Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 16
The quantum mechanics of Hydrogen atom – Part III

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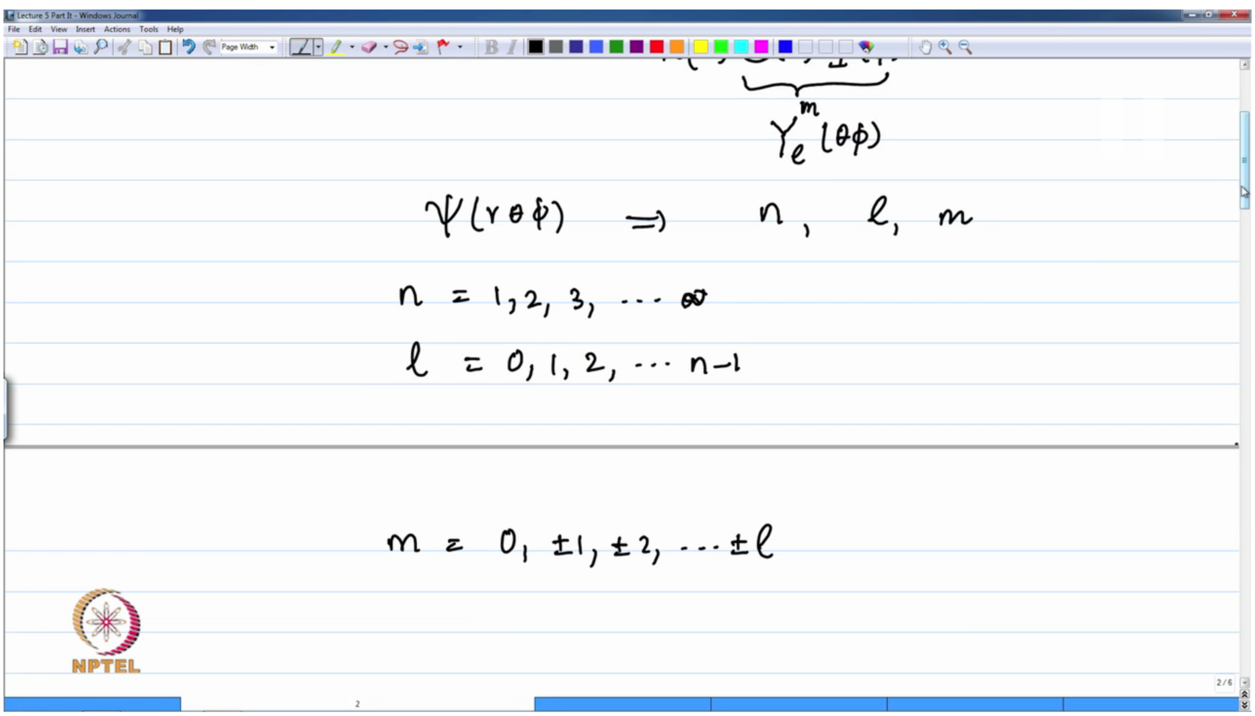
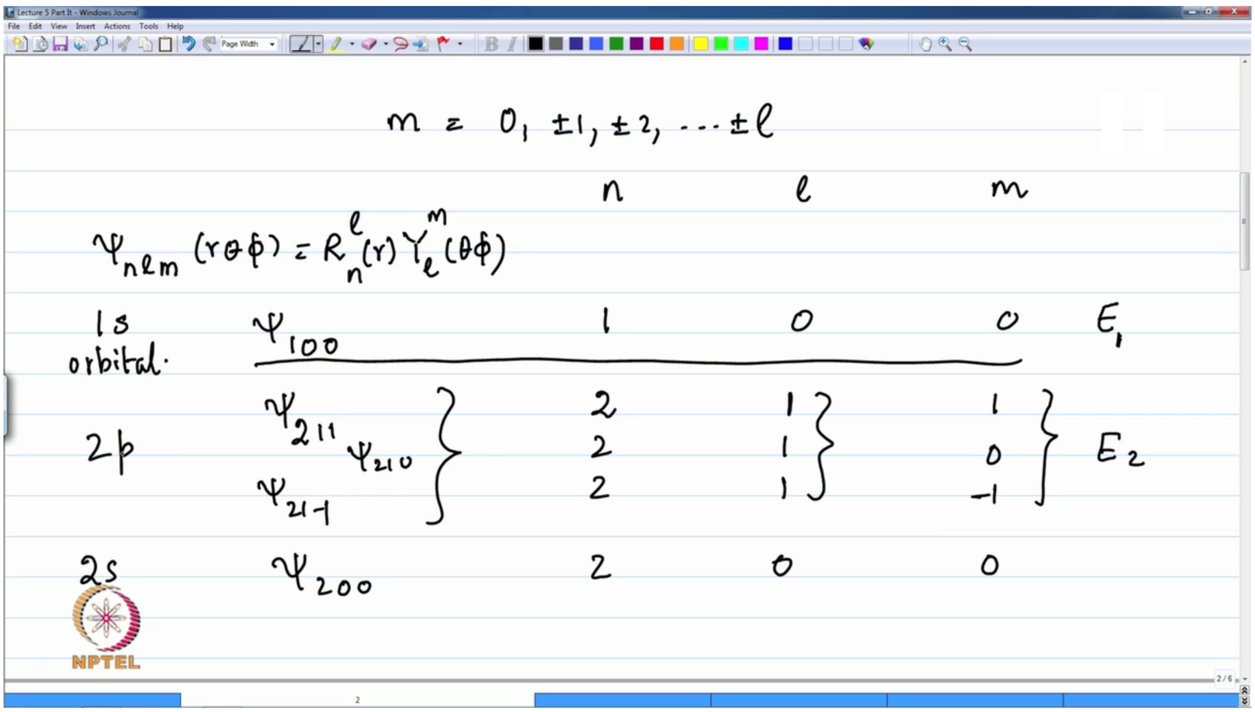
Prof. Mangala Sunder Krishnan: Welcome back to the lecture. We will continue with the analysis of the solutions that we have proposed for the hydrogen atom.

