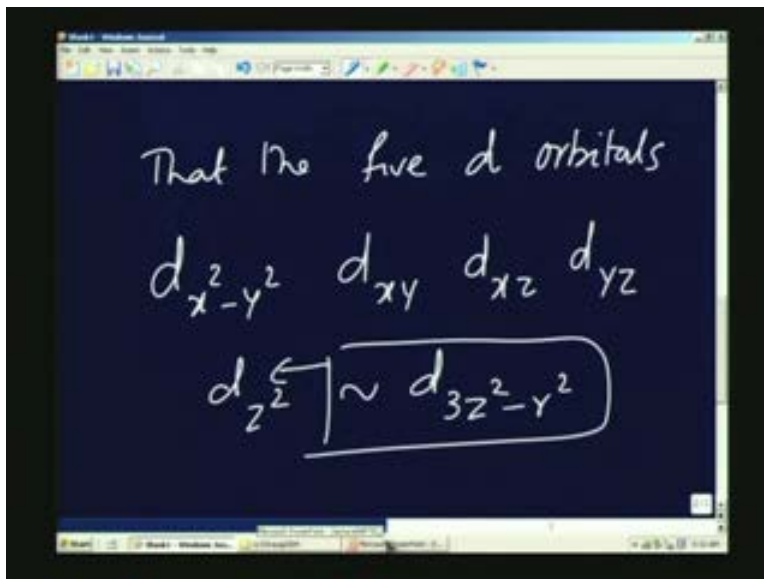
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For l = 2, m = 2 the spherical harmonics is $\sin^2\theta\, e^{2i\phi}$. Now what is the real part of this function? The real part of this function is $\sin^2\theta\, \cos2\phi$, and the imaginary part is $\sin^2\theta\, \sin2\phi$, let us look at

those; $\sin^2\theta\,\cos2\varnothing$ this is the real part of spherical harmonics $Y_2{}^2$. This is nothing but $\sin^2\theta$ $[\cos^2\varnothing - \sin^2\varnothing]$. And if you recall that this is nothing but $(\sin\theta\,\cos\varnothing)^2 - (\sin\theta\,\sin\varnothing)^2$. What is this?

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This is $x^2 - y^2$. Therefore the label $d_{x^2-y^2}$ corresponds to the real part of $Re[Y_2{}^2]$ which is real part of $Y_2{}^2$ with $l = 2$, and here $l = 2$ for d the real $Y_2{}^2$ is for this $x^2 - y^2$. So you remember that these labels x^2, y^2, xy, xz they are not arbitrary. In fact you go back further in Mathematics you will find that these spherical harmonics have a certain degree of symmetry and they have a property of what is called the irreducibility under the group representation and all those things anyway.

There is a Mathematical firm basis for the way the spherical harmonics come out as solutions for the Schrödinger equation part the angular equation part and we see that the Chemist make absolutely perfect use of these orbitals in describing the Chemistry of what goes on.

Let us look at the shape of these orbital now. What is d_{xy}? It should be obvious now that it is $\sin\theta\cos\phi\sin\theta\sin\phi$. Therefore this is nothing but $\sin^2\theta\sin2\phi$, where $\sin2\phi$ is of course the imaginary part of $e^{2i\phi}$ and this is of course what you see is Y_2^2 where the subscript 2 is for the $l = 2$ the degree $2 \sin^2\theta$. And the superscript 2 is for the $m = 2$ for the exponential function. So again the imaginary part of Y_2^2 gives you d_{xy} and the real part of Y_2^2 gives you $d_{x^2-y^2}$. Therefore there is no more mystery regarding these labels from the table of spherical harmonics.

If I go further in this quickly I will show you that association.

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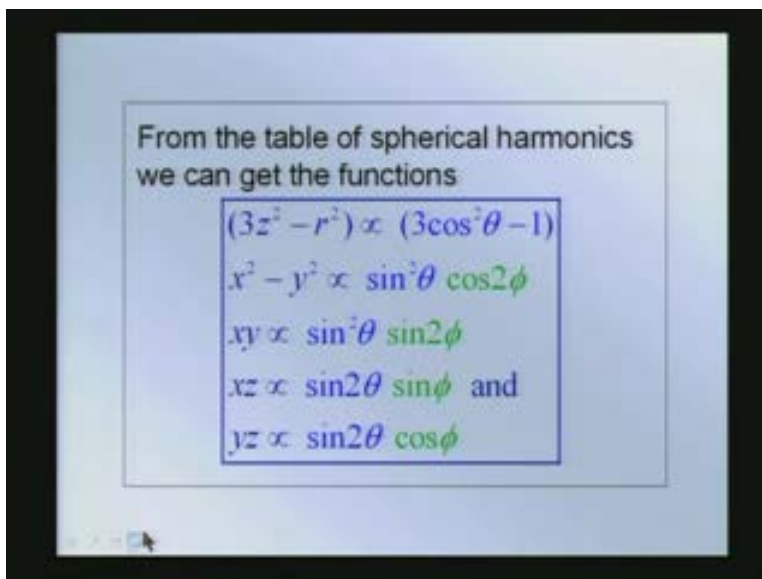
This is the table you have to remember. In fact you can construct that right away $(3z^2 - r^2)$ is $(3\cos^2\theta - 1)$ that is what you get from the Y_2^0. And $x^2 - y^2$ is $\sin^2\theta \cos2\emptyset$, xy is $\sin^2\theta \sin2\emptyset$, and xz, yz therefore likewise come from the $\sin\emptyset$ and the $\cos\emptyset$. You remember that the $\sin\emptyset$ comes from $e^{im\emptyset}$ where m is 1. Therefore these two correspond to the spherical harmonic Y_2^2 but with the m value + 1 and – 1. Real and imaginary parts of Y_2^1 are obtained by the linear combinations of these two functions. Therefore all the five spherical harmonic or harmonics give you these five different functions namely $3z^2 - r^2$, $x^2 - y^2$, xy, xz and yz.

In Inorganic Chemistry, to study the chemistry of materials and the materials of molecules that the materials are made of you will realize that these labels are extremely important in the field known as the coordination compounds.

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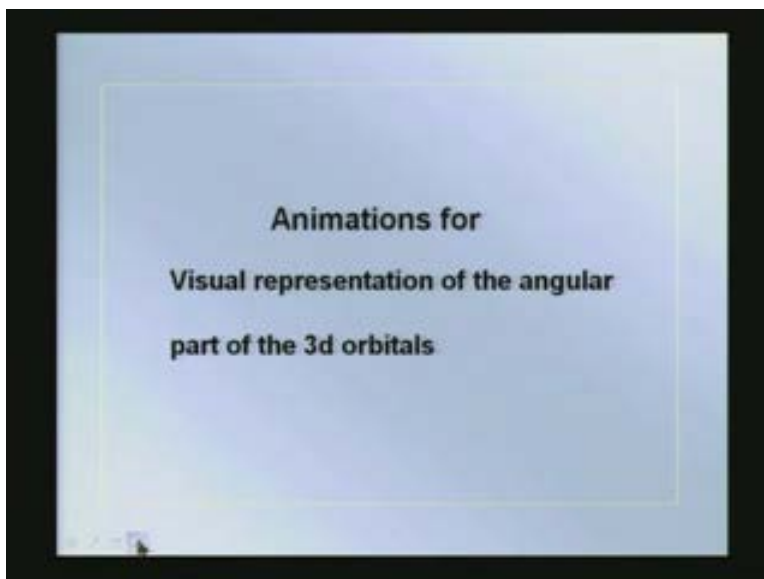
So these are not trivial labeling but let us look at the objective namely the representation of these orbitals one by one. We will also see all these five orbitals or the angular representations closely. First the d_{xy} orbital: My strategy for today's lecture is to first show you what the picture looks like and then go back and build this picture from the elementary plotting parts of the two variable functions like we did in the last lecture so that you see that the picture that you saw is not something that it is arbitrary but it is built up from very solid Mathematical plotting. Let us look at the d_{xy} orbital first.

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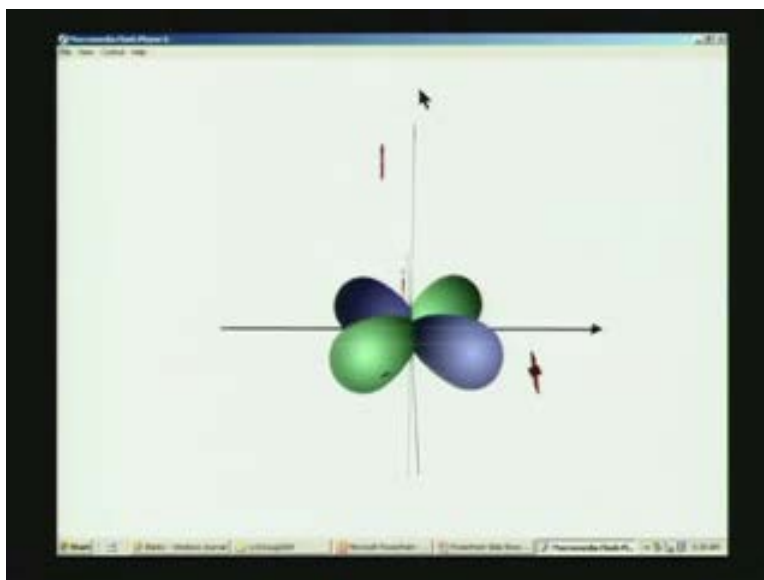
d_{xy} orbital corresponds to two pairs of lobes with two different colors you see the green and the blue here that these pairs of lobes pointing along the diagonals of the x, y axis system. You see that they are in the xy plane of course they also come out of the xy plane but they are pointing along the diagonals of the xy plane. What about the next one? The d_{yz}: you should not expect anything strange here you should expect that it is pointing now along the yz plane but along the diagonals of the yz plane as you see here.

The d_{yz} is pointing the two lobes here and the other two lobes the green lobes they are both pointing along the diagonals. Let us look at the d_{xz} orbital. Again you get the picture that the lobes are pointing along the xz plane but along the diagonals of those planes not along the axis themselves. Next one is $d_{x^2-y^2}$ orbital. Now it looks exactly like d_{xy} except that now the orbitals point along the axis the lobes point along the axis here the plus and the – axis. The last one in this the 5th one is the $d_{3z^2-r^2}$ orbital which looks like having a pair of lobes pointing along the z and the – z and the ring surrounding.

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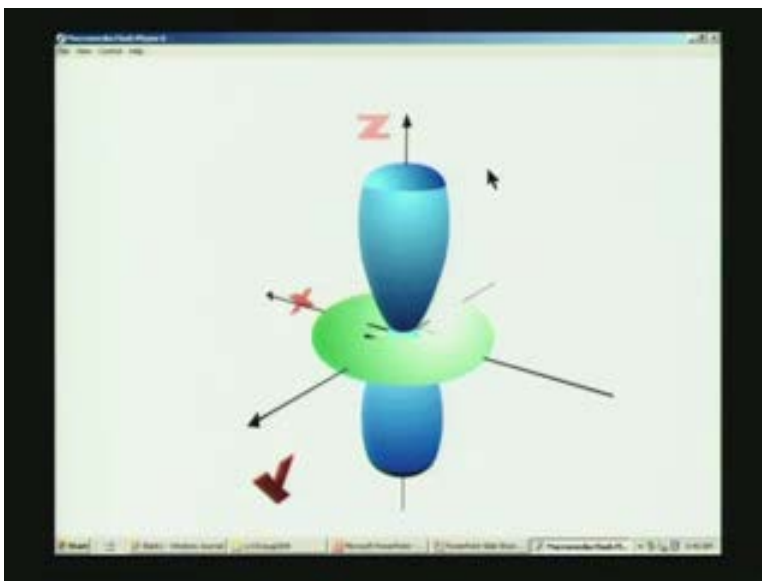
This ring is obviously symmetric in the (x, y) plane so you see that there is something which appears somewhat different from the other four sets. Now, these are the final pictures, these kinds of animations you can find anywhere but what you will not find is the method of building these animations by looking at the function and then plotting them in the polar graph.

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The angular part	2D	3D
$\mathrm{Re}\left[Y_2^2\right] = \sqrt{\dfrac{15}{32\pi}}\cos 2\phi \, \sin^2\theta$	Flash file	3D file
$\mathrm{Im}\left[Y_2^2\right] = \sqrt{\dfrac{15}{32\pi}}\sin 2\phi \, \sin^2\theta$	Flash file	3D file

That is the step that we will follow next. So let us look at the Y_2^2 which is $\sin^2\theta \, \cos 2\phi$. First we will plot this for one value of ϕ and then $\sin^2\theta$ for all the values of θ and then we will extrapolate that plot to all the values of ϕ just as we do in a three dimensional plot. So let us look at the flash file for this particular function. So what I have here is $\sin^2\theta \, \cos 2\phi$.

Now, recall the definition of θ and the ϕ. The θ is obviously along the z to the – z-axis which is a polar axis, you remember the pictures we had earlier. The variation is $\theta = 0$ here value slightly one value and so on and obviously 90° and then when you go to – z it comes to 180°. The ϕ is for a given value of θ. Of course anywhere if you go across the sphere through a circular path that is the value of ϕ going from the x axis as $\phi = 0$ and to y axis $\phi = 90° – 180°$ for the –y axis, 270 for the y axis and then back to 360° and then 0° for the x axis.

