Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 17
The quantum mechanics of Hydrogen atom – Part IV

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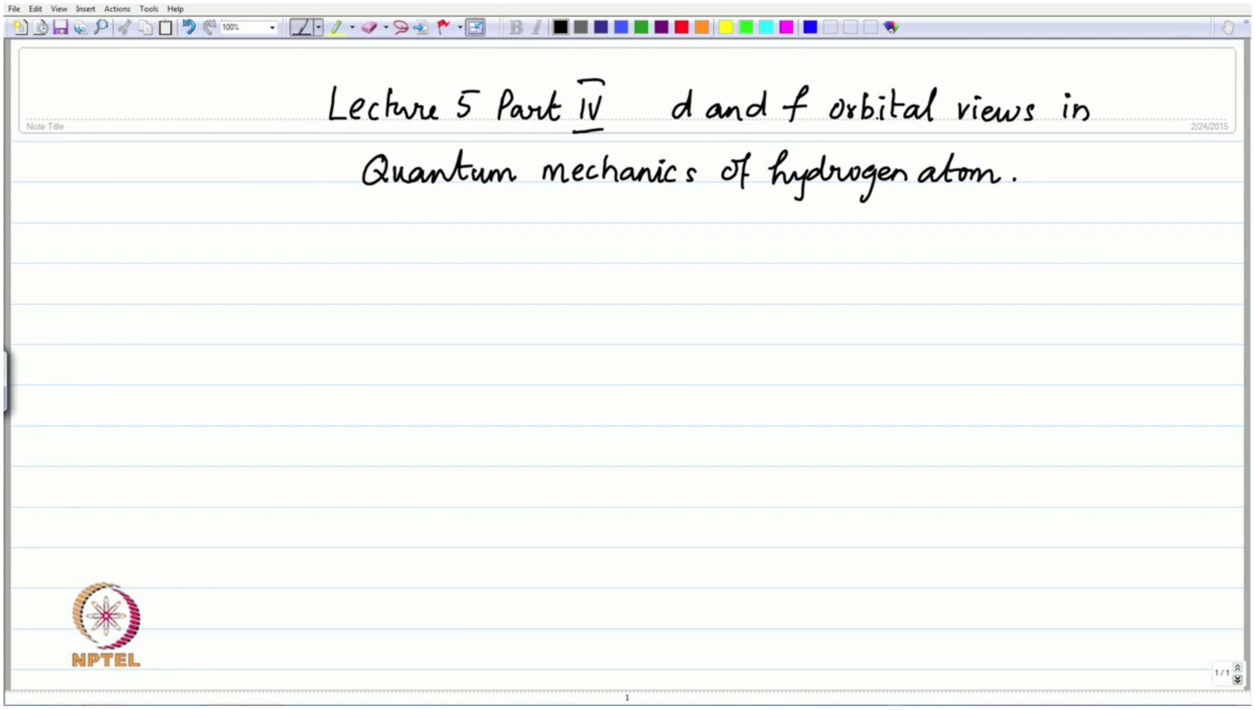
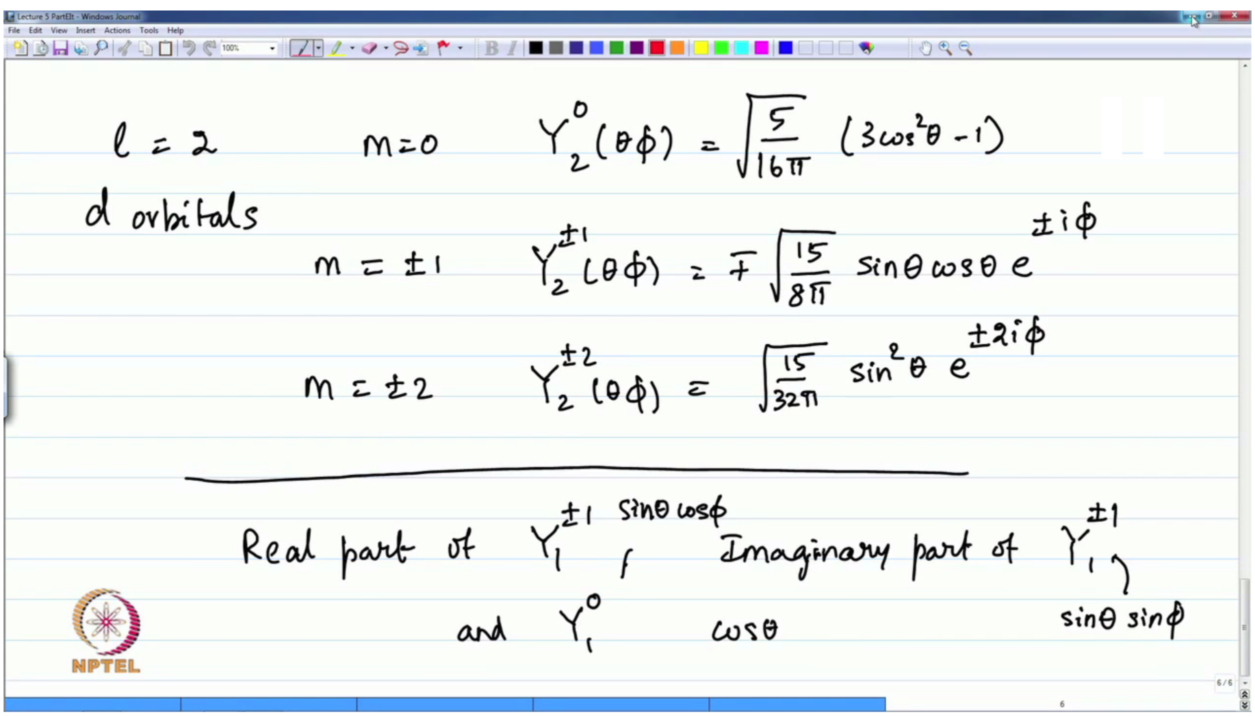
Prof. Mangala Sunder Krishnan: Welcome back to the lectures on the hydrogen atom. The lecture today is on the animated view and visualization of the D and the F orbitals. As I said in the part of the last lecture, this is purely a visualization for some of the orbital or some of the angular parts of the orbital. D orbitals and F orbitals are quite interesting for the molecular systems, particularly for the atoms in 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 ligands and the orbitals of the -- energies of the orbitals, you can see why the conclusions are important.