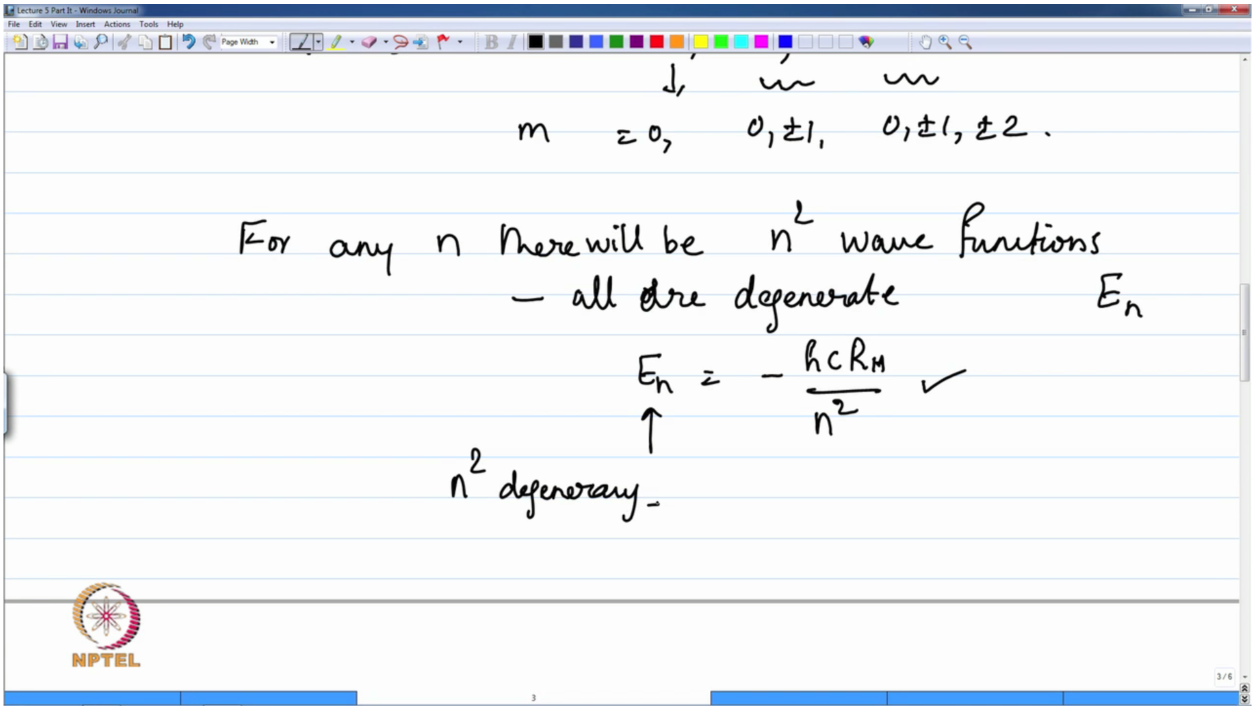


The equation beam the Schrodinger equation $H\psi = E\psi$ $\psi(r,\theta,\varphi)$ and we have proposed this to be a radial part and the angular part containing θ and φ and these two together written as a spherical harmonics of two dependents, okay. So this is the formal structure that we have for the solutions and the wave functions, when we solve these differential equations, the wave functions will depend on three quantum numbers n, l, m, these are the standard representations for the quantum numbers. The values for these quantum numbers are n goes from 1, 2, 3 to ∞ and the value of l is limited by the choice of any n it goes from 0, 1, 2 up to n-1, and the value of m is also chosen by the values of l, namely 0, ±1, ±2 up to ±l. Therefore, the wave functions are given by these three quantum numbers.