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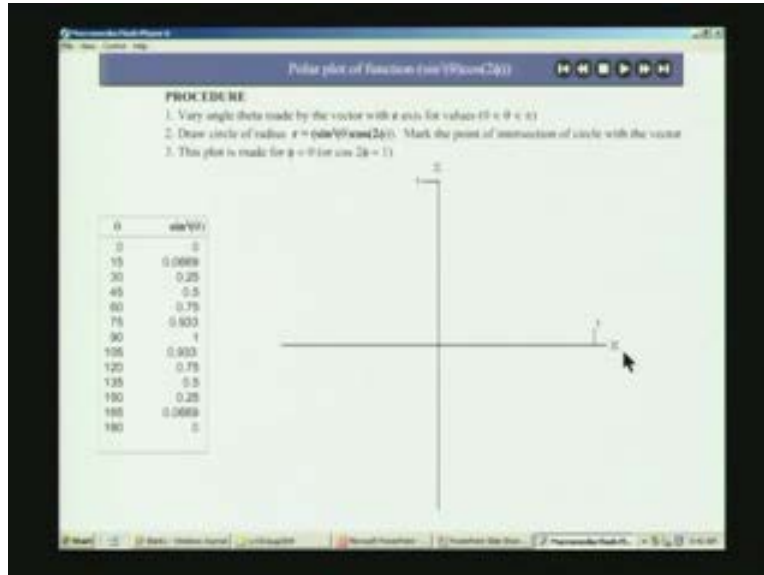
So we now plot this for one value of $\cos\phi$ namely $\phi = 0$ which means we are plotting this function along the x-axis. And the value θ is $\sin^2\theta$ so the functions are given here. Now θ is given from 0 to 180 and $\sin^2\theta$ is given from 0 to whatever is the corresponding value and the plot is for any value of θ the magnitude $\sin^2\theta$ is plotted along the radius as you have done in the previous p_x, p_y, p_z graphs in the last lecture are 15° then 30° here it is ¼, after 45° this is 1/2 and so on.
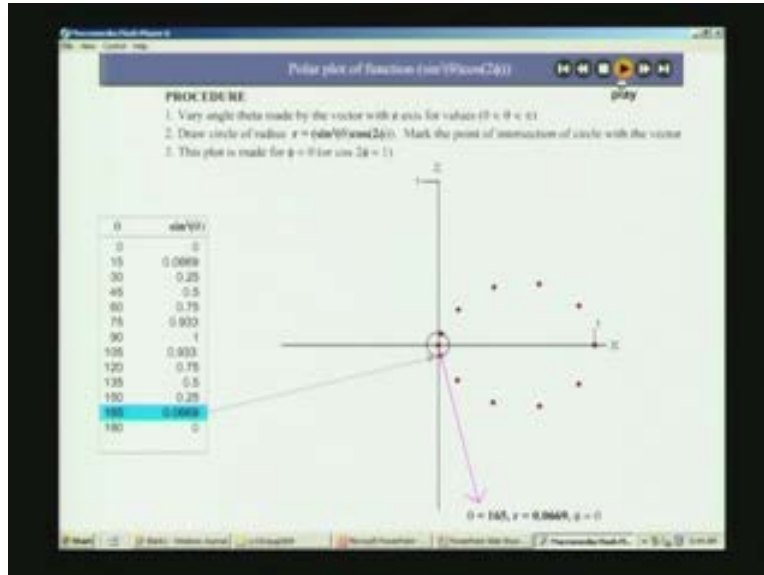
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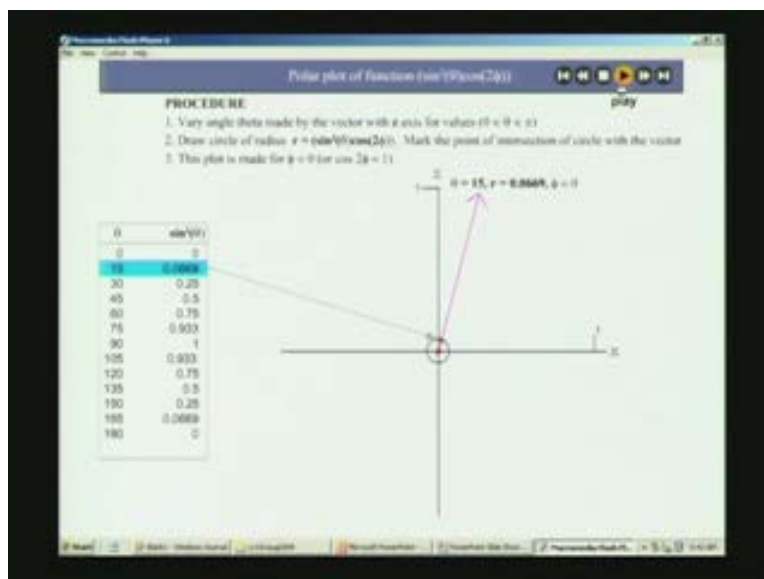
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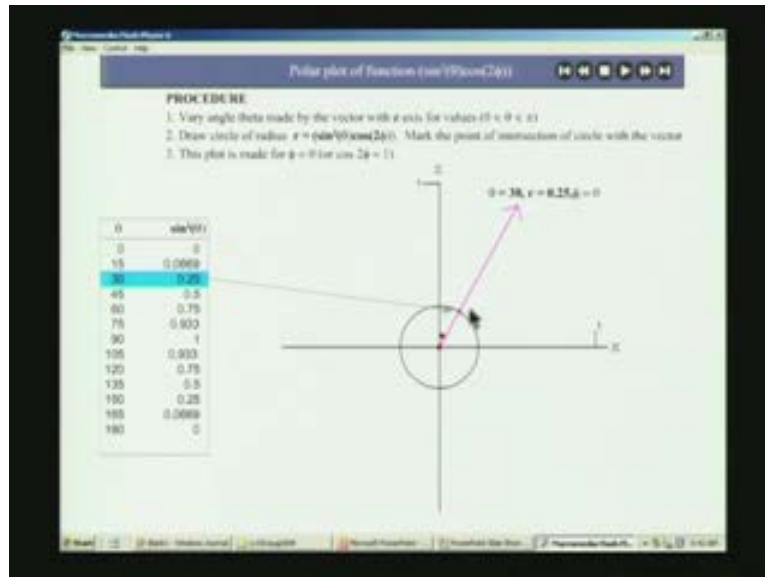
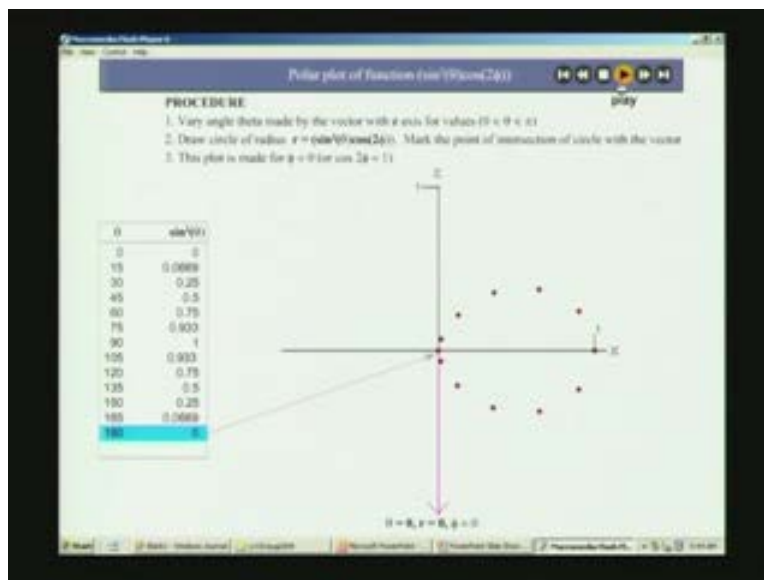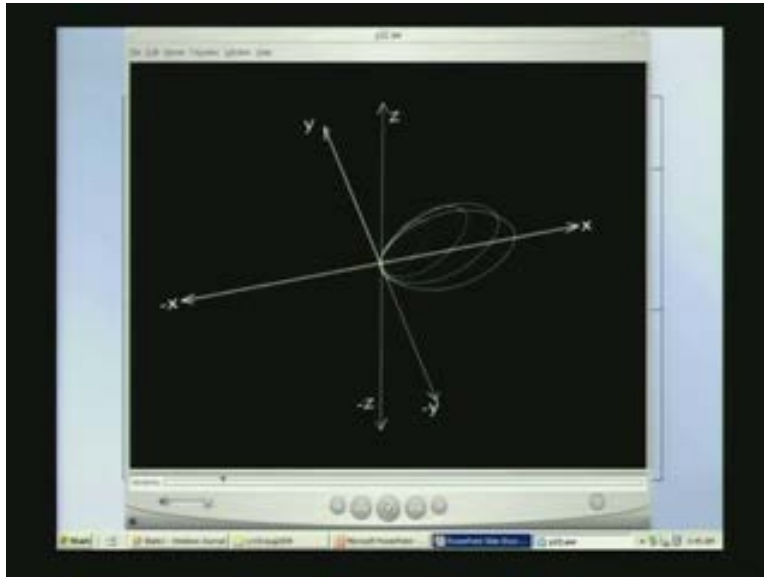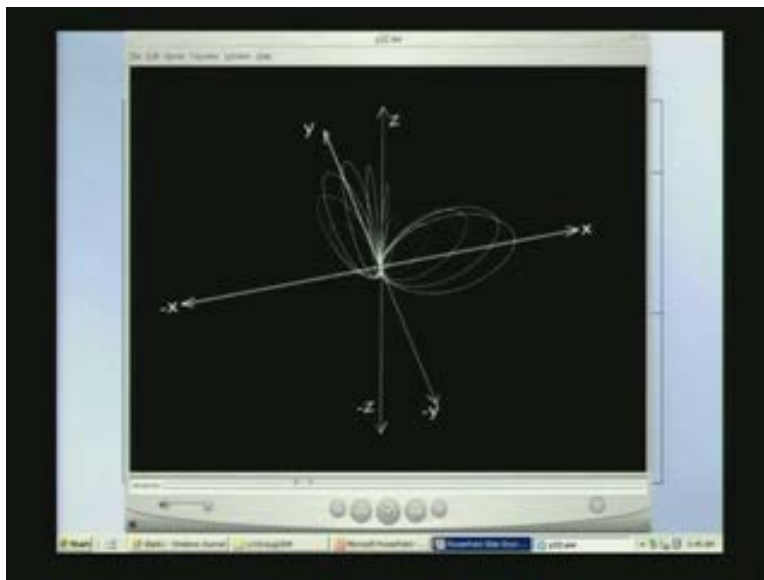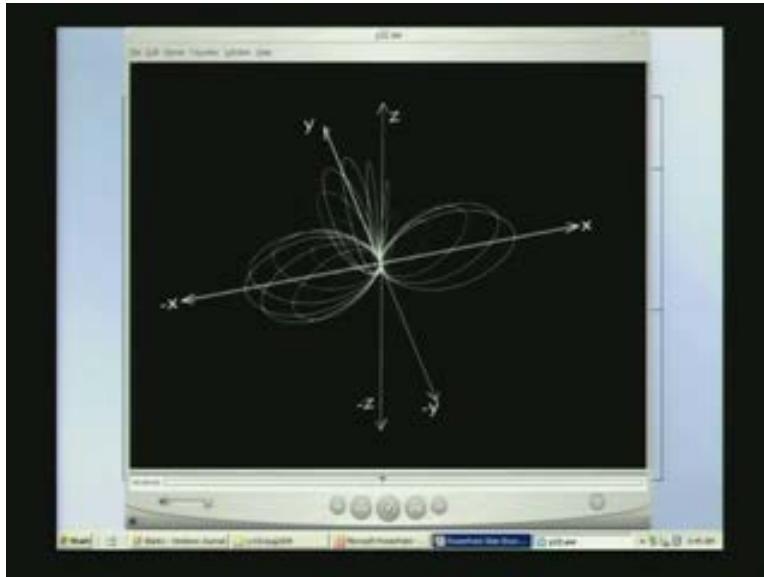(Refer Slide Time: 26:22 min)
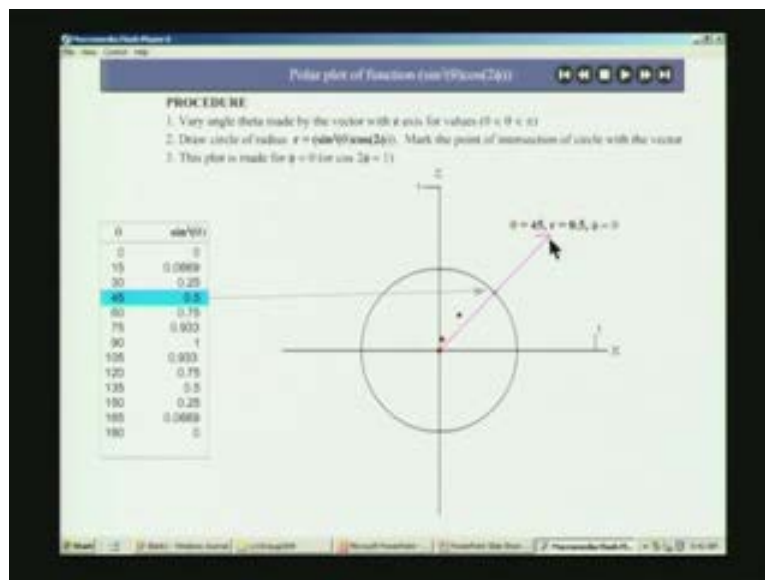
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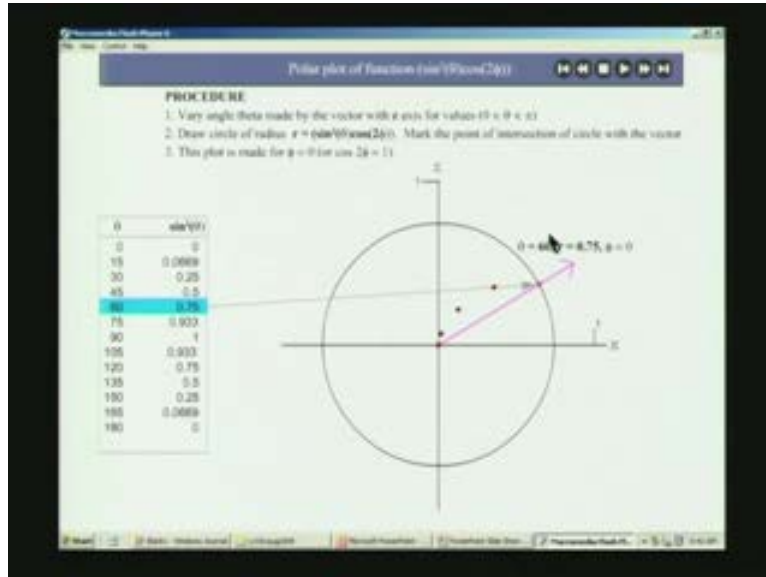
Whatever values are there for θ and $\sin^2\theta$ they are plotted.

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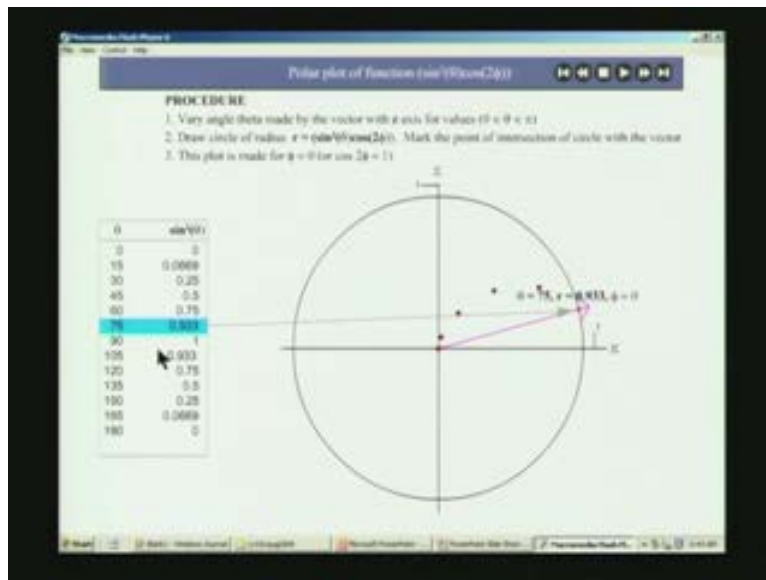
You know the value of θ if you go back to this graph.