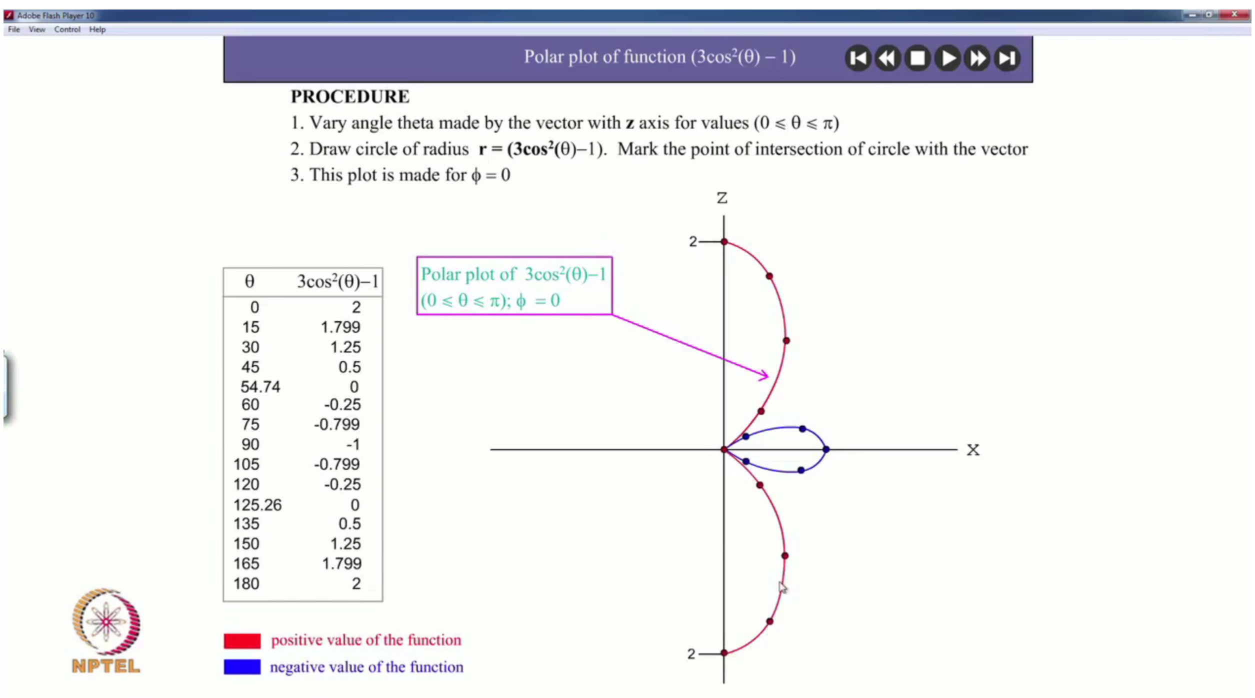


So let me start by recalling what the D orbital angular part of the function is. This is the part four of the lecture on the D and F orbital views in quantum mechanics.



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 ±1 or ±2 and the spherical harmonics. Second rank tensor with the spherical component 0. I've 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 all and understand them, but please take it from me that these are second-rank tensors representation in a spherical coordinate system with the component in the spherical coordinate system being 0 or ±1 or ±2, okay. Now that's the mathematics.

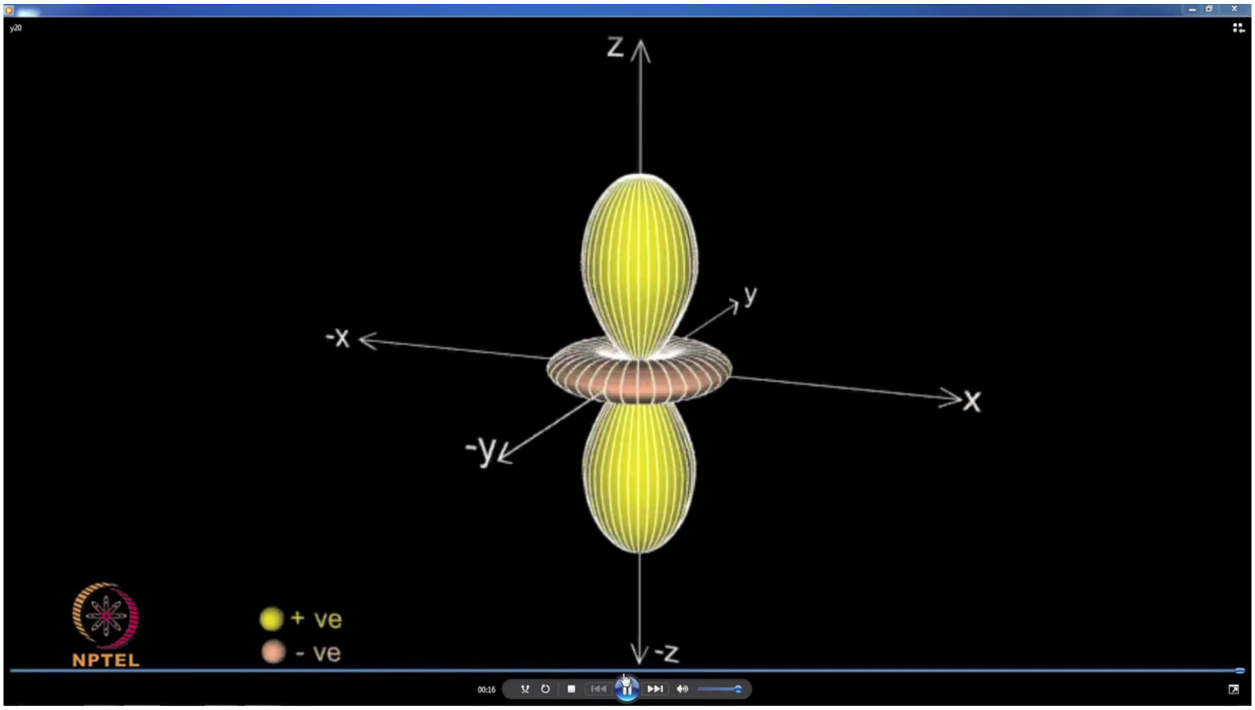
Now the circle harmonics Y 2,0 has the functional form ($3\cos^2\theta$ - 1) and m being 0, it does not have a φ dependent part, the exponential $e^{im\varphi}$ gives you 1 because m is 0, okay. The Y 2, ±1 (θφ) is quadratic in the trigonometric functions sinθ cosθ and if you think of (3cos2θ - 1), 1 is nothing but sin2θ + cos2θ. Therefore, this function is actually $2\cos^2\theta - \sin^2\theta$. So it's a homogeneous function, trigonometric function of order 2. And this is order 2 sinθ cosθ, but ±1 means exponential $e^{i\varphi}$ is ±iφ and likewise ±2 for the Y 2,2 tells you that the angular part has a trigonometric function, which is $\sin^2\theta$ and a φ dependent function, which is exponential $e^{\pm 2i\varphi}$, okay. We shall plot one or two of these, and let us start with the picture for Y 2,0.