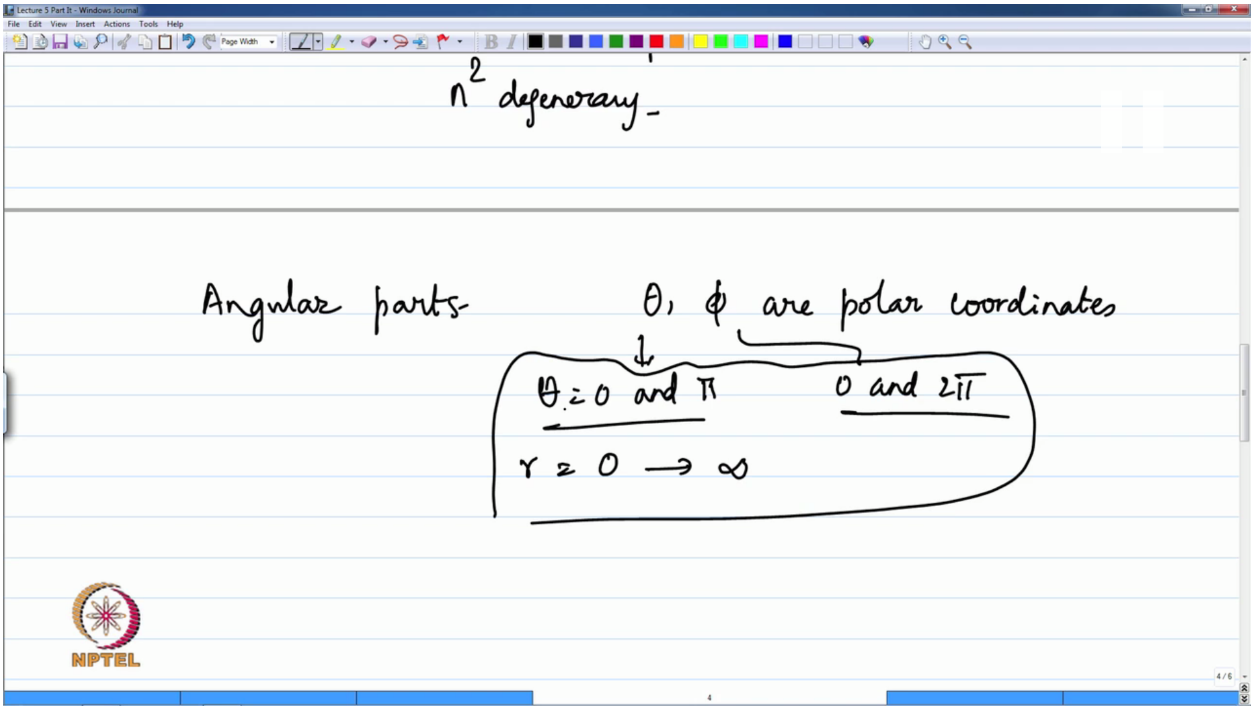


And if we write this ψnlm with n l and m or (r,θ,φ) as the radial function n l dependent on both the quantum numbers and the spherical harmonics ylm (θφ), the first value is ψ1, n=1, and the only choice that we have for the l an m are 0 and 0, 1, 0, 0. This is known in the standard representation as the 1s orbital. The next quantum number that we have is the n is 2, and therefore, we have the wave function that the n quantum number 2 and l can be 1 or 0, and if the L is 1 the m can take the three possible values namely 1, 0 and -1, 1, 1, 2, 2, and therefore, the three wave functions will have this representation 211 ψ_{210} and ψ_{21-1}, these three, okay.

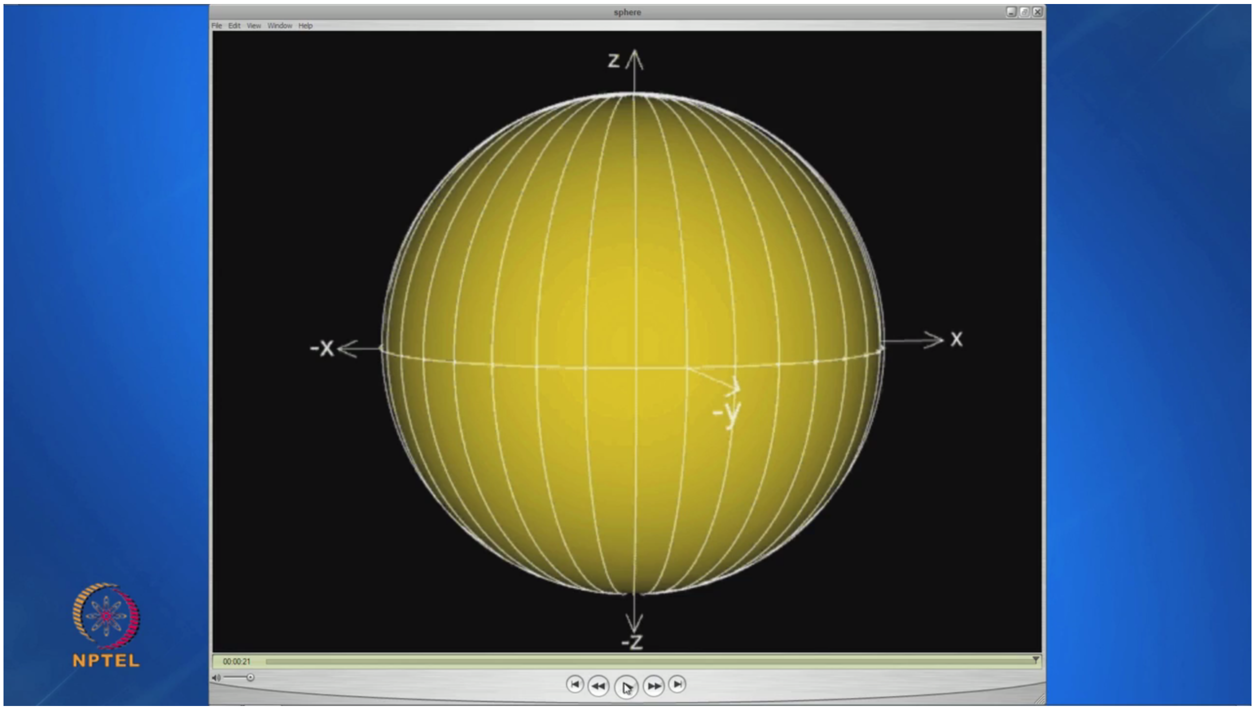
The overall energy is a solution in the radial part of the equation, therefore, this is the E_1, the overall energy will depend only on n, all of these will have the same energy E_2 and when n is 2 l can be 1 or 0, and therefore, m will be 0, other wave function ψ_{200}. This is to s orbital and the l=1, they are all known as P orbitals and this is the 2p orbital.