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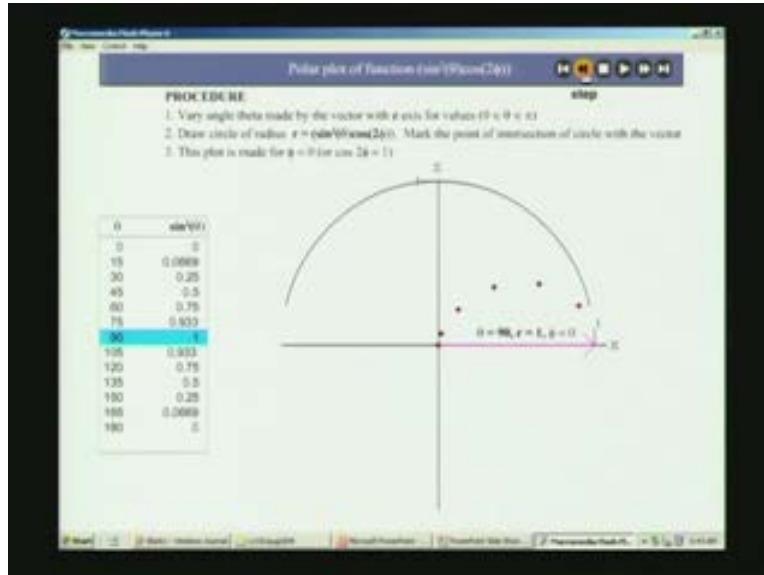
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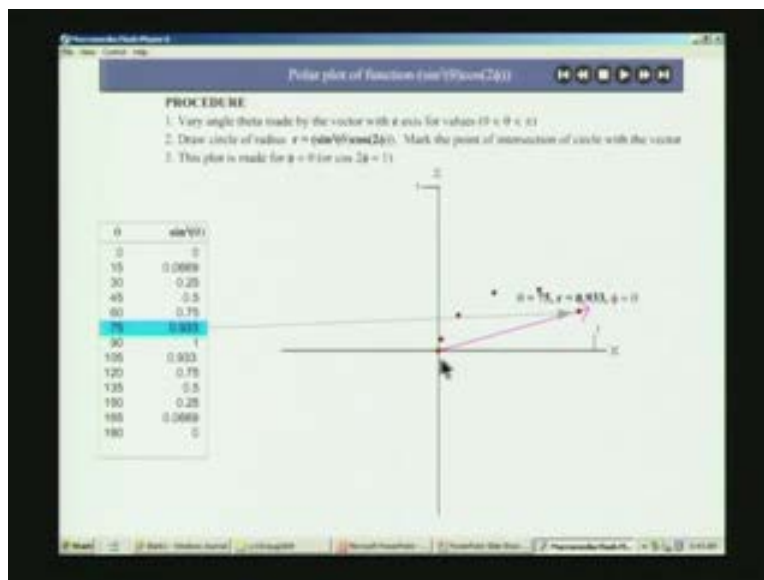
So what is the value? This represents the θ it is this angle, the θ is 75° and the corresponding value is 0.933 in a circle of radius 1 that you can mark. You saw that it is how you plotted it. You see this 0.93 is the value in a circle of radius 1 and that of course cuts the radius here so this value is also 0.93. So there should not be any doubt about how this plot comes about.

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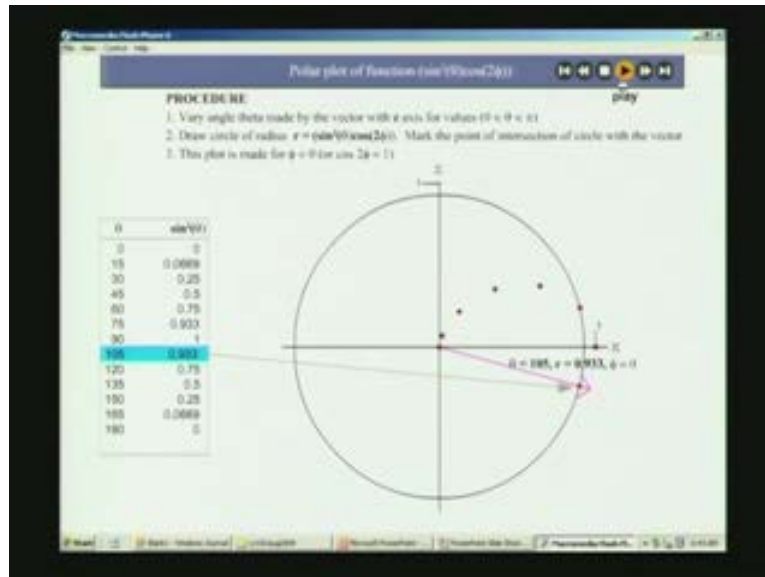
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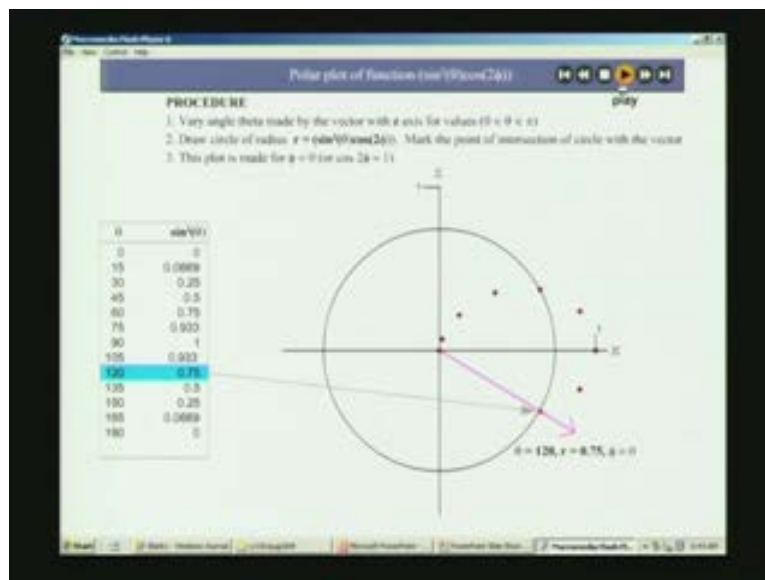
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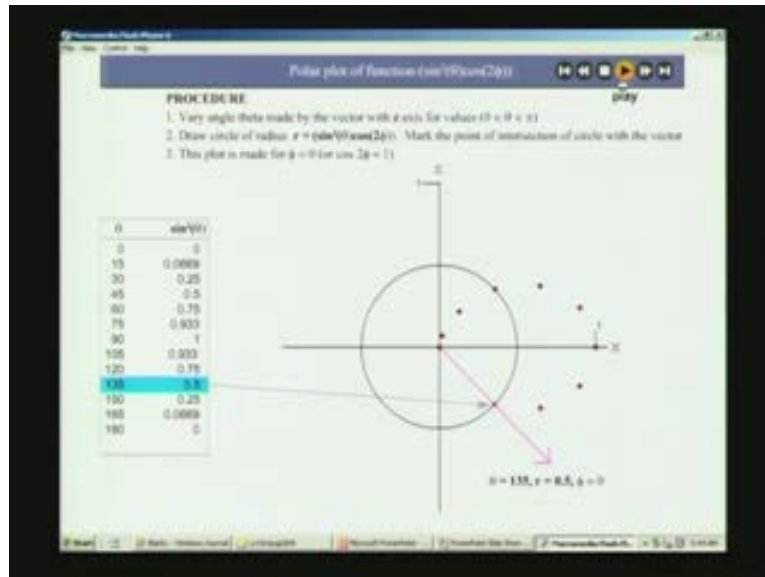
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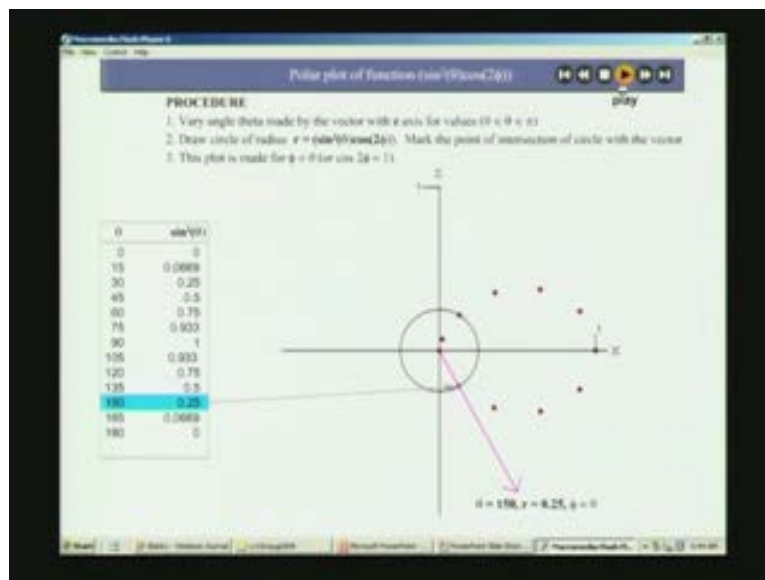
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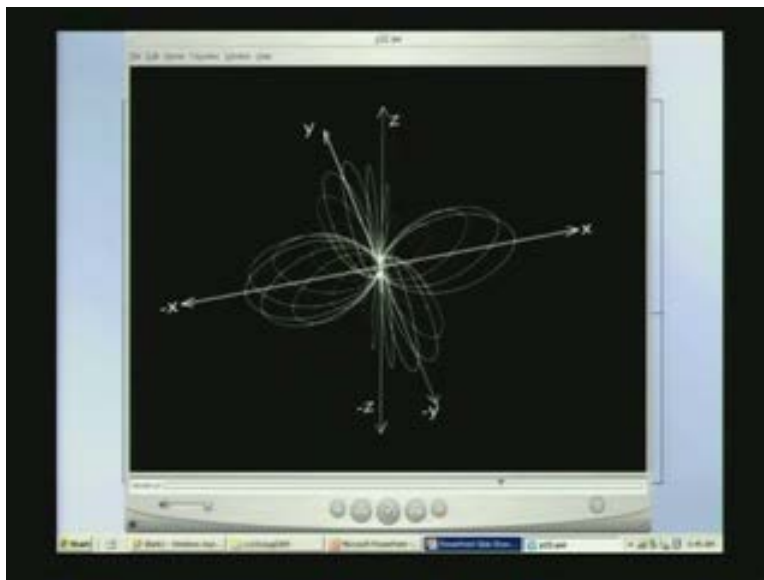(Refer Slide Time: 27:37 min)

(Refer Slide Time: 27:39 min)

So this is $\sin^2\theta$ and it is not spherical as in the case of $\sin\theta$ but it is some sort of a slightly distorted shape. Now this is for only value of ø namely cos2ø is 1 at ø = 0. This if we plot the same function same graph for every value of ø by multiplying that with cos2ø we get the three dimensional representation of the function $\sin^2\theta$ cos2ø that is the next plot in the 3D file.

(Refer Slide Time: 28:12 min)

So here have it along the x axis then this is now plotted along all the possible values of ø by taking a few samples and then connecting all of them together and that is multiplying at the same time with cos2ø

(Refer Slide Time: 28:26 min)

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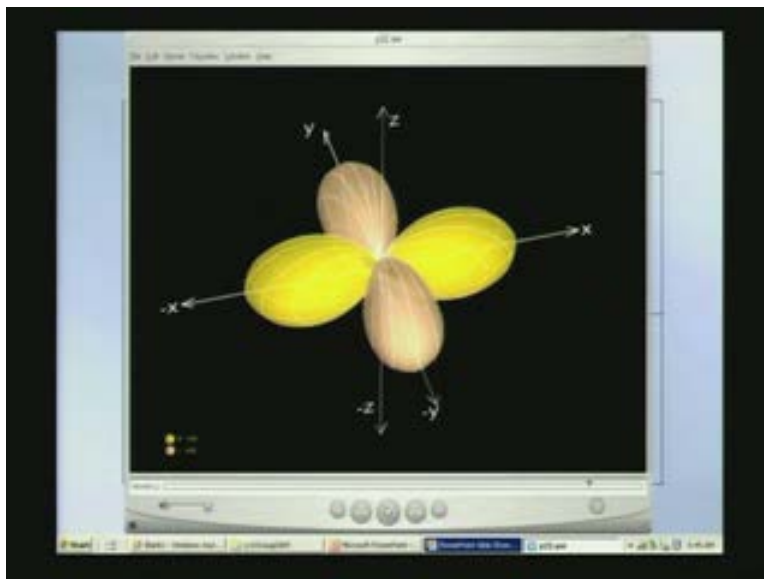
So that is the way the function looks like, just go back and see what it means. The nice thing about all these animations is that you can play them back and forth and learn at your own pace. Now, I have stopped at a point roughly where ø is 45°, at 45° of ø value the $\cos 2ø$ is 0 so you see that this function has disappeared completely (Refer Slide Time: 28:10 min) and at angles greater than 45° the $\cos 2ø$ is negative but it keeps building up. And ø = 90 means $\cos \pi$ which is – 1 that is the highest value in the negative side. So you see that the value again builds up and it becomes most negative along the y axis exactly like what it was along the x axis except that the function on this side is negative because of $\cos 2ø$, and $\sin^2 ø$ always positive having no problems. (Refer Slide Time: 29:41 min)

Now, as you go further $\cos 2ø$ goes from 180° to 270° as ø goes from 90° to 135°, and you see that it again goes to 0. So this whole part is negative, this part is positive and you continue this process until you go through the rest. And you see that the positive and negative part alternate leading to the two different colors of the function and this is typically what you write in your high school plots for the d orbital (x, y, z) and xy and yz and zx you put two '–'s on one pair of lobes and you put two '+'s on the other pair so what do they mean? They represent nothing but the signs of the function, the actual value of the function with its magnitude and the signs, so that is what you see here.

This is $d_{x^2 - y^2}$ and it points along the lobes and this is an agreement with the picture that we had earlier. (Refer Slide Time: 30:45 min) Next is the imaginary part of Y_2^2 is $\sin 2ø \sin^2 \theta$ that is the θ part and it is still $\sin^2 \theta$ but the ø part is $\sin 2ø$.
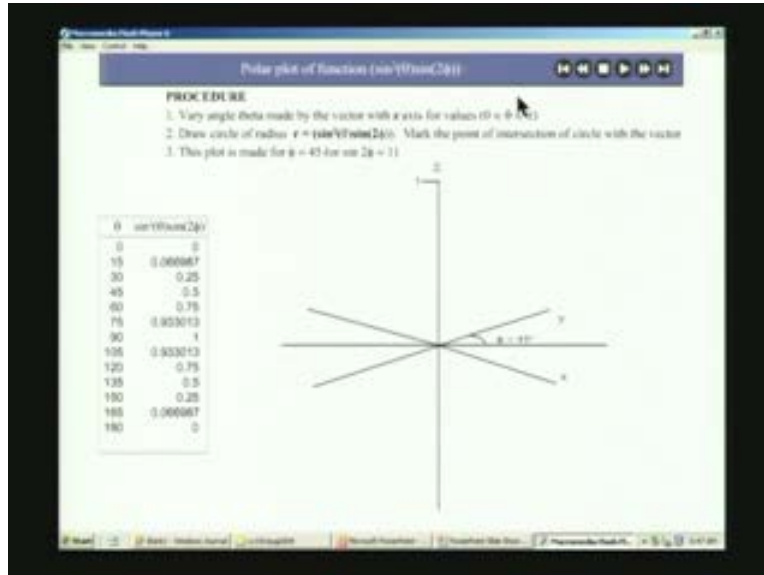
So if you look at the flash file the only thing that we have to do now is we should not plot this for $\phi = 0$ because for $\phi = 0$ the $\sin 2\phi \, \sin^2\theta$ is 0. Therefore, if you want to plot a particular value of ϕ keep the value and change the $\sin^2\theta$ for various values of θ. The most convenient point is $\phi = 45°$ but not 0. So if ϕ is 45° obviously you see that the x and y axis if you represent them somewhere from the middle this function starts its value and the final plot is a sin square theta plot which is the same as the previous plot, so let me just draw the final plot, the last frame.
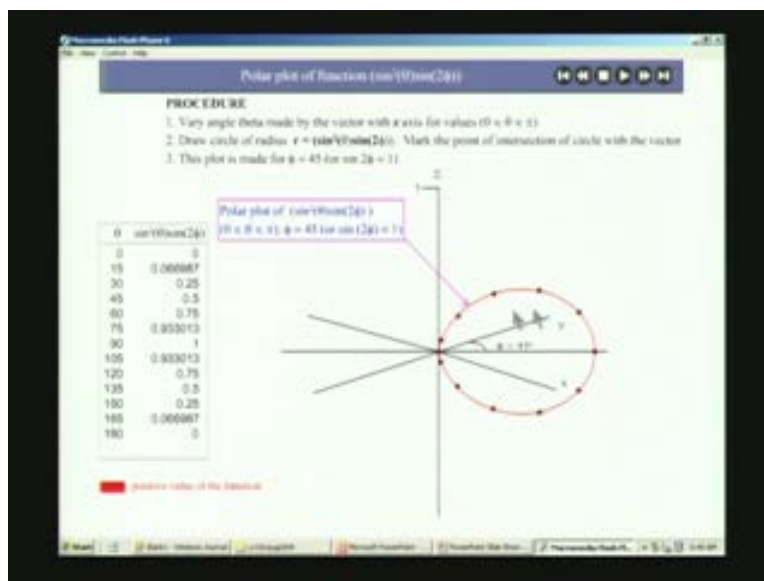
It is obviously along 45° is $\sin^2\theta$ with $\cos 2\phi$ is 1 at $\phi = 45°$. Now this plot obviously gets repeated by $\sin 2\phi$ modulation in the three dimensional picture.