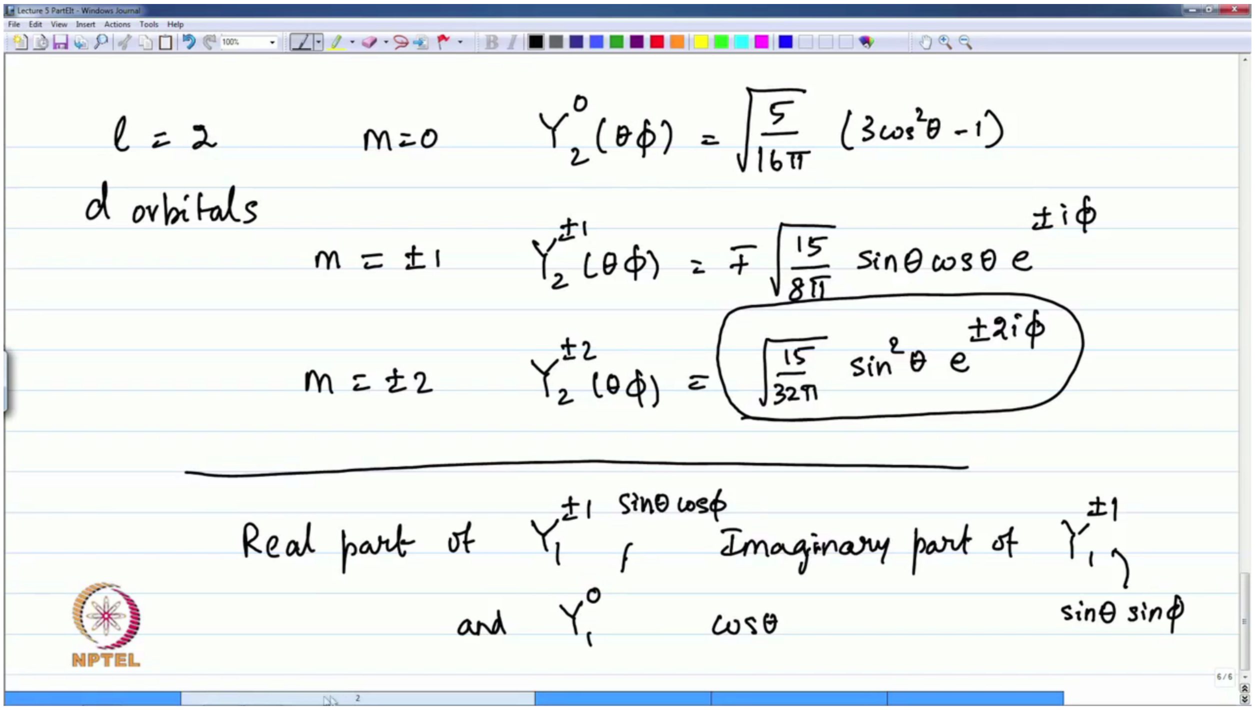
So this is ($3\cos^2\theta$ -1). I mean I'm leaving out what is called the pre-factor the normalization factor and all those things. I mean they will only change the extension but the shapes will remain the same. Therefore, we will keep ($3\cos^2\theta$ - 1) and we want to plot this in the polar system with the θ axis going from 0 to 90 to π to 180 degrees. The values of ($3\cos^2\theta$ - 1) for various values of θ are given here in this table, and you can see that ($3\cos^2\theta$ - 1) goes to 0 at $\cos\theta = \pm 1/\sqrt{3}$. Therefore, you see the $+1/\sqrt{3}$ corresponds to $\theta = 54.74$ and the $-1/\sqrt{3}$ corresponds to $\pi-\theta$ and that is 180 - 54.74, which is 125.26. In between 54.74 and 125.26 $(3\cos^2\theta - 1)$ is negative, because $\cos^2\theta < 1/3$ and at 90 degrees this is 0, therefore, this whole function is -1, maximally negative, okay.

So from the magnitudes given here, the variation is between 2, 0, -1, 0, 2. Let's see the function plot. Remind yourself that we are plotting the value of $(3\cos^2\theta - 1)$ one on the radius that makes an angle θ with the Z axis. That's a plot, please recall that. So at 54.74, it goes to 0 and then the function is negative so I have a different color for the points with the blue dots and that's -1, exactly half of the height. Again, the function goes back to 0 and starts increasing to larger values and reach 2.

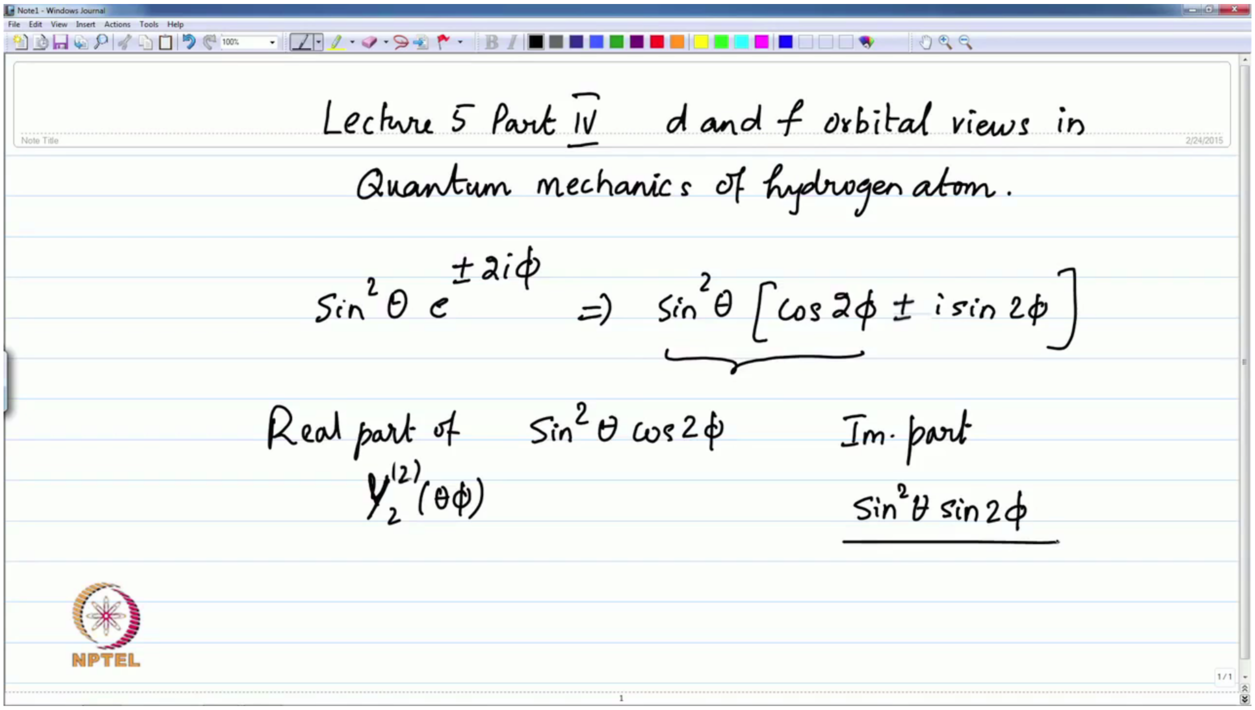
So the graph is drawn by following the θ values namely θ = 0 up to 54.74 and then between 54.74 up to 126.26, and then for the increased value of θ you have. So this is a continuous plot.