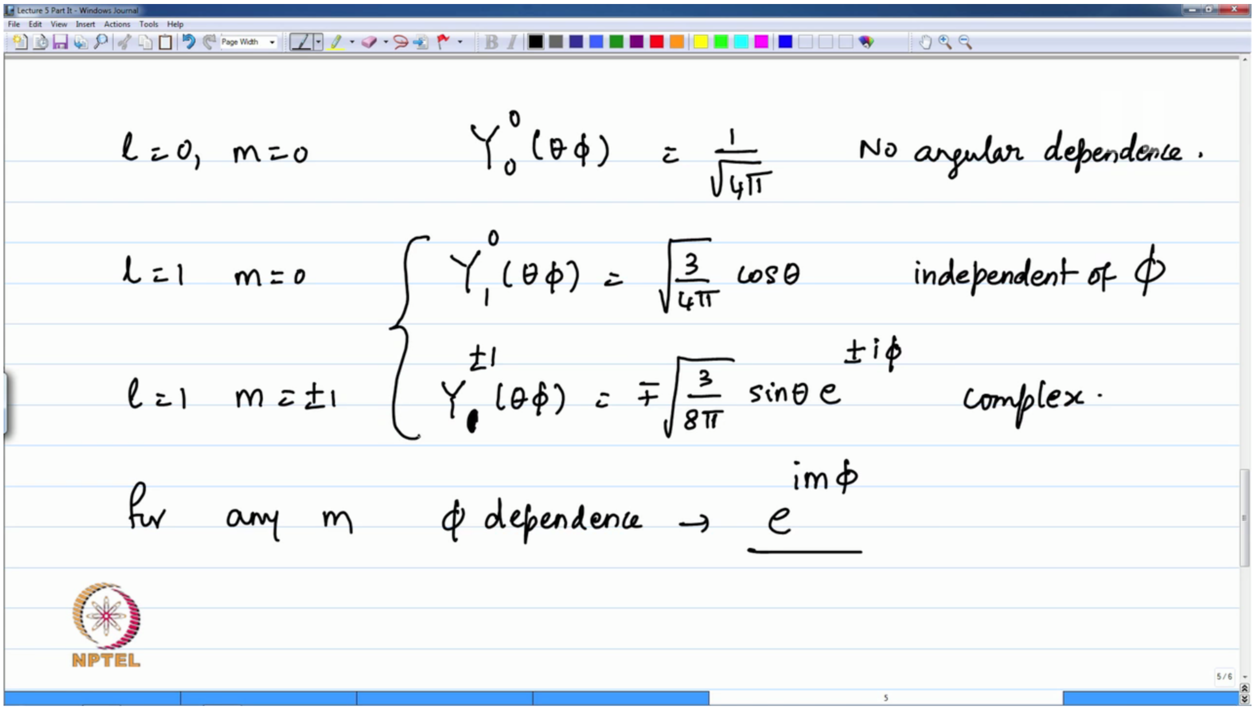
Likewise for n=3, you will have l = 0, 1, or 2 and l=0 will give you m=0. This will give you three values 0, ±1, this will have five values 0, ±1, ±2. Therefore, for any n, there will be n^2 wave functions. All of which are degenerate. They all have the same energy according to the formula that E_n given by the standard formula $-hcRm/n^2$ where H is the Planck's constant c is the speed of light, okay. This is something that you are familiar from the Bohr's model and also from the Schrodinger equation gives exactly this as the solution except to that, it has n2 degeneracy for every n, and the wave functions are given according to this particular format.