(Refer Slide Time: 32:13 min)
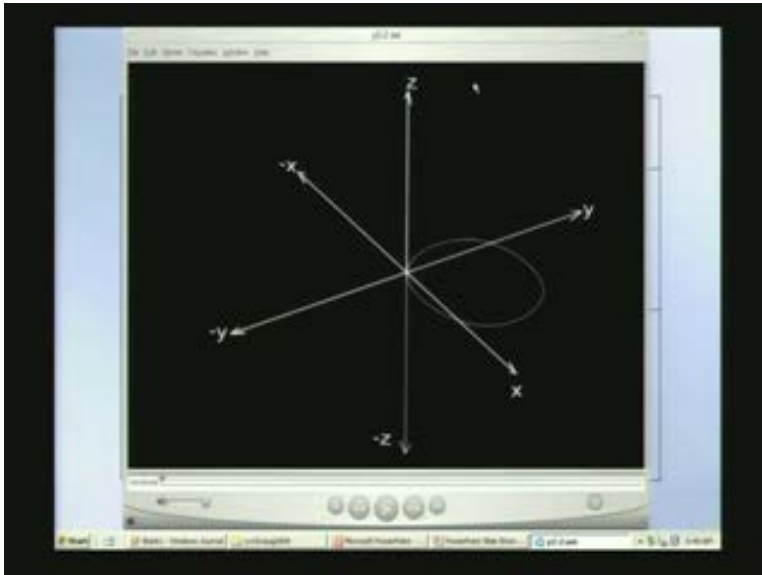
So when we go to the 3D part of the imaginary part of Y_2^2 everything is the same as the previous one except that now the maximum lies along 45° not along the x axis because at the x axis sin2ø is 0. So all that seems to happen is that the previous plot which you saw as between x and y seems to have been tilted by about 45° because of the value sin 2 phi and that is exactly what is reflected in this picture of imaginary the part of the Y_2^2. Well, it is very easy to remember and if you remember that sin function and cosine function are essentially different from each other by a phase angle of 90°. This is sin2θ and therefore the phase angle here is 45° instead of 90°. So what you have here is d_{xy} which is the orbital pointing between the axis with the maxima between the axis and along the diagonals and again with two positive parts and two negative parts.

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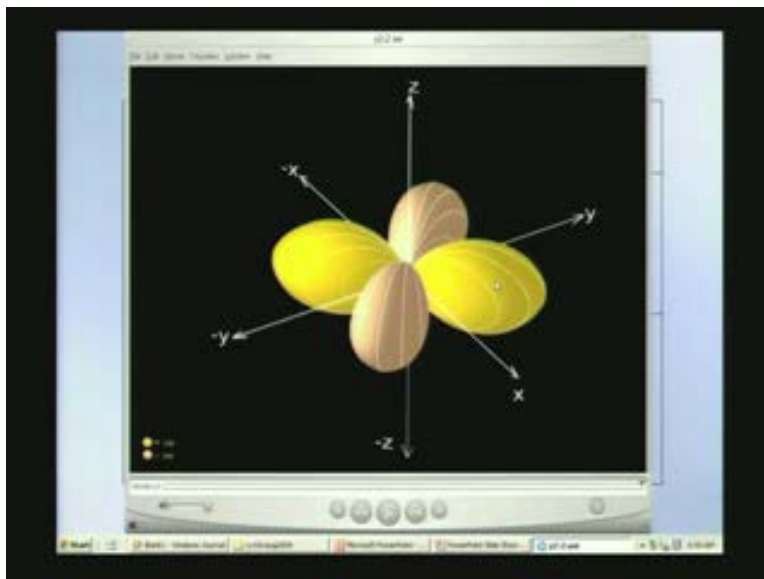
The yellow is positive and the slightly brown or grayish ones are negative. This is for $Y_2{}^2$ imaginary part or what we call as d_{xy}. Now there should not be surprises regarding what should be the imaginary part and real part of the $Y_2{}^1$ and $Y_2{}^{-1}$.

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The angular part	2D	3D
$Re[Y_2{}^1] = \sqrt{\dfrac{15}{8\pi}} \cos\phi \, \sin\theta \cos\theta$ $= \dfrac{1}{2}\sqrt{\dfrac{15}{8\pi}} \cos\phi \, \sin2\theta$	Flash file	3D file
$Y_2{}^0 = \sqrt{\dfrac{5}{16\pi}}(3\cos^2\theta - 1)$	Flash file	3D file

They correspond from this function as you see cosø sin2θ where sin2θ is cosθ sinθ and sinθ cosø is x cosθ so this is xz orbital.

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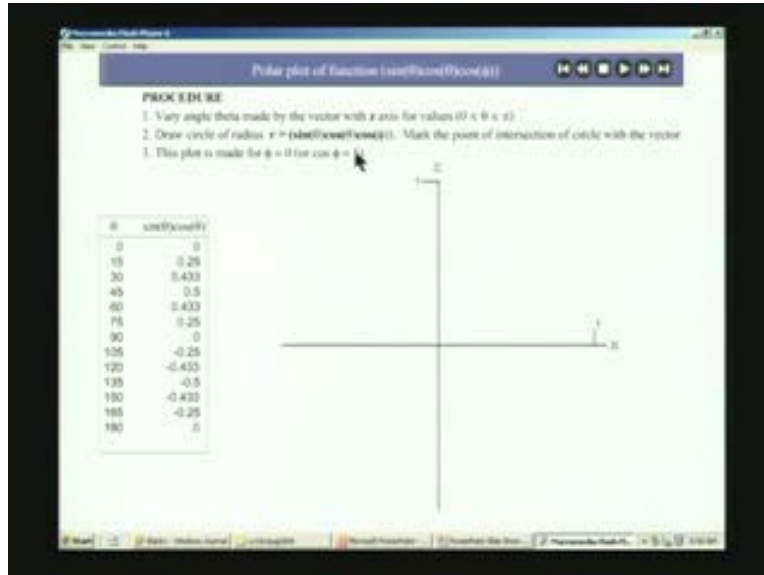
We are going to plot this for $\phi = 0$ because it is a $\cos\phi$. And $\cos\theta \, \sin\theta$ plot has something slightly different from the previous plot so it is worth going through the plotting routine again.

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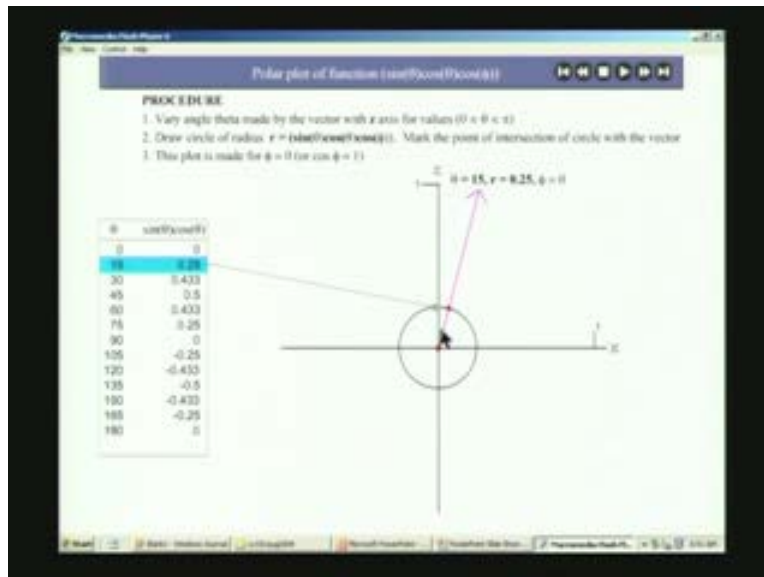
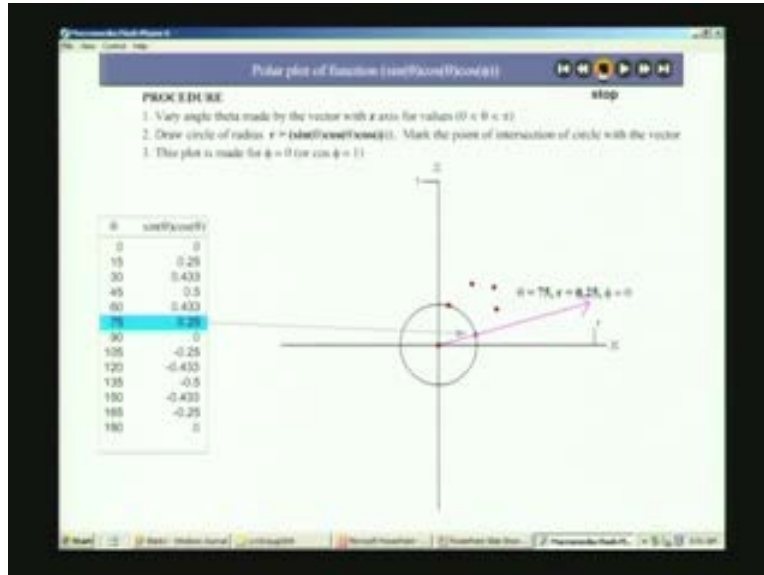The values are given here and the points are plotted along the radii making the angle θ.
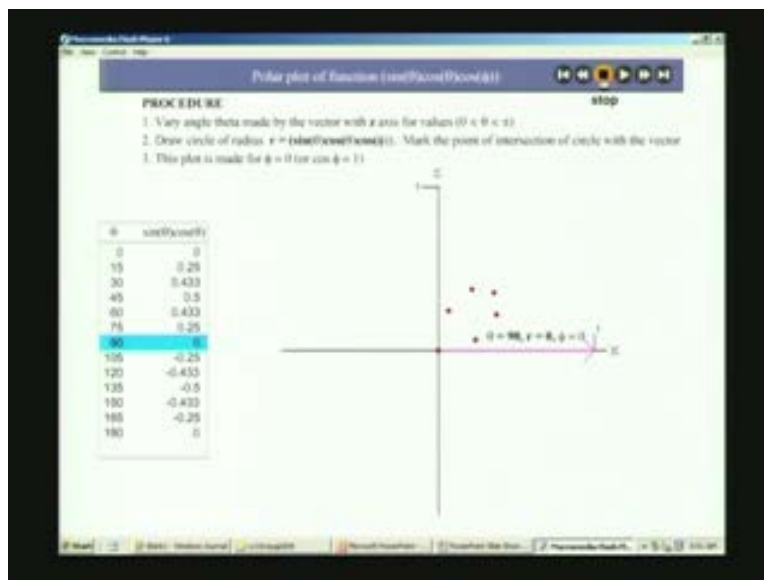
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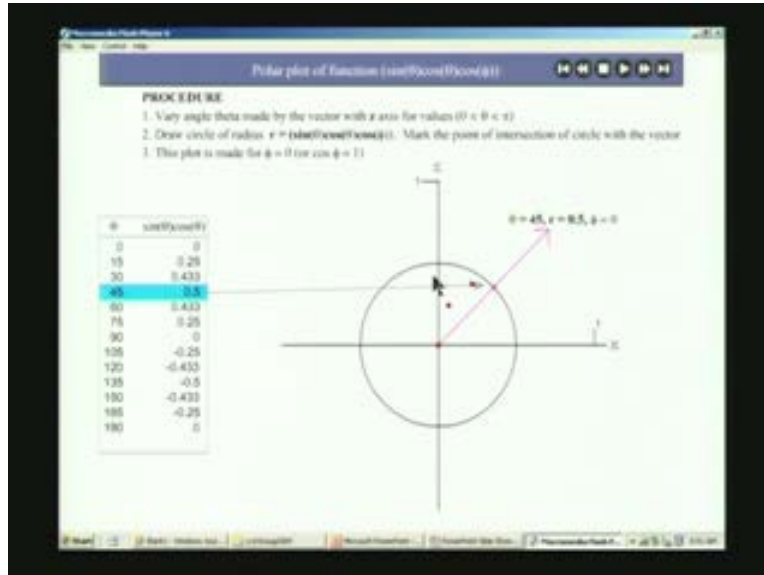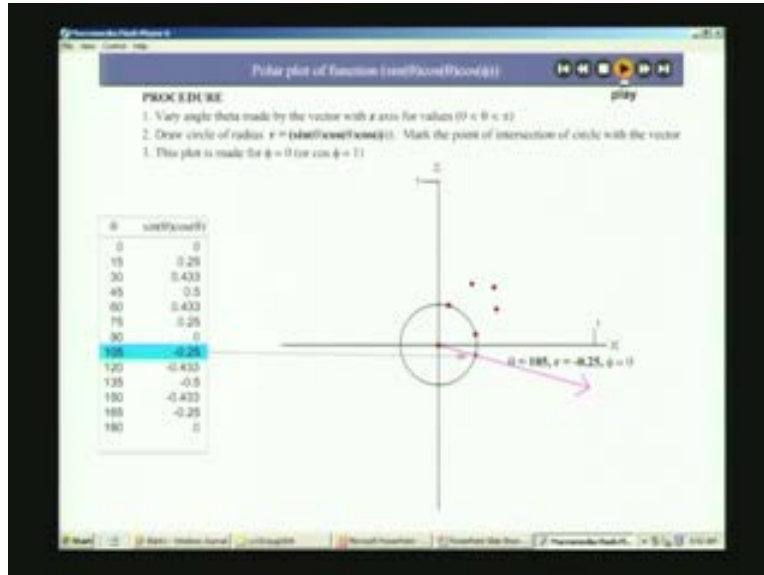

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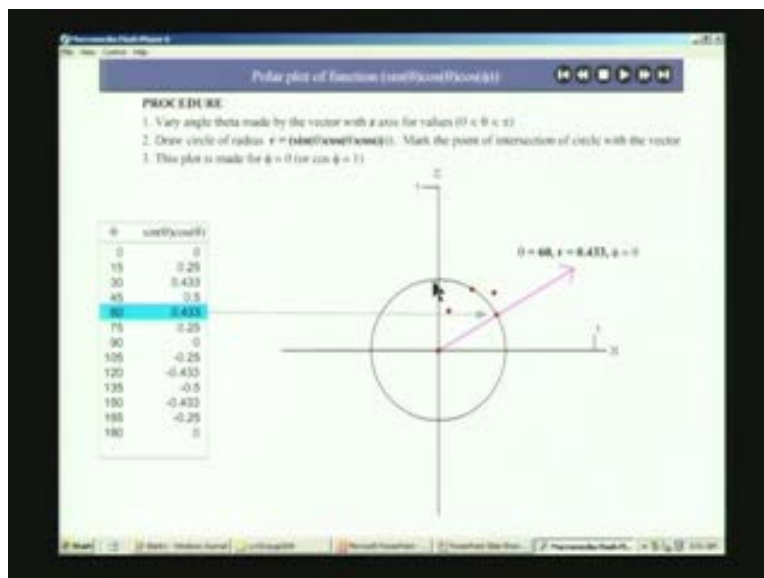
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So let me stop at the half way point. The reason for the half way point break is $\cos\theta\,\sin\theta$ obviously it goes to 0 when $\theta = 90°$ so you see that the function starts from 0 and it goes to some maximum and then it comes back to 0 and throughout this part the function remains positive. But now as θ increases $\cos\theta\,\sin\theta$ going to be negative and again it goes through the same except that now it is along the bottom part of the axis system, let us play that now.