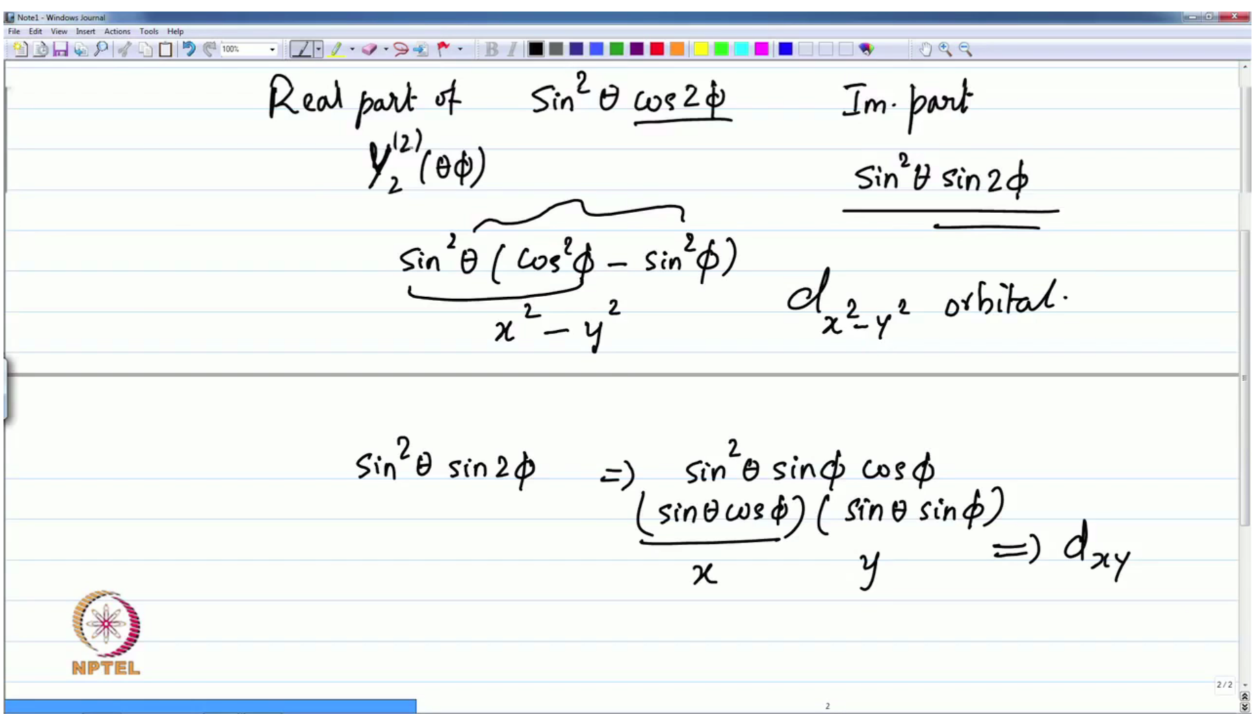
Now this is φ independent, therefore, it's the same plot for all values of φ, because the function is φ independent. Therefore, for 0 to 360 degrees, you get the familiar picture of the D orbitals with two balloons connected to each other by the ring in between and in some pictures you might see that the ring is standing out and the balloons are not touching the ring, but that's wrong. This is the mathematical representation. The ring is tangential at 54.74 top the plus part and also at the bottom 125.26 it is tangential. Therefore, you see that this is a continuous surface. This is the D orbital, which you call as the Dz^2 orbital sometimes. As you might find in textbooks, but it's essentially $3z^2 - r^2$ and we have not considered the r, we had only worried about the fact that $(3\cos^2\theta - 1)$, okay. So it's easy to visualize.



Let us take m=±2 and find out what this picture is, ±1 in a similar way you can find out yourself. ±2 contains an imaginary -- there is a complex part. So let me get my function into real and imaginary parts and let me leave the $\sqrt{15/32\pi}$ for the moment, we don't need to worry about that.

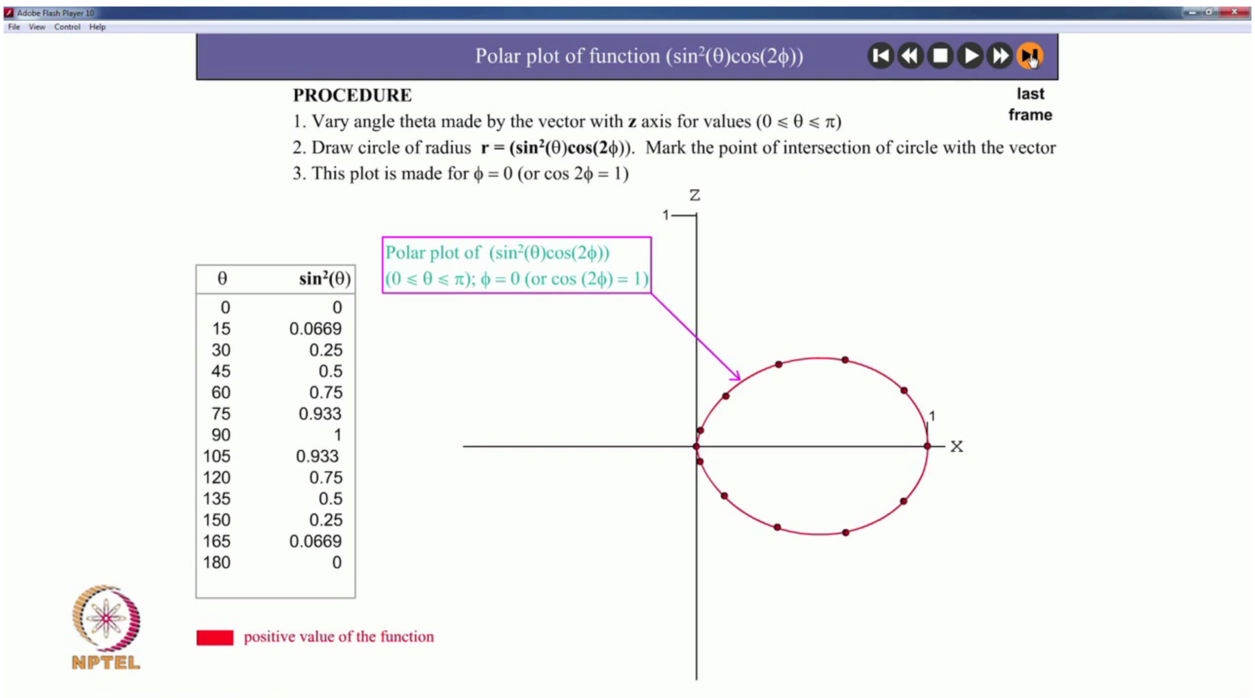


So we have $\sin^2\theta\, e^{\pm 2i\varphi}$, which is $\sin^2\theta\,[\cos 2\varphi \pm i\sin 2\varphi]$ and the real part is $\sin^2\theta \cos 2\varphi$, this is the real part of Y 2,2 (θφ). The imaginary part is leaving the i out. Obviously, the imaginary part is $\sin^2\theta \sin 2\varphi$, okay.