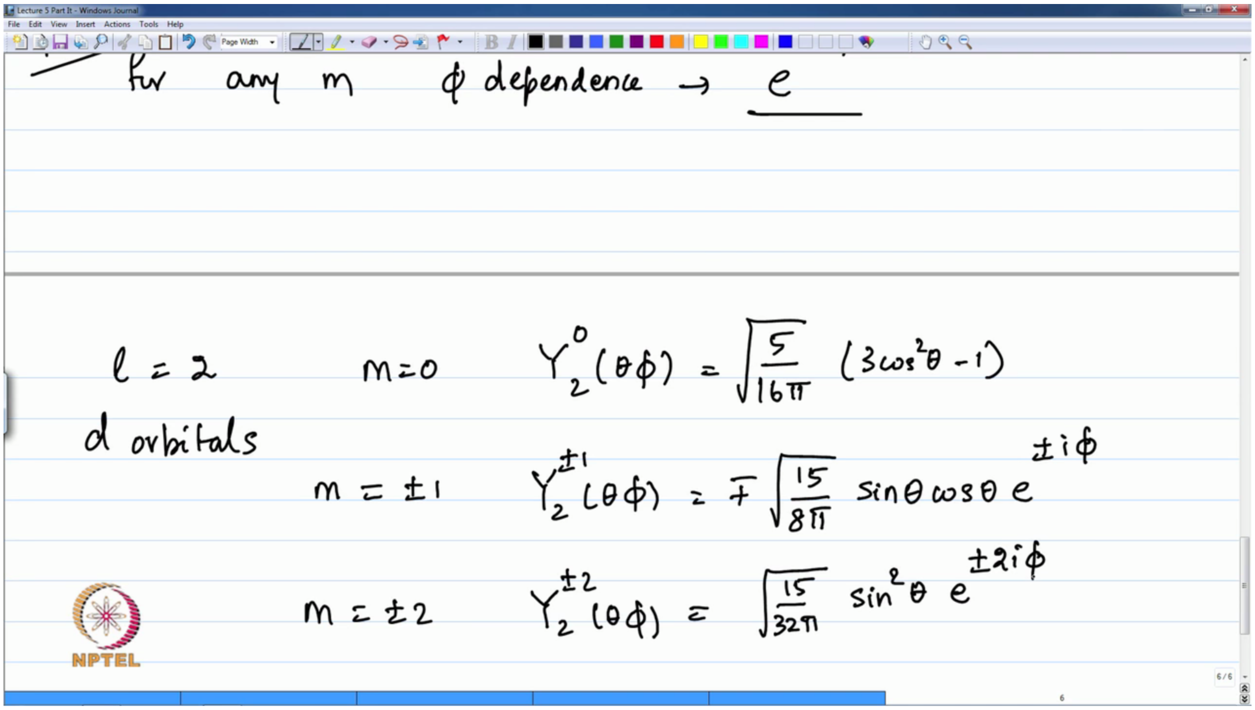
Now what we will do is, we will see these wave functions in two parts, the angular part first, which brings to you the results in some familiar form to what you already know, namely the orbital forms that you have seen, the shapes of the various atomic orbitals are given by the angular parts, okay. Now remember θ and φ are polar coordinates and in sphere θ and φ have the limits of θ=0 and π and φ has the limits of 0 and 2π. So with these variations we can create a spherical surface. Therefore, these are what is called the maximum values, the maximum -- this is the range of the θ and φ. The radius of course goes from a sphere of 0 radius to infinite radius, therefore radius goes from 0 to ∞. So this collection of the coordinate system that we have reproduces the boundary conditions that we have, namely 0 radius to infinite radius and for each radius a spherical surface enclosing a spherical volume, therefore the entire three-dimensional volume is reproduced.



This is seen by a very simple animation that one came view here. So let me show you that these are the θ and φ. The polar coordinate has 0 to π, so it ranges that way and then the φ coordinate taking the semicircle throughout. It generates the whole spherical surface. Therefore, please remember the angles are limited by this unsymmetrical or asymmetrical choice. One is from 0 to π, the other is from 0 to 2π. If you put both of them 0 to 2π, you will generate the spherical surface twice. You will generate the infinite volume twice. Therefore, you do it you get the value two times that, therefore it's not correct. The spherical coordinates have this as the limits.