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And what you see here is the mirror image of that plot except that the values are all negative not by saying this is negative, there is nothing called negative here but the function is negative.
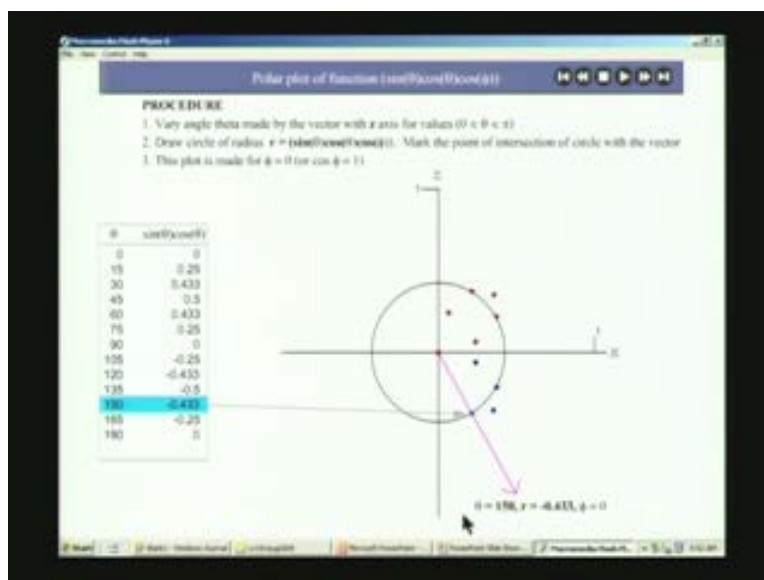
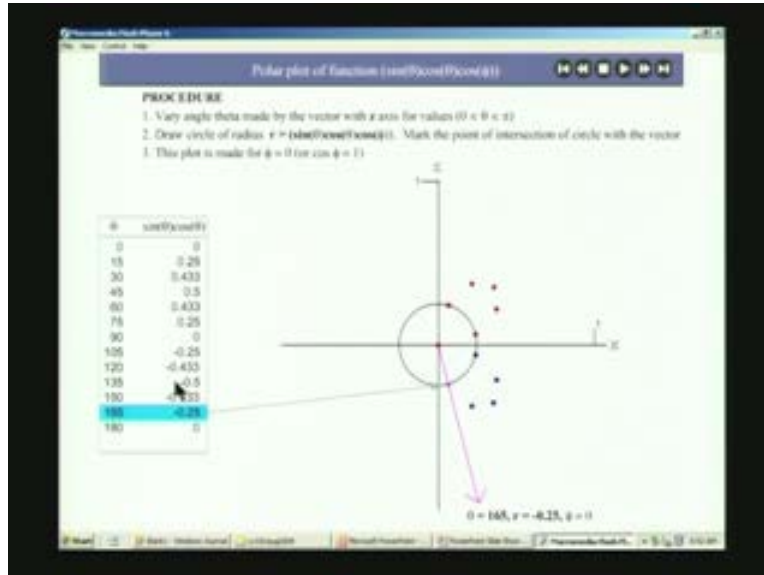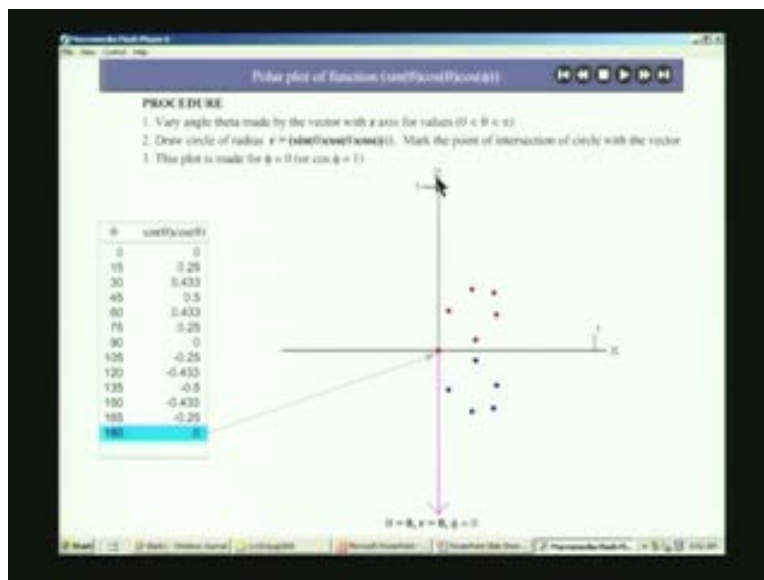(Refer Slide Time: 35:23 min)
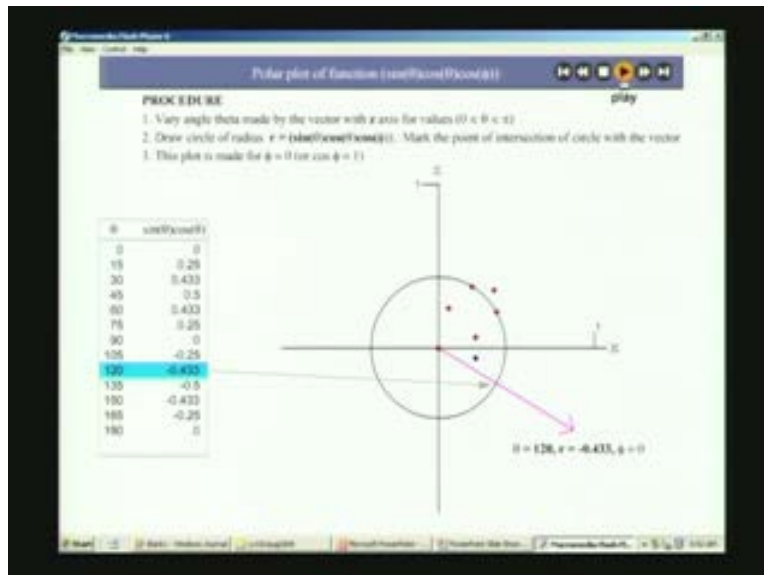
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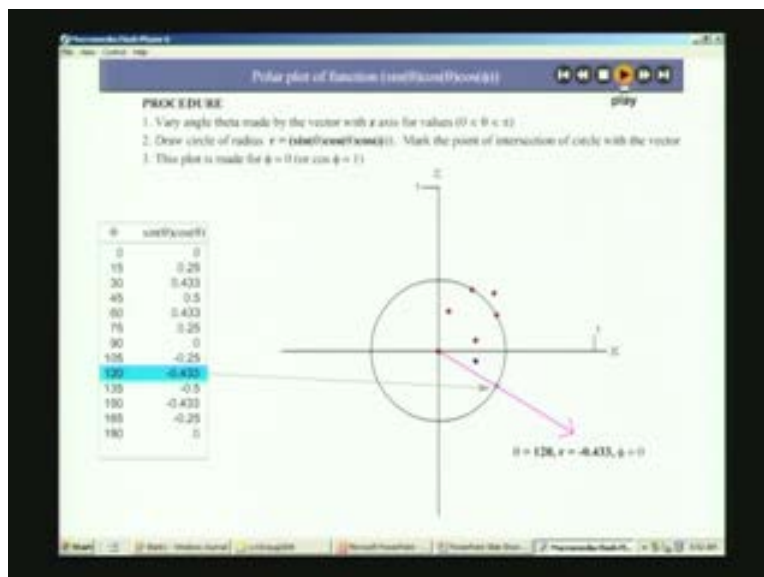
(Refer Slide Time: 35:31 min)
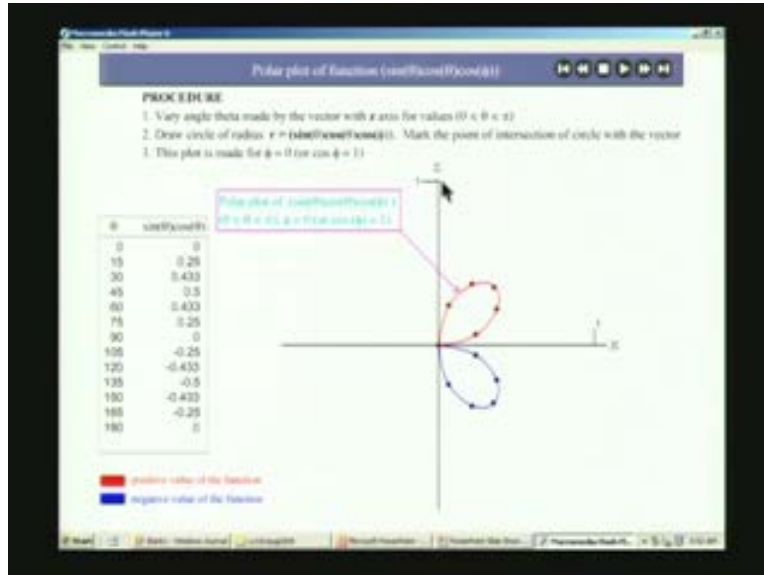
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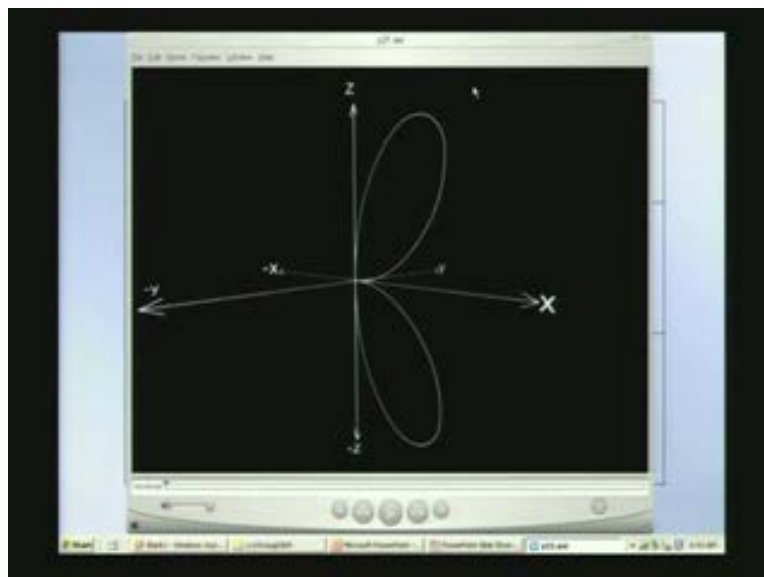

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This z-axis does not make any meaning right now, this axis is only to reference 0° angle and 180° angle.
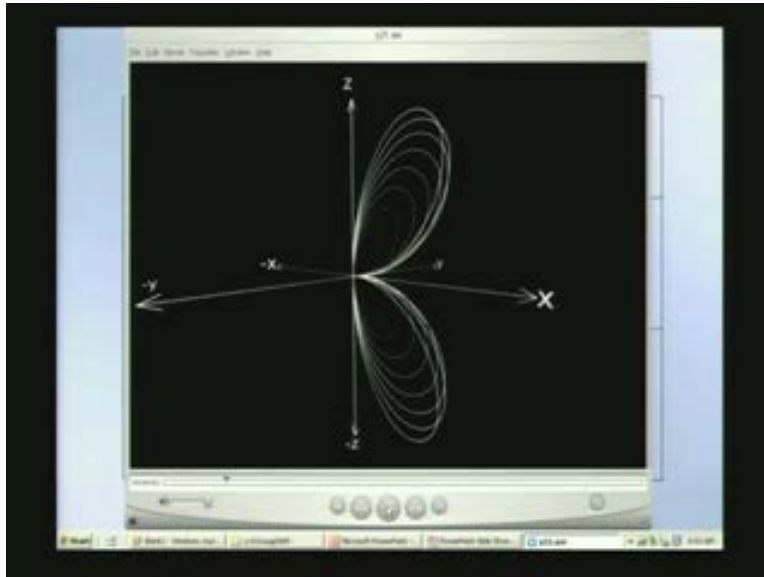
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The z axis is 0 and the angle $\theta = 0$ is here, the angle $\theta = 180$ is here that is the only reference. You cannot mark anything along the axis this is not a Cartesian plot but this is a polar plot so only the radius and the length along the radius are important. So now you see $\cos\theta \sin\theta$ has this positive and the negative lobe where the red is positive and the blue is negative and this has to be plotted as a function of $\cos\phi$ for all values of ϕ which is given in the three dimensional file.
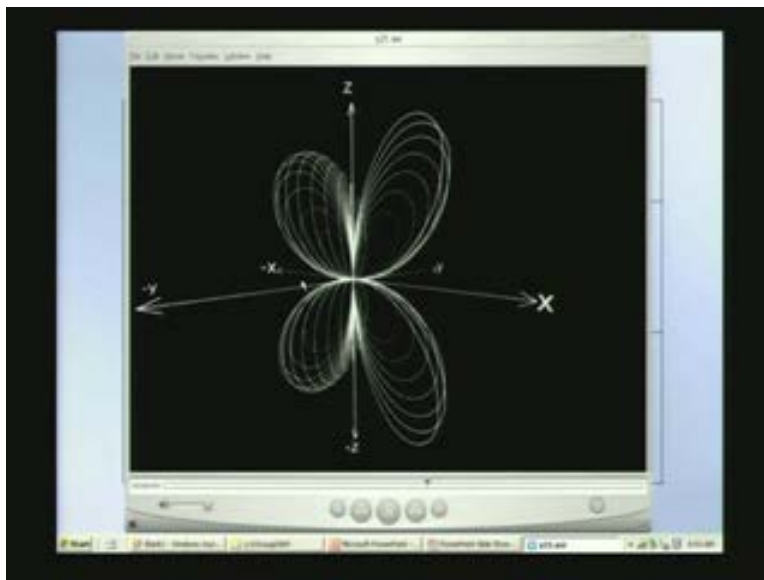
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You see, this is a slightly more expanded version $\cos\theta \sin\theta$ here along the x axis and then you plot this it is modulated by $\cos\phi$ so it goes to 0 at $\phi = 90°$, and goes to -1 at $\phi = 180°$.
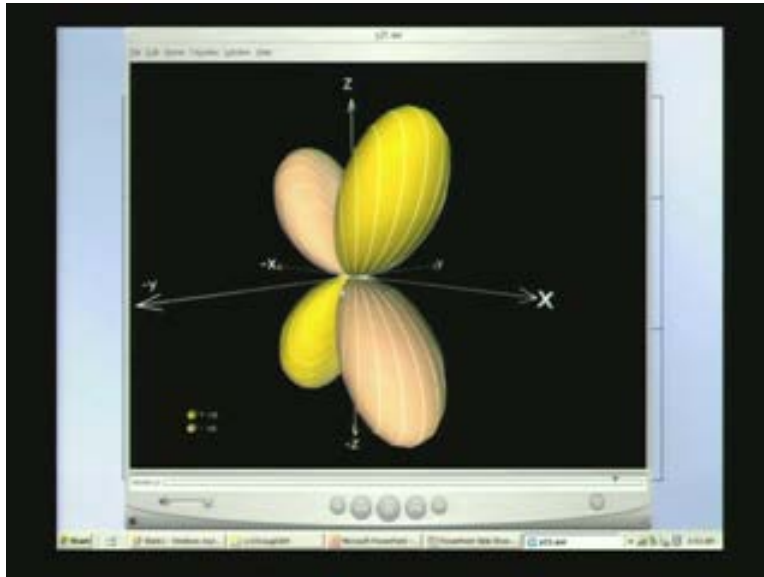
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You see that the lobes are pointing in the xz plane and there is nothing along the y axis because at y the ø value is 90 therefore cosø is 0 so you see that these lobes are identical to the xy lobes except that now they are in the xz plane. And let me do one more plot here on the Y_2^0 namely $(3\cos^2\theta - 1)$ it is a slightly interesting plot.
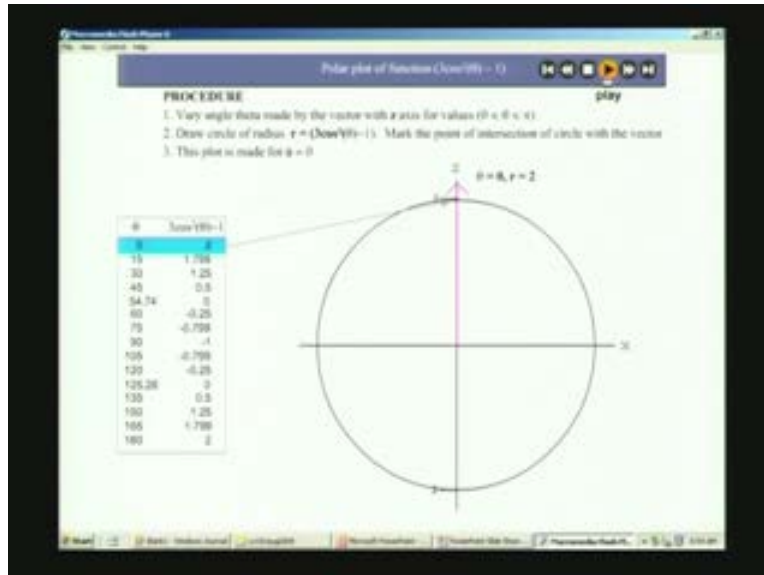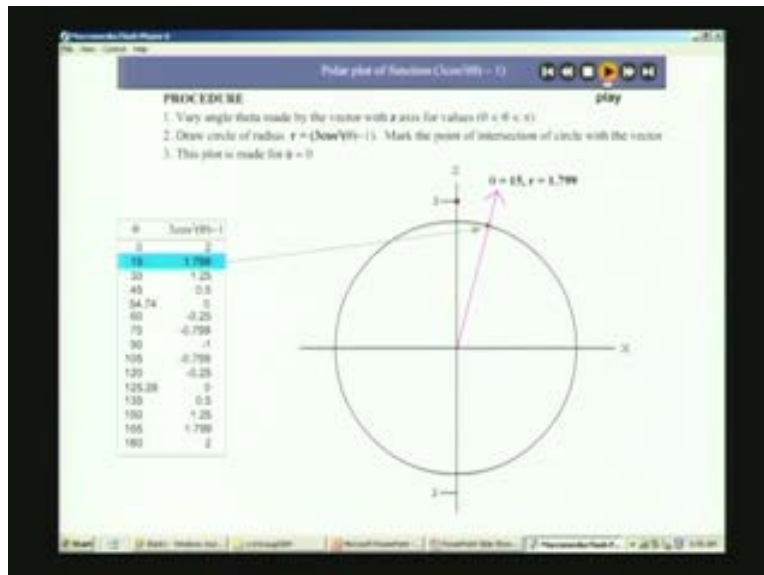
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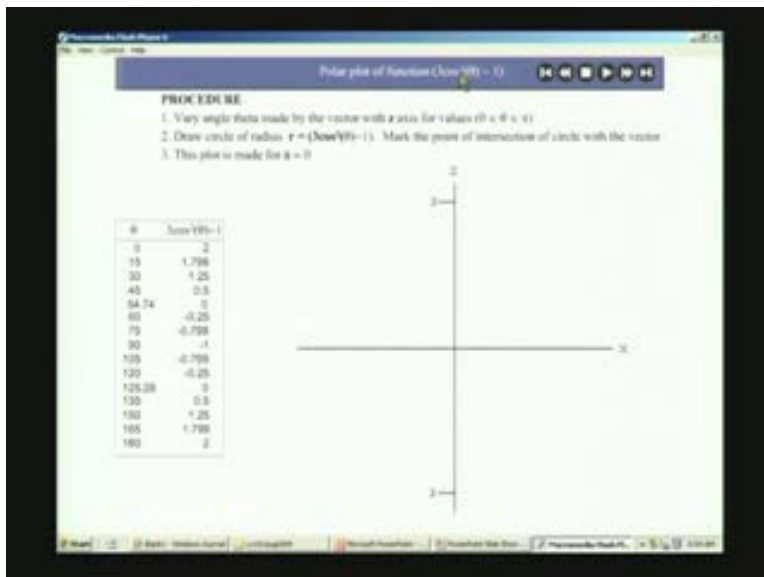
There is no ø dependence for this function and $(3\cos^2\theta - 1)$ when you calculate for various values of θ the table is here. for $\theta = 0$ 3 then $(3\cos^2\theta - 1)$ is 2. And there is a value of θ for which this goes to 0 which is $\cos\theta = 1/\sqrt{3}$ for $\theta = 54.74°$. Also $\theta = \pi - 54.74°$ both of them for which this function goes to 0, and in between the $3\cos^2\theta$ is less than 1 therefore the function takes a