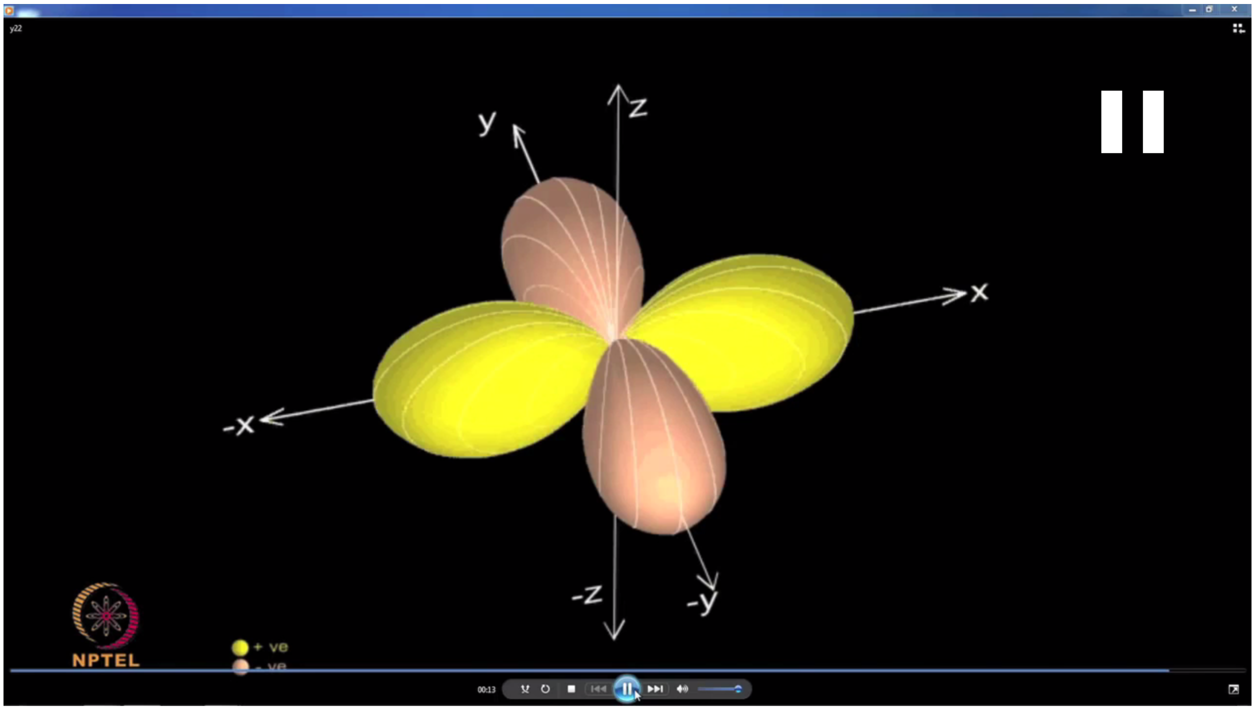


Recall that cos2φ -- so this function is $\sin^2\theta\,(\cos 2\varphi - \sin 2\varphi)$ and remember sinθ cosφ is like x, therefore, this is x^2 and sinθ sinφ is like Y, and therefore, this is $-y^2$. So this part is often referred to in your textbooks as dx^2-y^2 orbital. And in the same way if you look at $\sin^2\theta \sin 3\varphi$, this is barring the numbers out I mean there's a 2 here, but what is important is it's $\sin^2\theta \sin\varphi \cos\varphi$, which is ($\sin\theta \cos\varphi$) and s($\sin\theta \sin\varphi$) multiplied to each other. So remember this is x and this is y. So this is often the dxy orbital that you see. And you see the difference between the two functions is essentially the difference between $\cos 2\varphi$ and $\sin 2\varphi$, okay.

$\text{Cos}2\varphi$ and $\sin 2\varphi$ differ by $\pi/2$ or $\pi/4$, if you change φ by $\pi/4$ $\cos 2\varphi$ becomes sin2phi. Therefore, you see that whatever the shape that you will have for dx^2-y^2 will be only rotated by 45 degrees to get the shape of the $\sin^2\theta \sin 2\varphi$ that is the dxy. We will see that.