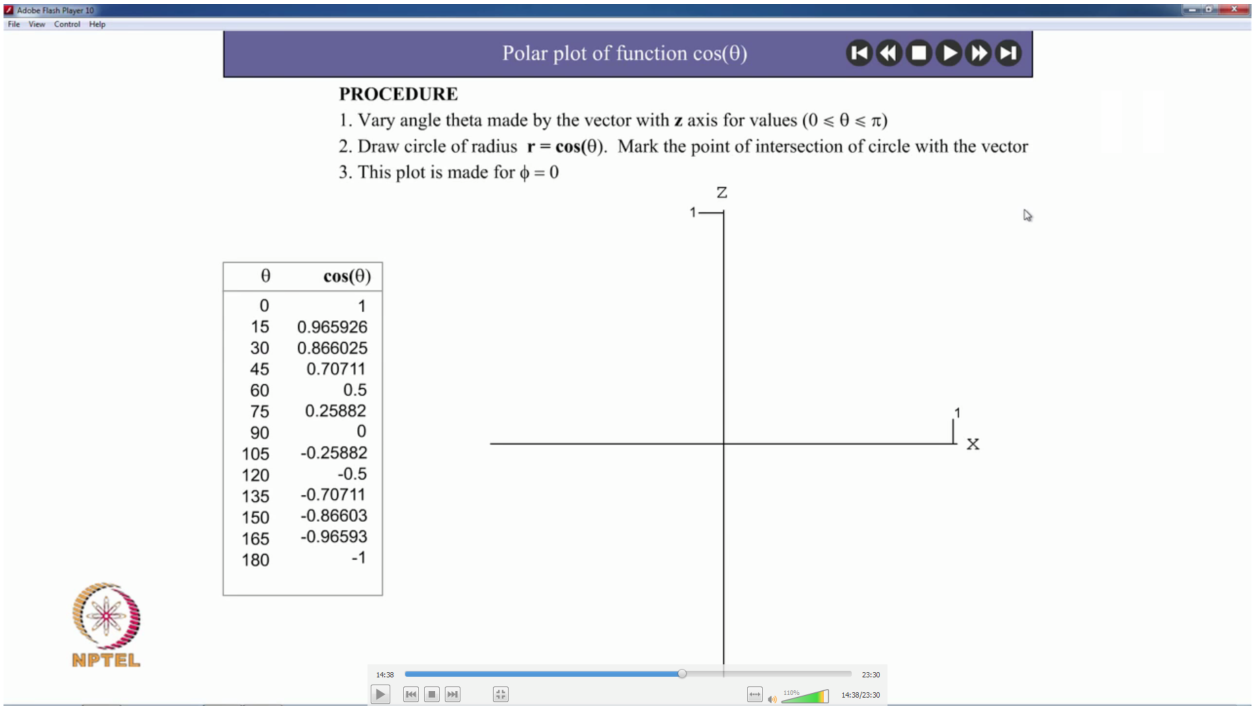


Now let's look at the series of functions that we wanted to see pictorially, okay. So let me write some of these spherical harmonics as solutions. When $l=0$ and $m=0$, the spherical harmonics Y is 0, 0 is not dependent on any angle and it has a value $1/\sqrt{4\pi}$, no angular dependence. When $l=1$, and $m=0$, the spherical harmonic is Y l, m is 1, 0 $(\theta\varphi)$ and it has the value that $\sqrt{3/4\pi}$ $\cos\theta$ independent of φ. When $l=1$ and $m=\pm1$, the spherical harmonics is Y1 ±1 $(\theta\varphi)$ and it has the form $\pm\sqrt{3/8\varphi}$ $\sin\theta$ $e^{\pm i\varphi}$. This is π, this is φ, complex functions. In general, for any m, the φ dependence is given by this function $e^{im\varphi}$, and you can see that here, this is $\pm1\varphi$ -- 0φ,which is of course 1. Therefore, these are what are called the spherical harmonics for the P orbital.