negative sign between these two 0s otherwise the function is positive. Let us see what the plot looks like.
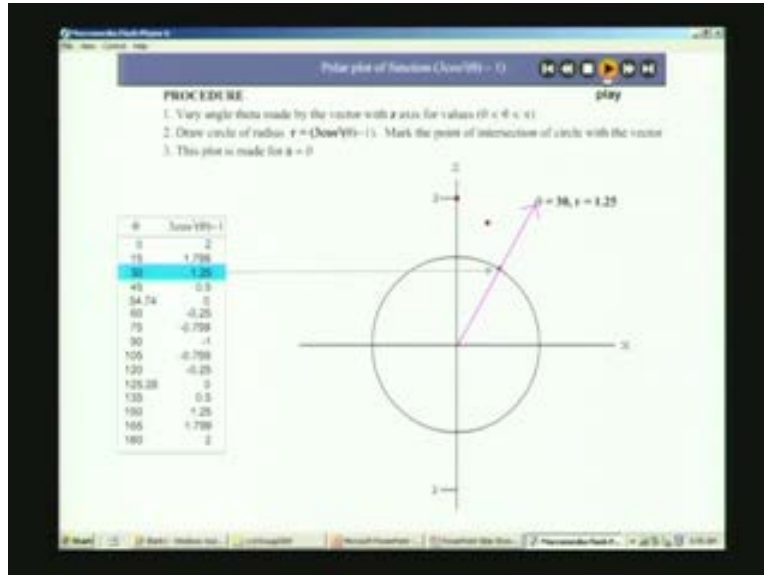
(Refer Slide Time: 38:12 min)
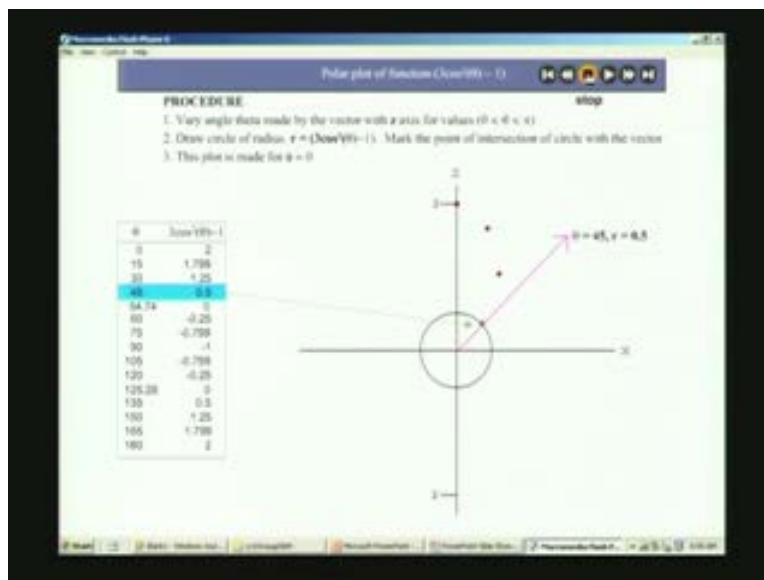

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The function is already 0 at this point, this angle θ is 54.74° and the function up to now is positive but now it becomes negative it increases and then goes back to 0 again.

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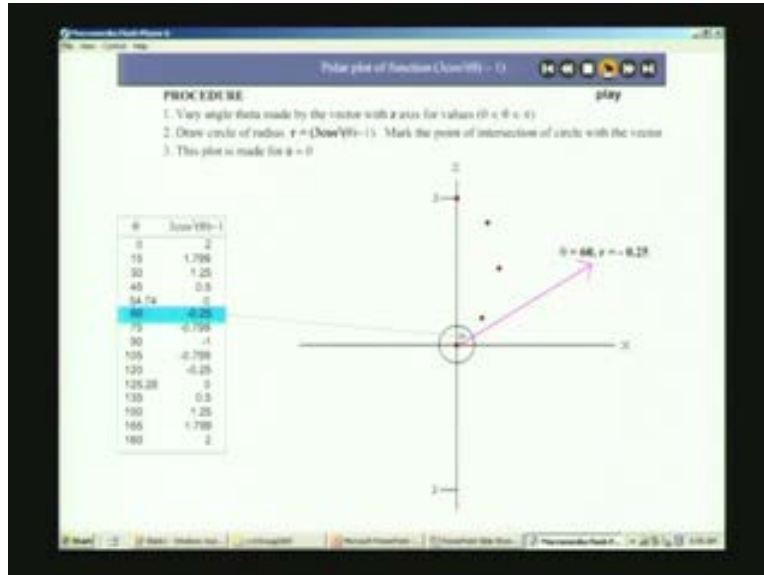
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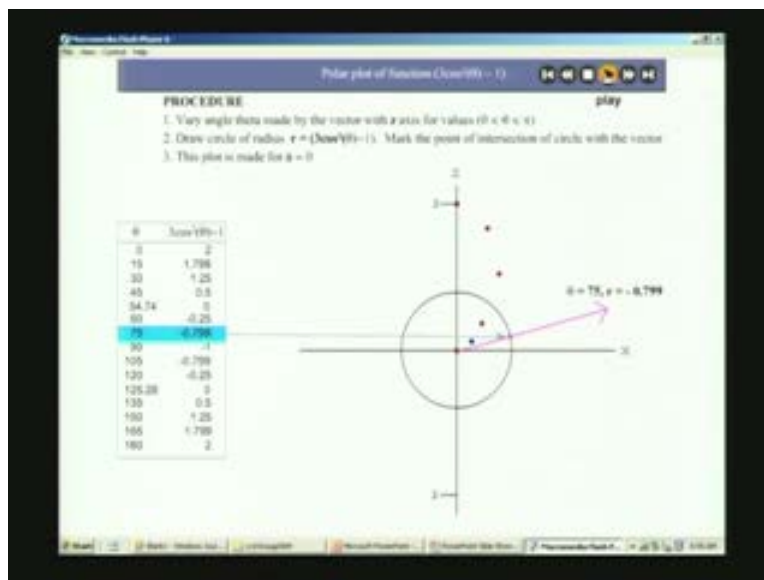
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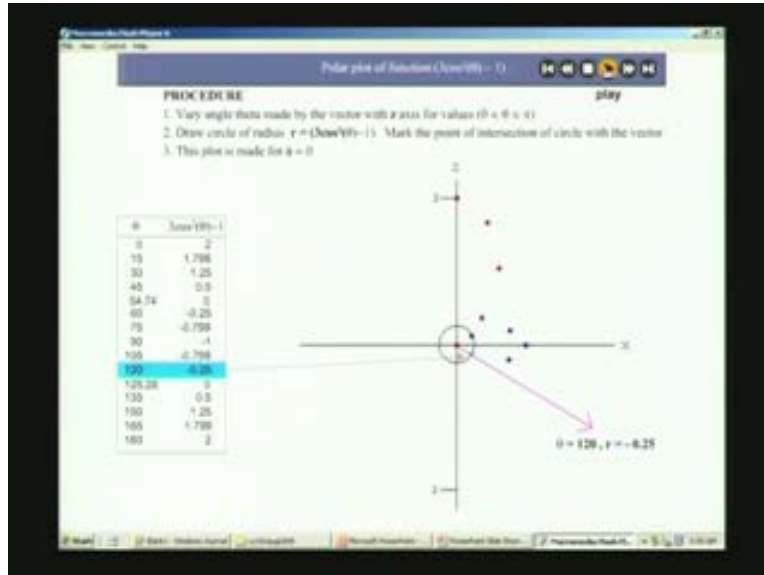
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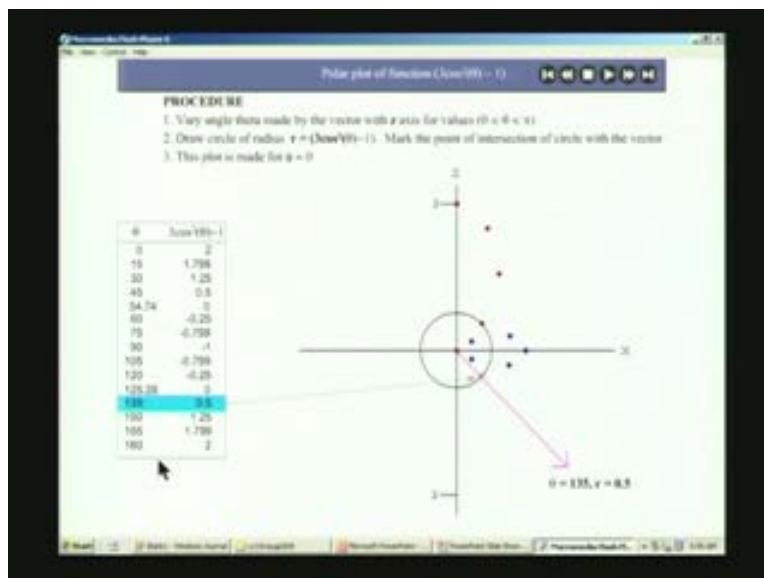
So let me complete this plot.