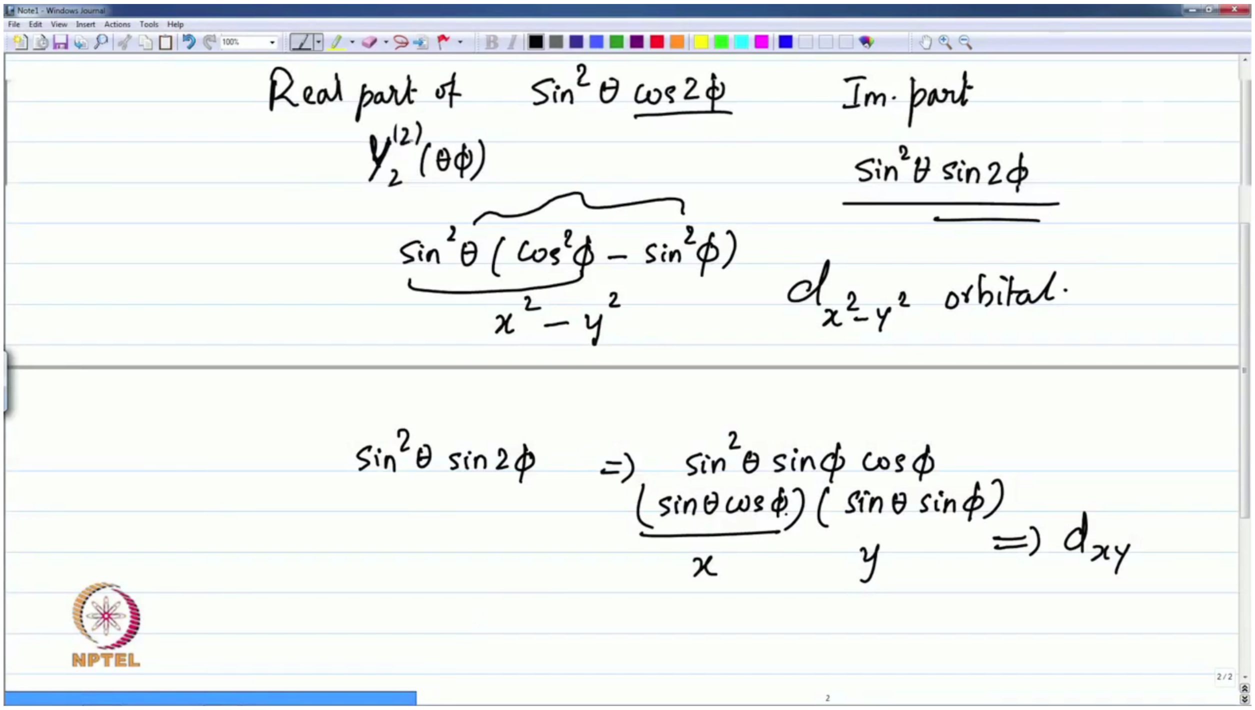


So let's start with the real part for the D orbital, the $\sin^2\theta \cos 2\varphi$, and since $\varphi = 0$ gives you $\cos 2\varphi = 1$, and therefore, you get the maximum value for $\sin^2\theta$. Let's plot it along the X axis and then plot it for various values of φ in going around, so that for each value of φ, the $\cos 2\varphi$ multiplying $\sin^2\theta$ will change the shape to get you the full three-dimensional picture, okay.

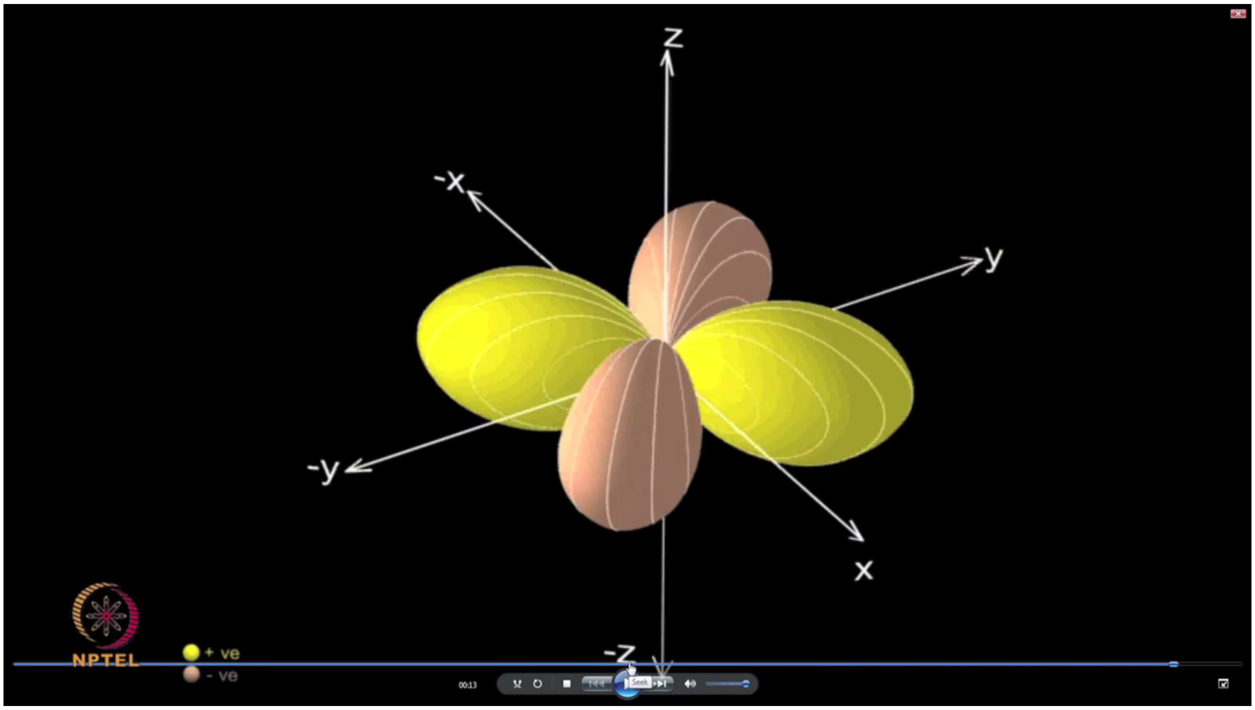


This is $\sin^2\theta$ with $\cos 2\varphi = 1$. I don't have to go through this. Let me go to the last frame, that's what you will get, okay. If you want to play around and stop and see that it plots the right thing. This is $\sin^2\theta$ and then what you have is this is modulated by $\cos 2\varphi$ and it's modulated by $\cos 2\varphi$ with $\cos 2\varphi$ being 1x where φ is 0, $\cos 2\varphi$ being -1 at y where φ is 90. So in between $\cos 2\varphi$ goes to 0 namely at $\varphi = 45$. Therefore, this graph goes to 0 at 45 and then it increases, but becomes negative, because $\cos 0\pi$ is negative in that quadrant, in that part of the -- in that range of φ. And then when it comes to -x axis, this is 135 somewhere around. Again, $\cos 2\varphi$ goes to 0 at 135, but when φ is greater than 135 and 180 and 225, $\cos 2\varphi$ goes to positive values. See for yourself.