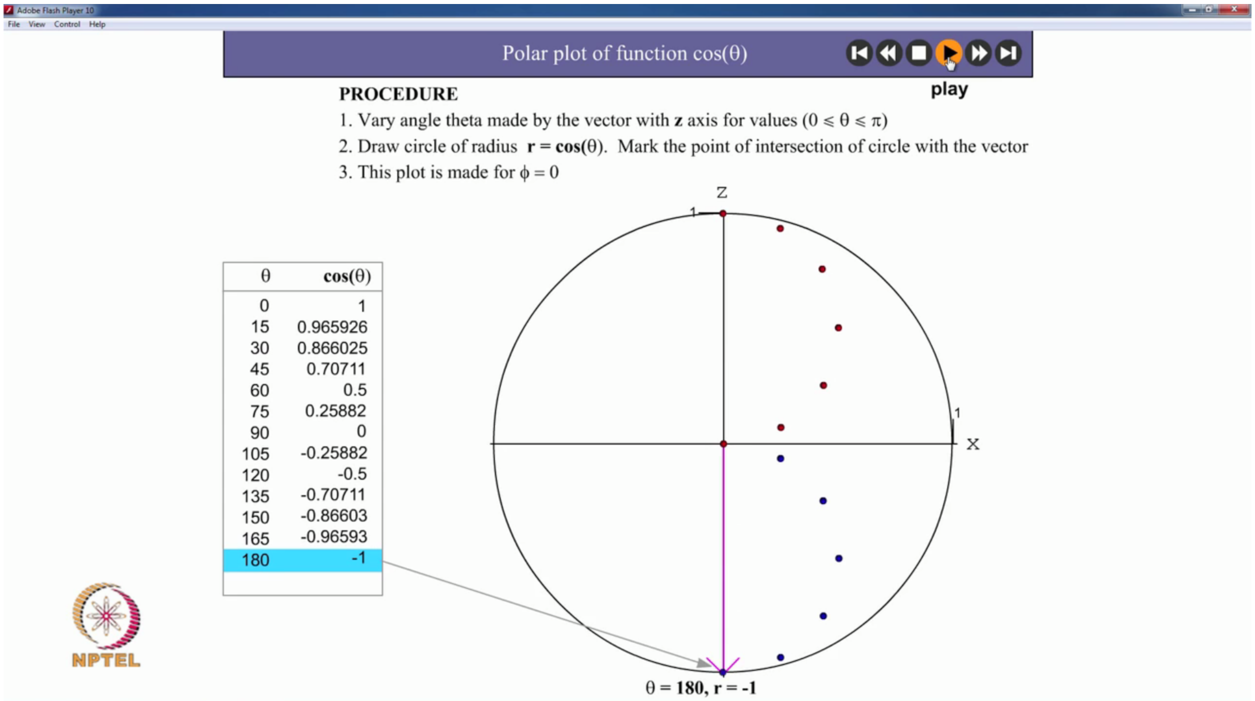


And what are the values for the n=2, which are known as the D orbitals. All three of these are P orbitals and these are D orbitals. You have l=2 if m=0, you have the spherical harmonics Y 2,0 (θφ) and the value is given by √5/16π (3cos2θ - 1) and when m is ±1, Y 2, ±1 (θφ) has a ∓√15/8π sinθ cosθ e±iφ, and when m is ±2, the spherical harmonic is Y 2,±2 (θφ) and that's given by √15/32π sin2θ $e^{\pm 2i\varphi}$, okay. So you can see that P orbitals are all functions of cosθ or sinθ raised to the power 1, that is the -- it's a monomial. If l=2, you can see that it's 3 $\cos^2\theta$, but one is nothing but $\sin^2\theta + \cos^2\theta$, therefore it is $2\cos^2\theta - \sin^2\theta$. So it is a function of cosθ sinθ, but degree 2, polynomial of degree 2, and likewise, for sinθ cosθ, $\sin^2\theta$. So all the ls, the spherical harmonics, for each and every l, you will have the θ dependent part as a lth degree polynomial homogeneous. It will involve sinθ and cosθ but the total power of sine and cosθ will be n.

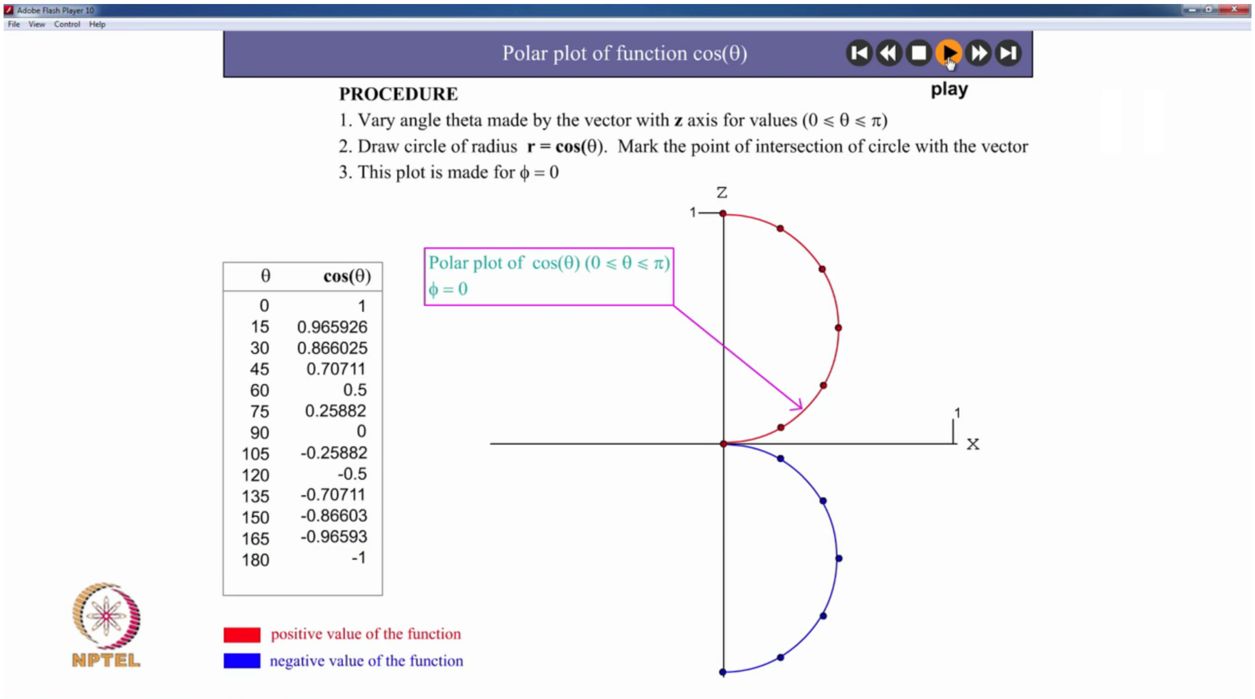
The φ part is Y l,m the φ part is $e^{im\varphi}$, that's it. Therefore, the structure of the spherical harmonics and the patterns are clear. How do we get these constants in front of it and how do we get the ±signs et cetera, that's more mathematics, but this is through the normalization of the spherical harmonics to unity over the sphere, and therefore, these constants would be shown in the next part as the actual numbers that come out when you normalize the spherical harmonics like the way you normalize the wave functions by taking ψ*ψ, dτ, the integral as 1. Here, you would take the spherical harmonics Y l,m * Y l,m and taking through the spherical volume elements, namely θ = 0 to π and φ = 0 to 2π, and the spherical differential element, sinθ dθ dφ. When you do that, you will get all these constants clearly, okay.