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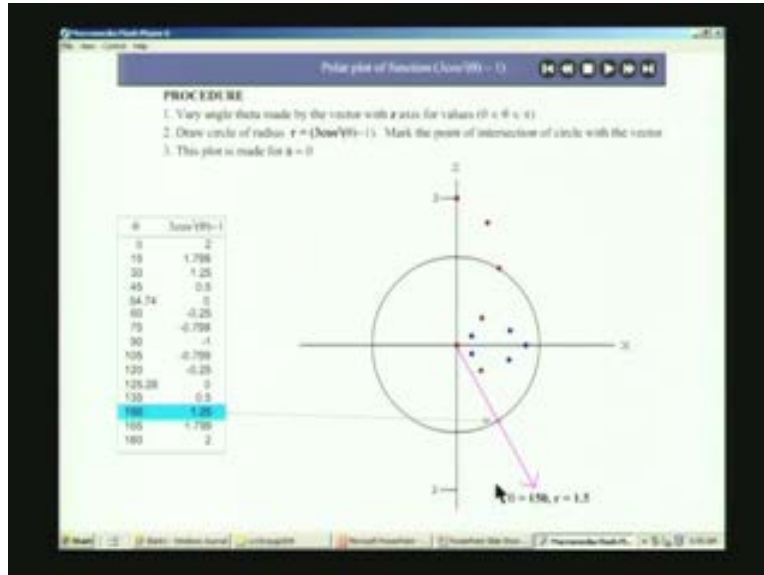
(Refer Slide Time: 39:10 min)
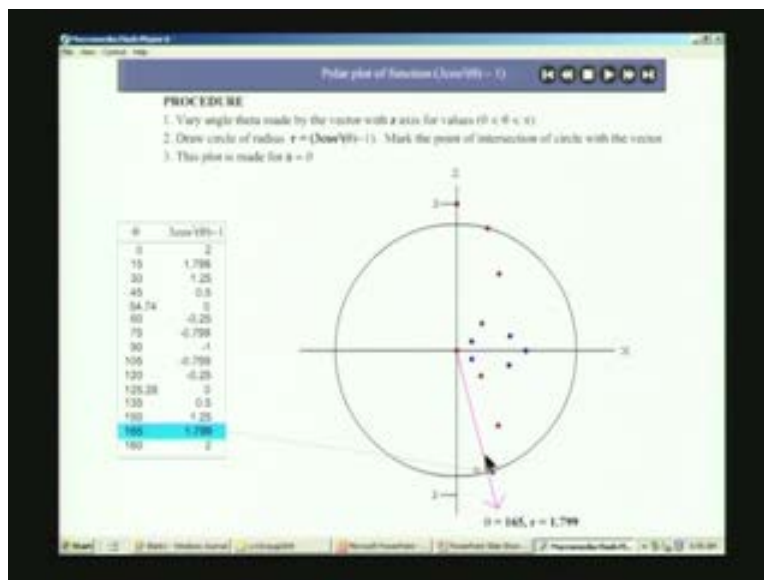
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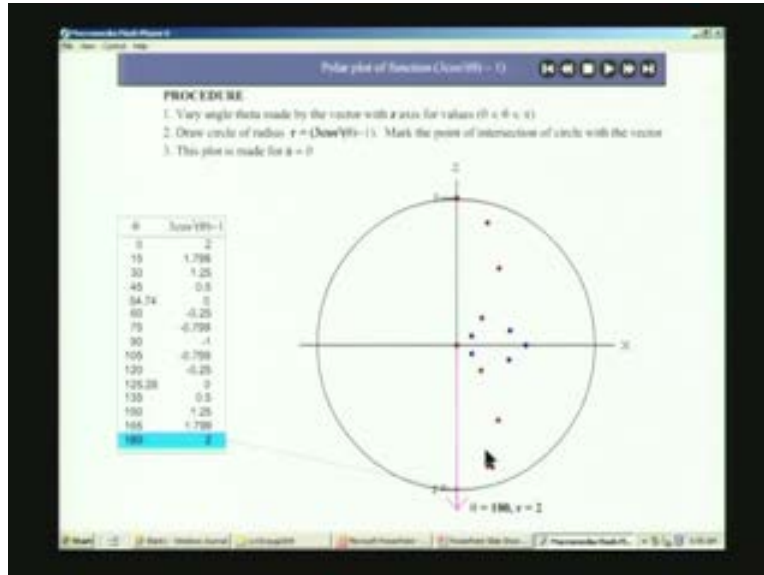
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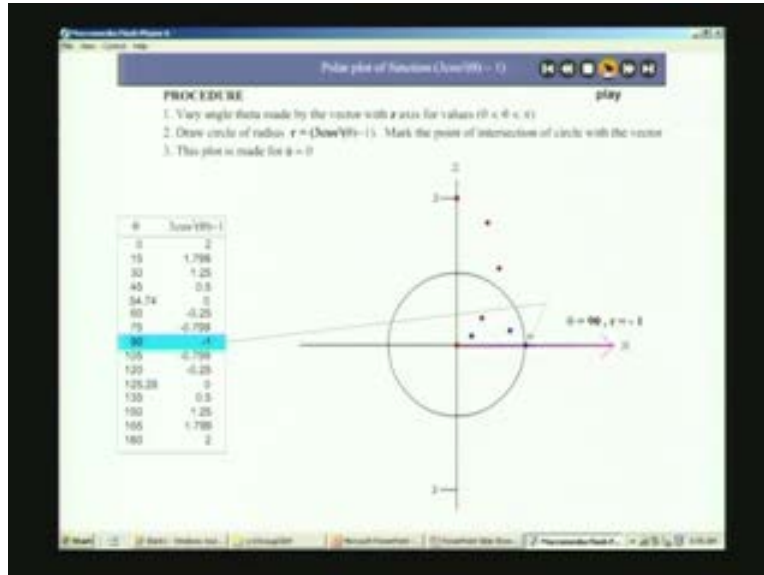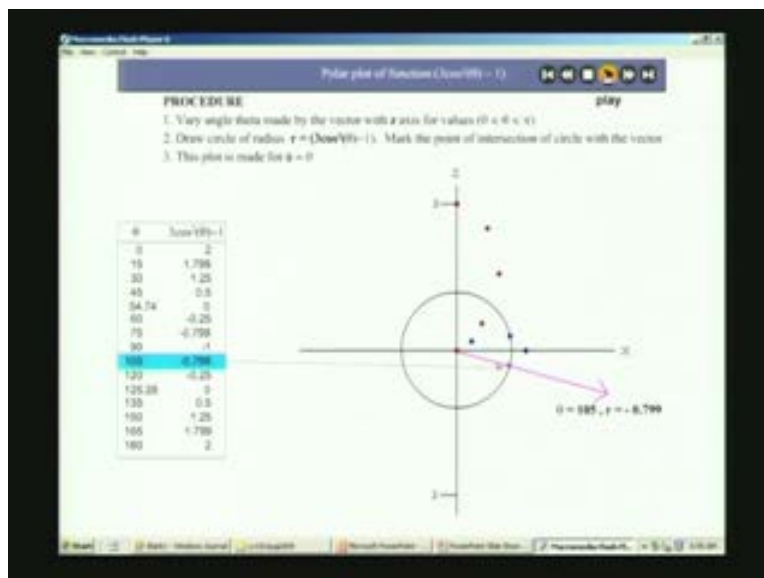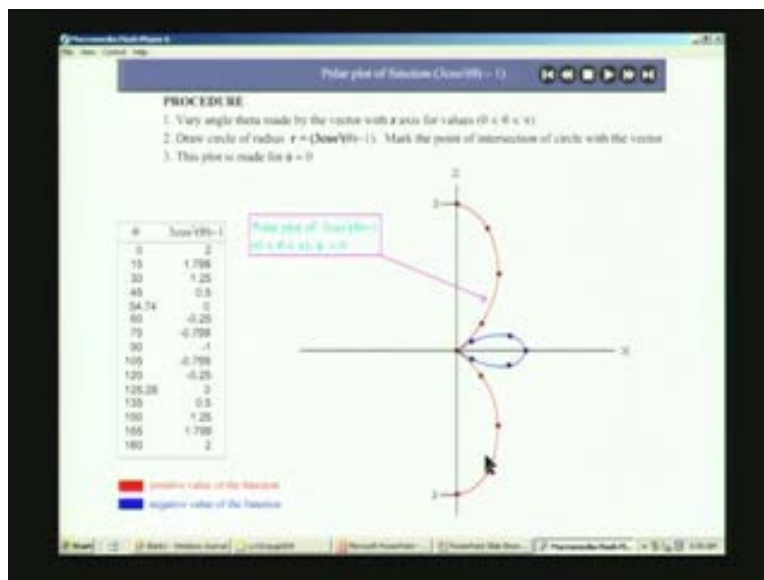The rest of the plot is identical to what we have on the top. So the function looks like, see the plot when you connect all these points the function goes to 0 then there is a negative part, there is a linear positive part and this is independent of ø therefore when you plot this in the three dimensional axis system $3\cos^2\theta -1$ in the spherical polar representation you get the picture that we saw in the beginning namely the lobes with a ring in the middle, ø independent so it is a same plot and we simply repeat that for all the values of ø.

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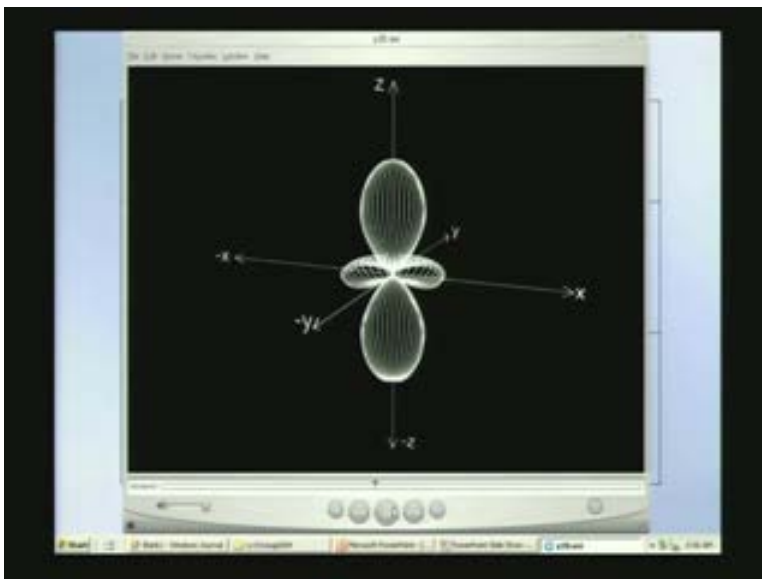
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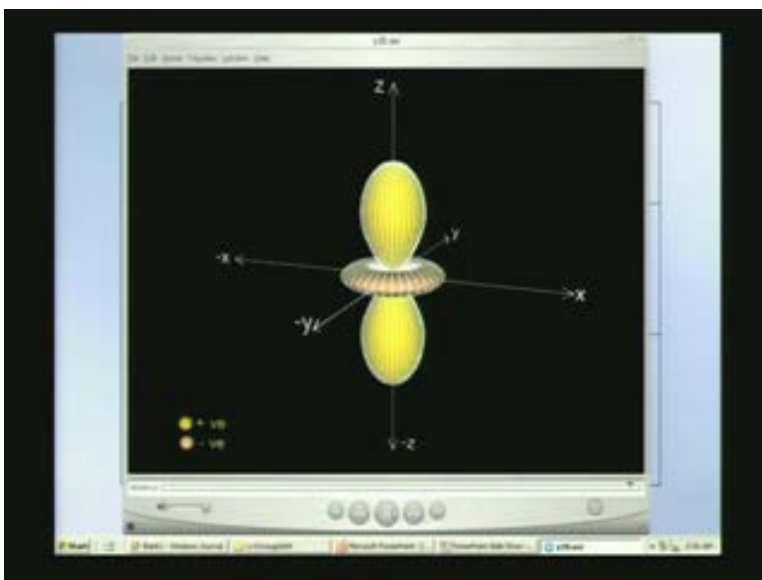
So you get two lobes and a ring in between. And the ring is negative the lobes are positive. Now, having done this if you go back and look at the $d_{3z^2 - r^2}$ orbital you see that this was a slightly different colored representation but you see that two lobes and the ring in between gave you how to build these functions from scratch once you know how to plot them in the polar graphs. (Refer Slide Time: 40:29 min)

All of the orbitals that you see as pictorial representations in textbooks in Quantum Mechanics textbooks and any Physical Chemistry textbooks which are called the orbitals are not exactly orbitals. But what you see are basically the angular functions, the real and the imaginary parts of

the angular functions being plotted on the polar graph. This gives you for a given radius r value how is the wave function distributed along its sphere. And the spherical polar coordinate system is a fundamentally useful coordinate system for hydrogen atom because the electron nucleus interactions is the same for any give distance irrespective of where that axis is or where on the sphere of radius the electron is moving around. But that is a classical picture.

One assumes the electron to be like a dot moving around a sphere having an interaction with the nucleus. Now that picture does not have any meaning the moment you associate a wave function with the electron through the solution of Schrödinger equation. All that you have is a function which itself not a very meaningful function because you know that wave function does not have an interpretation in Quantum Mechanics. It is the absolute square of the wave function calculated in a small region of space that is related to the probability that the system in that region, that is the only interpretation of this. So what is the meaning of all these plots and why should we go through representing functions so elaborately and so carefully when we know that in the end these functions themselves are a meaningless quantity.

The reason is, when you do the Quantum Chemistry when you want to see how the atoms react to form molecules and the atomic orbitals are interpreted as combining to give molecular orbital the linear combination of atomic orbital which is a procedure by which we understand chemical bonding requires us to understand the functional forms of these orbitals very clearly. One has to understand how a p orbital looks like.

One has to know a d orbital looks like from one atom to another atom and when the two comes together what kind of an overlap between these orbitals takes place. Chemical bonding is interpreted as nothing but the overlaps of the atomic orbital constructive overlaps. If the overlaps are destructive we do not call them chemical bonding but we call them chemical anti bonding. The interpretation of the molecular nature and the associations of atoms to form molecules go back to the use of these wave functions based on the hydrogen atom atomic orbitals.

A carbon atom nucleus of course does not have the atomic orbitals like that of a hydrogen atom. In the case of the hydrogen atom there is only one electron. When you go to carbon atom you have got six electrons and there is the electron repulsion. But then there are theories which build on these approximations and treat the atomic orbitals as useful and fundamentally important quantities from which you build the atomic orbitals of the other atoms and from which you also build the molecular orbitals of various molecules. In that sense, in understanding, visualization, a mental pictorial representation of the hydrogen atom orbitals is extremely important even though the functions themselves do not have a physical interpretation.

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The angular part	2D	3D
$Re\left[Y_3^1\right] = -\sqrt{\dfrac{35}{64\pi}}\ cos3\phi\ sin^3\theta$	Flash file	3D file
$Re\left[Y_3^2\right]$ $= \sqrt{\dfrac{105}{32\pi}}\ cos2\phi\ sin^2\theta\ cos\theta$	Flash file	3D file

We have to keep this in mind when we go through the Mathematics of all these things without deriving the Mathematics. We are treating this very carefully on waters whose depth we do not know but we want to understand how the surface looks like.

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Lecture Summary :

•Solutions for the angular equation

Plots of angular functions.

Let me summarize this part of the angular function and let me go back to the plots of the radial functions in a few minutes.