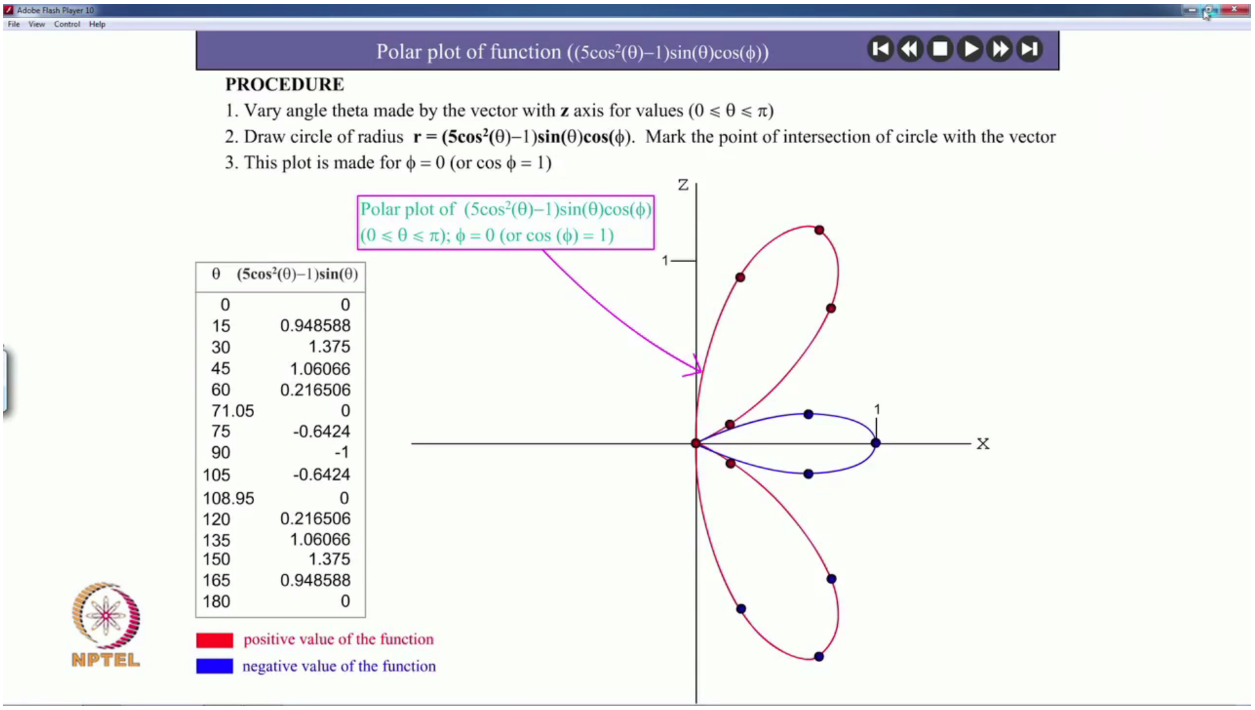
So that's essentially how we picture so you see the picture of the $dx^2=y^2$, which is a pair of lobes along the x axis as well as along the y axis, but with opposite signs, because of the $\cos 2\varphi$ modulation 2φ modulation, and this is an even function, you can see that. The x and -x, y and -y, they both have the same sign, okay.



Now what about the other function? The other function is (sinθ sinθ) (cosφ sinφ), therefore, it’s $\sin^2\theta$. So the plot of $\sin^2\theta$ is the same as what we had before, but since it is (cosφ sinφ), we don't want to plot it along the x axis because it's obviously 0 at φ=0. You can see that it is a maximum at φ = 90 -- I am sorry at φ = 45 not 90, because at φ = 45, cosφ is 1/√2, sinφ is 1/√2, they both have the same value. Therefore, you see this function actually is between the two axes, it's not split by the axis. At both the axis the function is actually 0, because φ is 0, φ is 90, φ is 180, and then φ is 270. So on all the axes, the function goes to 0, but between the axes the function goes to a maximum from 0 to 45 and then it goes to 0 from 45 to 90 and so on.

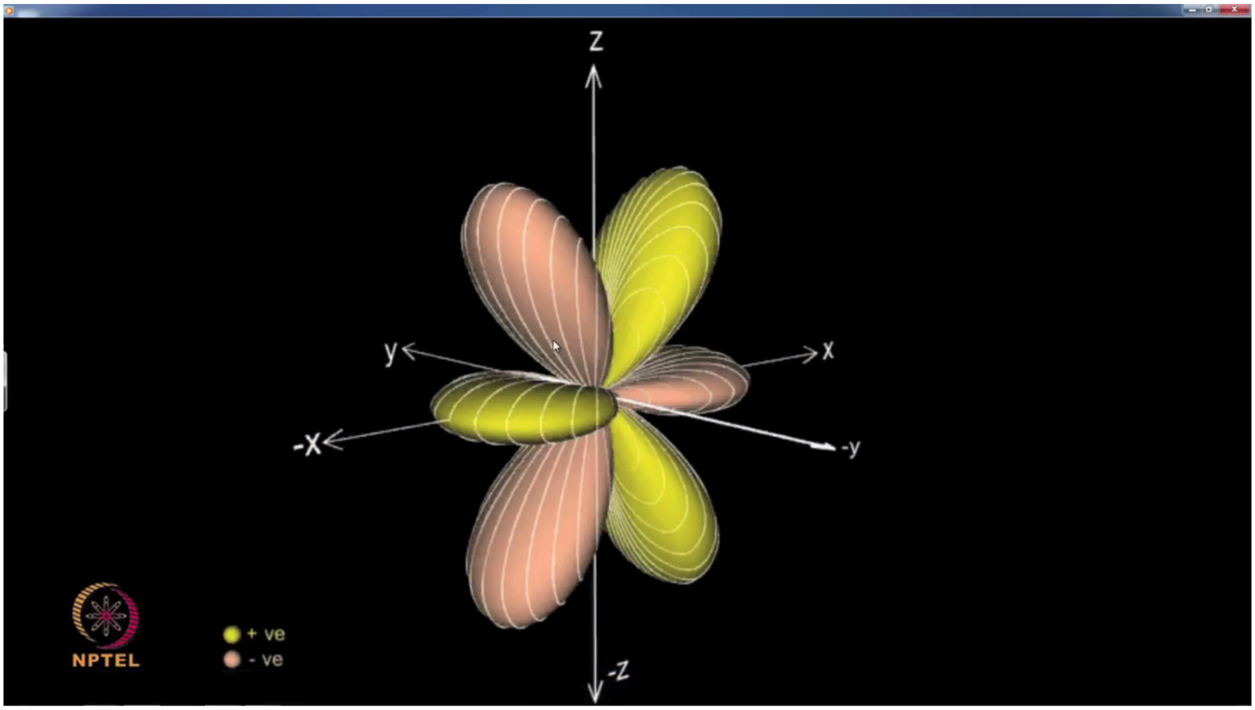


So the picture, you can see that the picture starts with the middle of the axis, at x it is 0 and at y also it is 0. So the bulk of the picture, bulk of the shape is in between the axis and it's only a 45-degree tilt, because the difference between the dxy and dx^2-y^2 is a 45-degree angle. So the shapes are determined by the way we represent the mathematical functions and then the way we plot them in a spherical axis system and the spherical polar coordinate system. So these are for the D orbitons.