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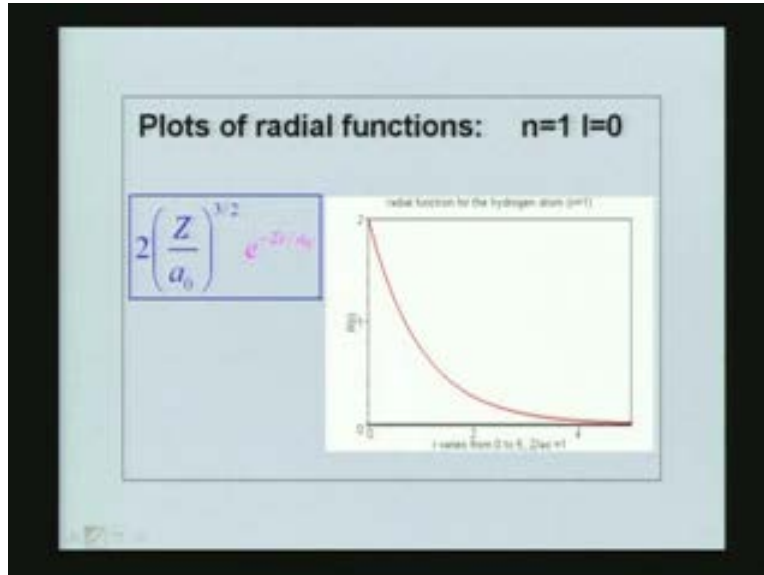
Now let us examine the radial part of the hydrogen atom solutions. The radial functions when we discussed the solutions for the radial part the radial functions were described for n as a principle quantum number for n = 1 that was one radial function, now recall the lesson about 1 ½ hours before th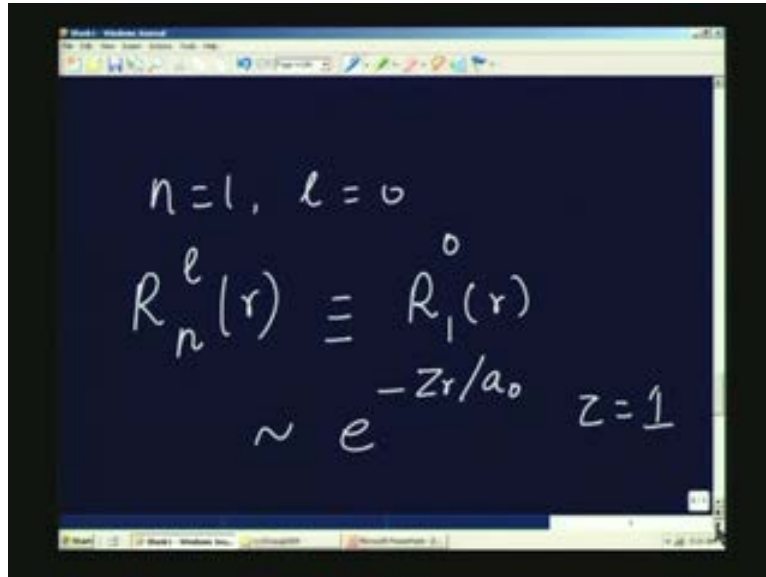is lecture for n = 1 there was one radial function and for n = 2 there were two radial functions namely with the quantum number l = 0 and l = 1. We have represented the quantum number l = 0 as the s orbital or spherical but ideally it is the labeled sharp chart and l = 1 also was a radial function for n = 2. (Refer Slide Time: 45:59 min)

When the principle quantum number the next number that n is 3 there were three radial functions and so on. So let us look at the functional forms of the radial function with the justification for the radial functions and the wave functions I gave a few minutes ago. The first one corresponding to n = 1 and l = 0 is a constant and let me read this out, it is the $\exp(-Zr/a_0)$. The n = 1, l = 0 the radial function is $R_n^1(r)$ and that is $R_1^0(r)$ is leaving the constants out, it is $\exp(-Zr/a_0)$, where Z is the charge on the hydrogen atom nucleus which is +1 and a_0 is the bore radius

a_0 has a constant value of 0.53 A° also known as the Bohr radius in honor of Neils Bohr whose discovery on the hydrogen atom was one of the most important developments in the history of Physics. Now, if you look at this form $\exp(-Zr/a_0)$, obviously r/a_0 is dimensionless it has to be dimensionless otherwise the exponential quantities do not make sense. So what you have is the radial functions decreases with respect to r like the exponential. This is what you see in the plot here it is an $\exp(-r/a_0)$. The function has the maximum value there is a constant in front of it therefore that takes the value and then it is a simple exponential decaying as r goes down goes to very large values. and you see that even though that r value in principle can take anywhere from 0 to infinity that is the radius of sphere can be from 0 to infinity you see that this functions drops by four to five atomic units here the function becomes negligibly small, it never reaches 0 until r goes to infinity but it is practically zero, for all practical purposes it is 0. So it does not mean that even though with respect to a hydrogen atom the electron has infinitely large dimensional degree of freedom that is radius can be 0 to infinity.

Now, you are in Madras and the electron coordinate in Los Angeles cannot be called as the electron belonging to the hydrogen atom in Chennai it does not make sense. Within three to four atomic units the wave functions are becoming more or less unimportant for this Mathematical limit to exist only as a Mathematical limit but with no real physical reasoning. So the value r is restricted for n = 1, l = 0 case to just about 2 to 3 atomic radii, what is the next one?

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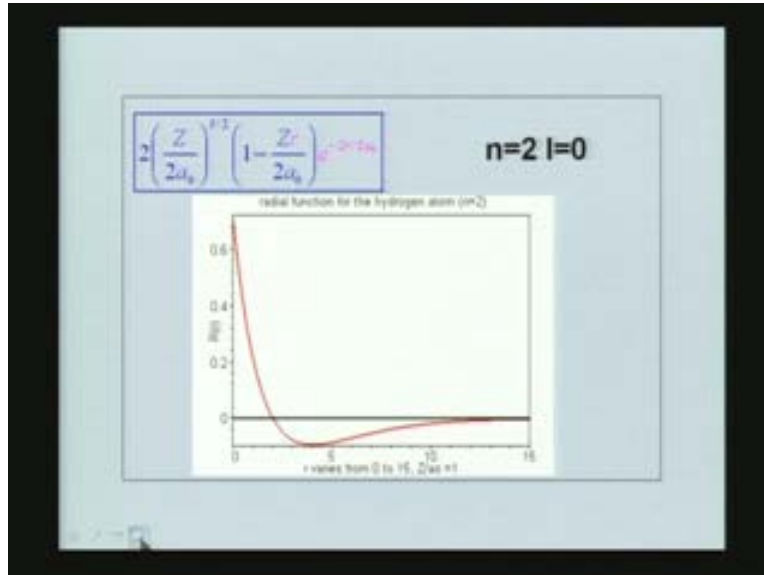
The next function for n = 2 and l = 0 the radial function is $R_2^0(r)$ is roughly $(1 - Zr/2a_0) \exp(-Zr/2a_0)$, do not worry about how we derive these things, this derivation comes from the solutions of the Laguerre polynomials which we did not solve we are only looking at the final solutions and trying to make sense out of it. So, again there is a dimensionless number here and then $\exp(-Zr/2a_0)$.

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In principle $R_n^1(r)$ will have an $\exp(-Zr/2a_0)$. So this number is indicative of what quantum number what atomic orbital that we are talking about where n = 1 corresponds to the shell k, l, m, n shells you might remember this the k shell, the l shell, the m shell and the n shell for the

hydrogen atom those are determined by the values of n. So $(-Zr/2a_0)$ tells you what shell you are in.

Now $R_n^1(r)$ looks like $(1 - Zr/2a_0) \exp(-Zr/2a_0)$ so what does it look like functionally when you plot them in a graph? The function has a graphical representation like this: at $r = 0$ and $(1 - Zr/2a_0)$ is 1and the exponential is 1 it is maximum and for as r increases for an intermediate value of r this function decreases but this is dominant in the beginning so it goes down and at the value $Zr/2a_0 = 1$ therefore this function goes to 0, this is called the radial node. Then for all the other values of r greater than this value the $Zr/2a_0$ is negative therefore the function is negative all along and eventually the exponential decreases much more than the increase here so the exponential eventually brings it to 0 that is from the most negative value to 0. You see that there is what is called a minimum and there is a node and this function has this feature.

The second radial function associated with n = 2 is the l = 1 case, the n = 2, l = 1 case the functional form is some constants $Zr/a_0 \exp(-Zr/2a_0)$. The functional form is $R_2^1(r) = Zr/a_0 \exp(-Zr/2a_0)$ obviously for r = 0 this goes to 0 and as r increases it keeps on increasing it is always positive but this keeps decreasing so there is a tug of war between the increase due to this r and the decrease due to the exponential and you see the graph.

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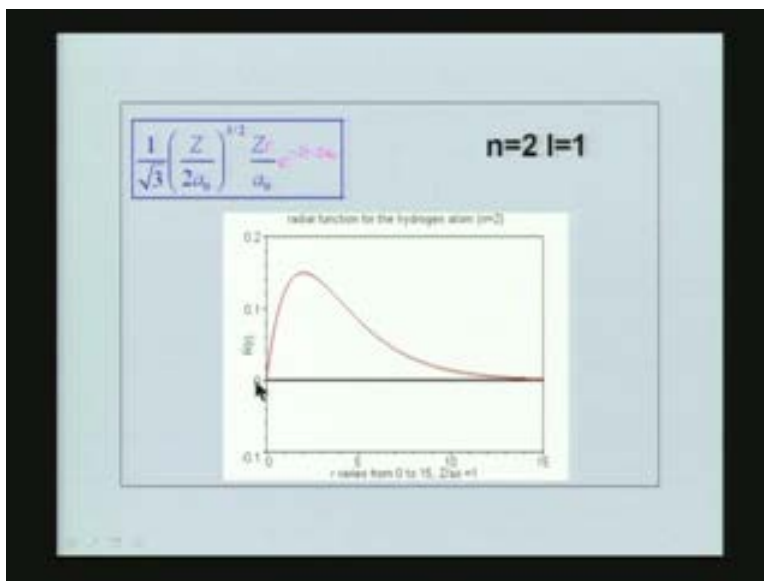
The graphical representation is that there is a maximum and then it goes to 0. Nowhere does it become 0 for any value of r in between 0 and ∞, there is no value there is node in between. The n = 3 radial function is somewhat complicated. Now one of the reasons why I did not want to derive all these polynomials is that the Mathematics is a separate course by itself, and what is important is how we interpret the algebraic results.

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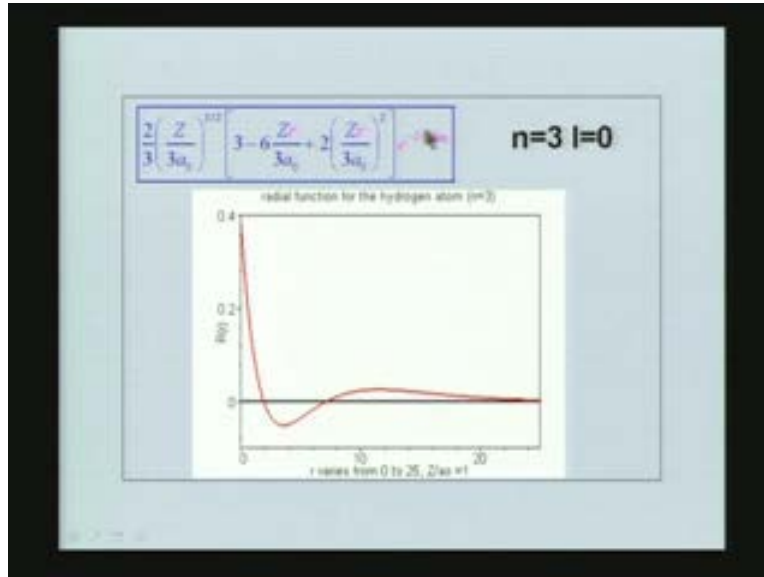
So $n = 3$, $l = 0$ is $\exp(-Zr/3a_0)$. And then there is a quadratic equation in front here is $[3 - 6(Zr/3a_0) + 2(Zr/3a_0)^2]$ so there is an r^2, r as a constant, so let me write that here in the generic form: $R_3^0(r)$ is $(a + br + cr^2) \exp(Zr/3a_0)$ where a, b and c are some constants in the form of quadratic in r. The quadratic has two roots and both of them are positive.

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The roots are such that you can write this as $R_3^0(r)$ as $(r - a_1)(r - a_2) \exp(Zr/3a_0)$ where a_1, a_2 are the first and second roots and then these are multiplied by $\exp(Zr/3a_0)$ such that $a_1 > a_2$. Now this is fairly clear as to how it should look when we plot them.

For all values of r less than the smallest of the two this is negative, this is negative, the product of the two negative therefore it is positive and this function is of course is always positive for all values of r which is from 0 to ∞ here (Refer Slide Time: 55:22 min) so the graph is positive from 0 to a_1, between a_1 and a_2 and greater than that the $(r - a_1)$ part is positive, $(r - a_2)$ part is negative and this whole is always unchanging in sign so what you have is at a_1 there is a 0 the function goes from positive to negative between a_1 and a_2 and for r greater than a_2 the function is again positive but at a_2 it again goes to 0.

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So there are two roots or two nodal points two nodes a_1 and a_2 are the two constants the two roots of that quadratic equation that we have here and for this the function is 0 but the radial function is positive, negative and then it goes to 0 because the exponential becomes dominant and it kills everything else, no matter what the increase is the exponential decrease kills any finite power to n so the radial function that you have has two nodes and alternates for $n = 3$, $l = 0$, let me just do the two other cases quickly and then conclude the lecture.

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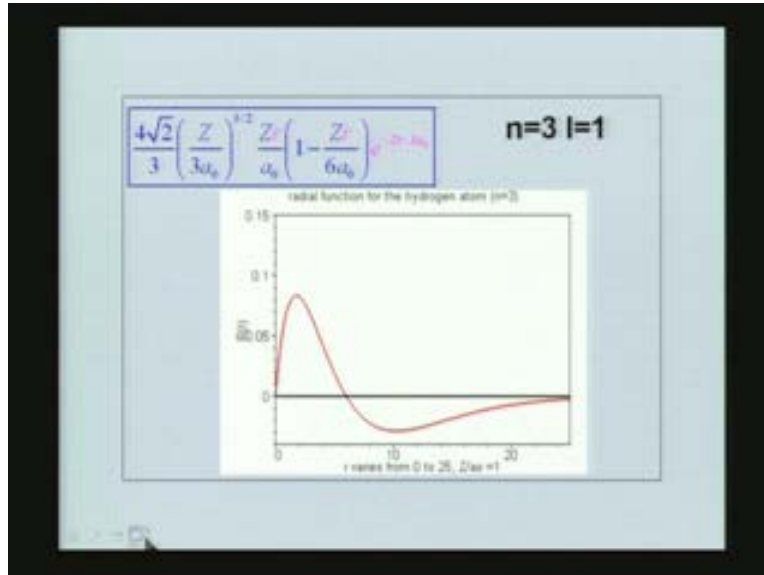
For n = 3, l = 1 it is easy from the functional form Zr/a_0 $(1 - Zr/6a_0)$ times $\exp(Zr/3a_0)$ that this has only one root and it starts from 0. Therefore you see that from 0 to reaches the maximum and then goes to 0 at $(1 - Zr/6a_0) = 0$ and then it becomes negative and it goes to 0 for very large values.

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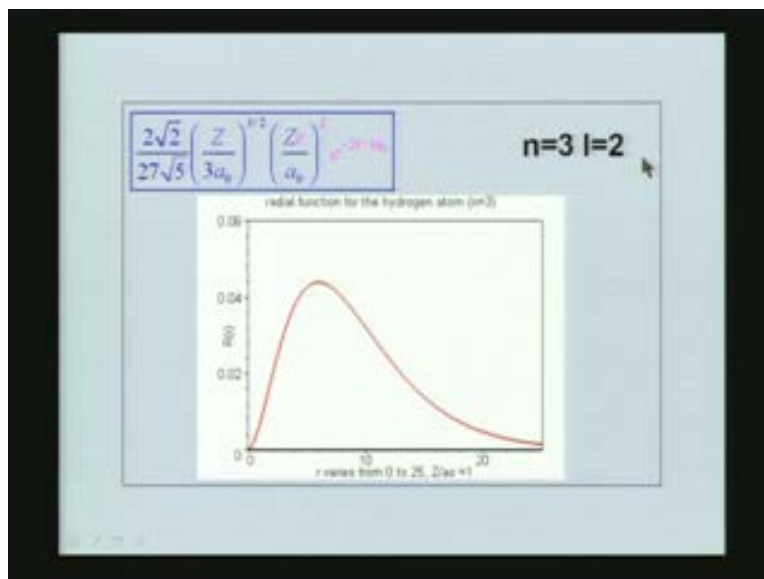
The last for n = 3, l = 2 you see that it is simply $(Zr/a_0)^2$ $\exp(Zr/3a_0)$ it never goes to 0 for any value other than 0 and ∞ so it is a simple node. Now, let us keep these things in mind, again the question will come in that for some values of r the radial function starts from r = 0, so r = 0

means what? It is the nucleus, that does not mean that the electron is there in the nucleus in the region where the nucleus is, r = 0 sometimes the function is 0 so what do these things mean?

Again the same answer, the wave function themselves do not have any interpretation when we take the absolute square of the wave functions all these conceptual difficulties we have with the wave functions will disappear and we will continue this in the next lecture where we will complete all these basic ideas about the wave functions as well as do some numerical calculations on what is called the electron probabilities, the electron distances, the average distances, the distances of where the electron probability is maximum and so on, until then thank you very much.