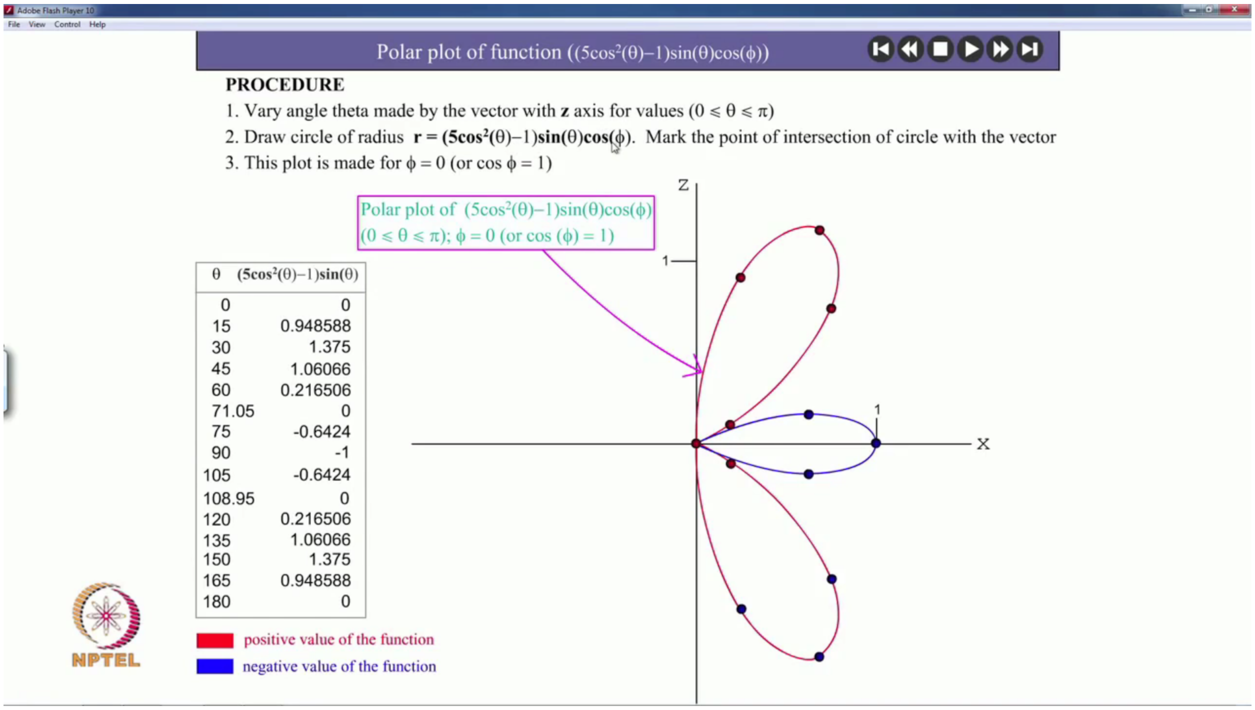


I'll show one F orbital as I mentioned in the last lecture, and then we will leave the rest to be seen by you, okay. The function Y 3,1 is $(5\cos^2\theta - 1)\sin\theta \cos\varphi$. This is a trigonometric function, homogeneous function of order 3, because 1 is nothing but $\sin^2\theta$ and $\cos^2\theta$ so it is $(4\cos^2\theta - \sin^2\theta)\sin\theta$, so everything is cubic, times $\cos\varphi$, and therefore, for φ, $\cos\varphi$, and therefore, for φ, we have chosen the value 0 that this is maximum, and so what you see is the plot of $(5\cos^2\theta - 1)\sin\theta$ on the polar coordinates.

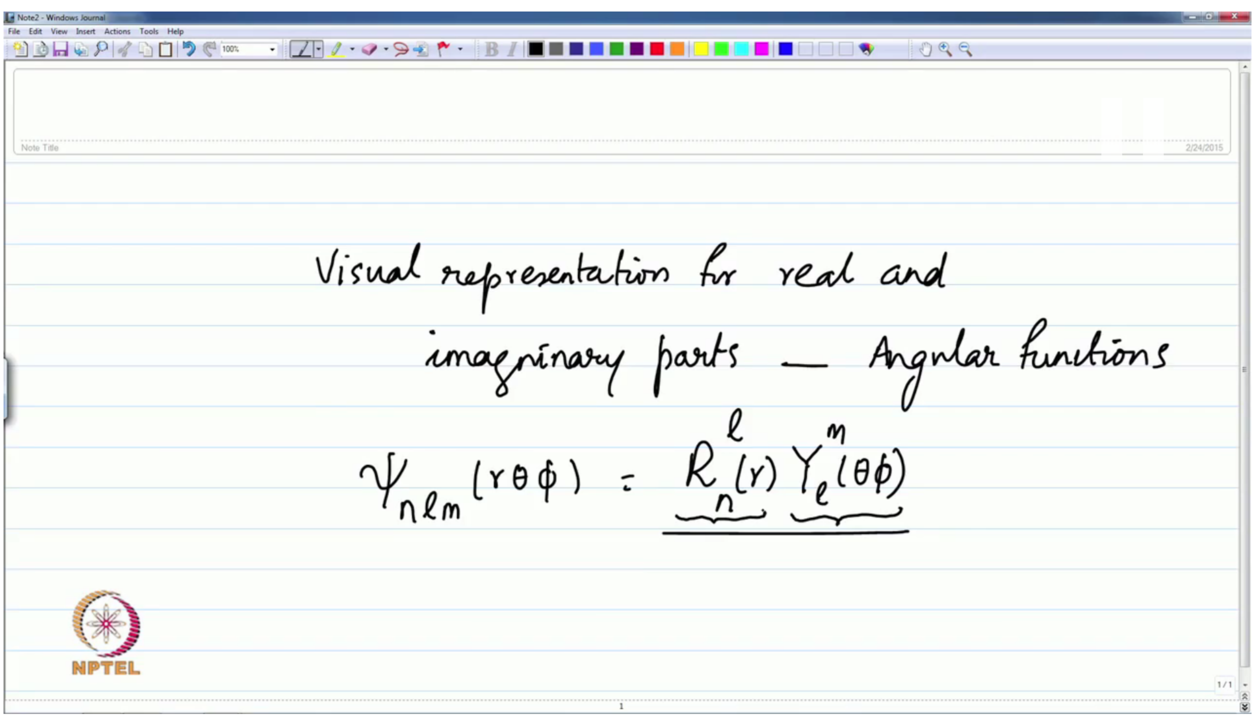
You can see that it goes to 0 at three places, $(5\cos^2\theta - 1)$, this is -1 when cos θ is 0 and this is again $(5\cos^2\theta - 1)$ that's 0, and at 180 degrees also, it is zero because there is a function $\sin\theta$. Therefore, the plot looks like the shape, you start from zero, as the θ value goes this way, the function increases to this point, and then as the θ becomes more and more, the function comes to 0, and then the function goes to this value and it comes back to this, and this is multiplied by $\cos\varphi$, 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 $\cos\varphi$.



So if we look at the cosφ part together, the modulation that you see is followed by that followed by that, but now in the whole φ 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, its opposite on this 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 5, it has the equation $(5\cos^2\theta - 1)\sin\theta\cos\varphi$. The $\cos\varphi$ comes from the real part of exponential $e^{i\varphi}$, therefore, what you see is this is Y3r -- this is 1 and if it is multiplied by $\sin\varphi$, that is Y3 - 1.



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 ψ_{nlm} (r,θ,φ) is the radial R n,l of (r) Y l,m (θφ). So what you have seen is only the visual representation 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. Until then, thank you very much.