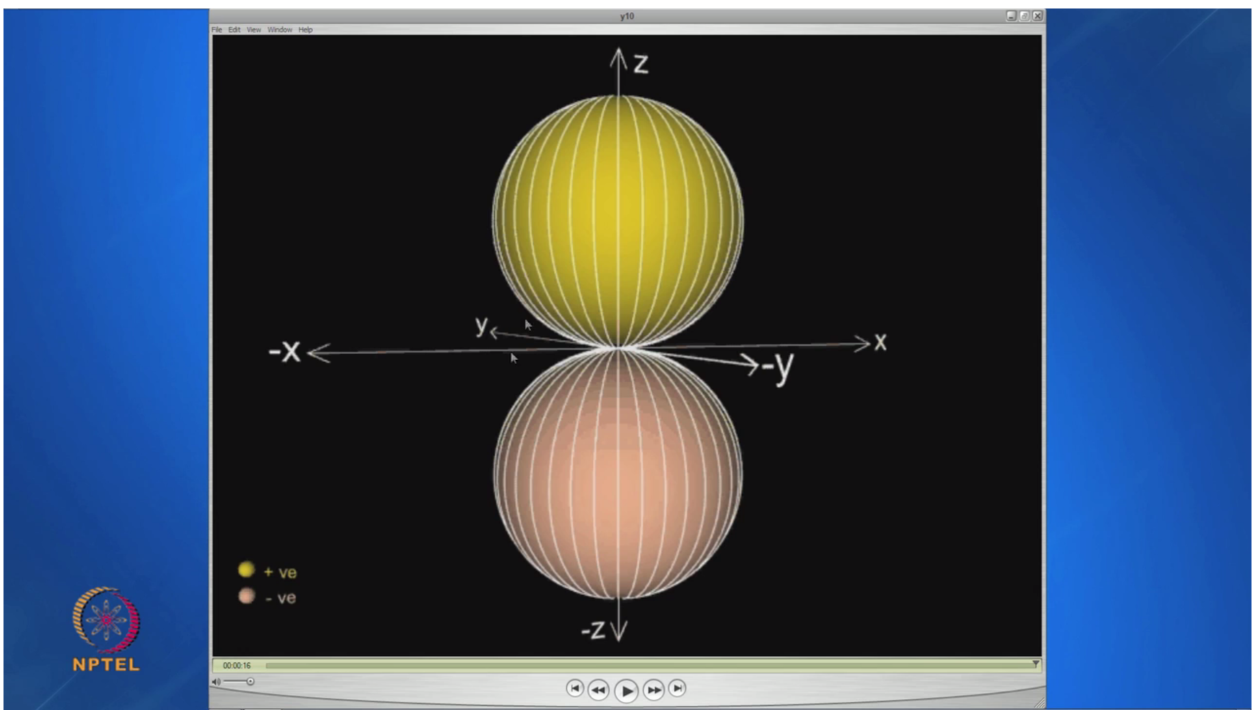
Now let us see the pictorial representation patience for the real part of Y 1,±1 and the imaginary part of Y 1,±1 and the function Y 1,0 which is real anyway. It is a function of cosθ. And here, this will contain sinθ, the real part will contain sinθ cosφ and the imaginary part will contain sinθ sinφ. So we shall see this in the spherical coordinate pictures, representations. Let's look at the Y 1,1. So first let me see Y 1,0. Here, I am plotting Y 1,0 on 1 value of φ, but this function you know is cosθ Y 1,0. Therefore, it's the same for all values of φ. So if you know the shape of this function for θ, then we can reproduce that shape for all the values of φ. And what is done here is cosθ is plotted on the θ coordinate.



Remember the θ coordinate for the polar axis system starts with some Z direction where θ is 0 and then θ is some value, some value, then it's 90 and then it's 180. So the value of cos θ is plotted on that value of θ radius, and then you connect them, okay. So this is θ=0 cosθ=1, 15 cosθ=0.8. You mark it on the radius, the entire length, okay, and then you connect all these points to get a representation for cos θ on polar system, spherical polar system. This is pollard. Once you do it for all values of φ, you will get it for spherical polar. I have given a different color, because cosθ is negative for θ>90 degrees, but the values are symmetrical on either side of the X axis, okay.

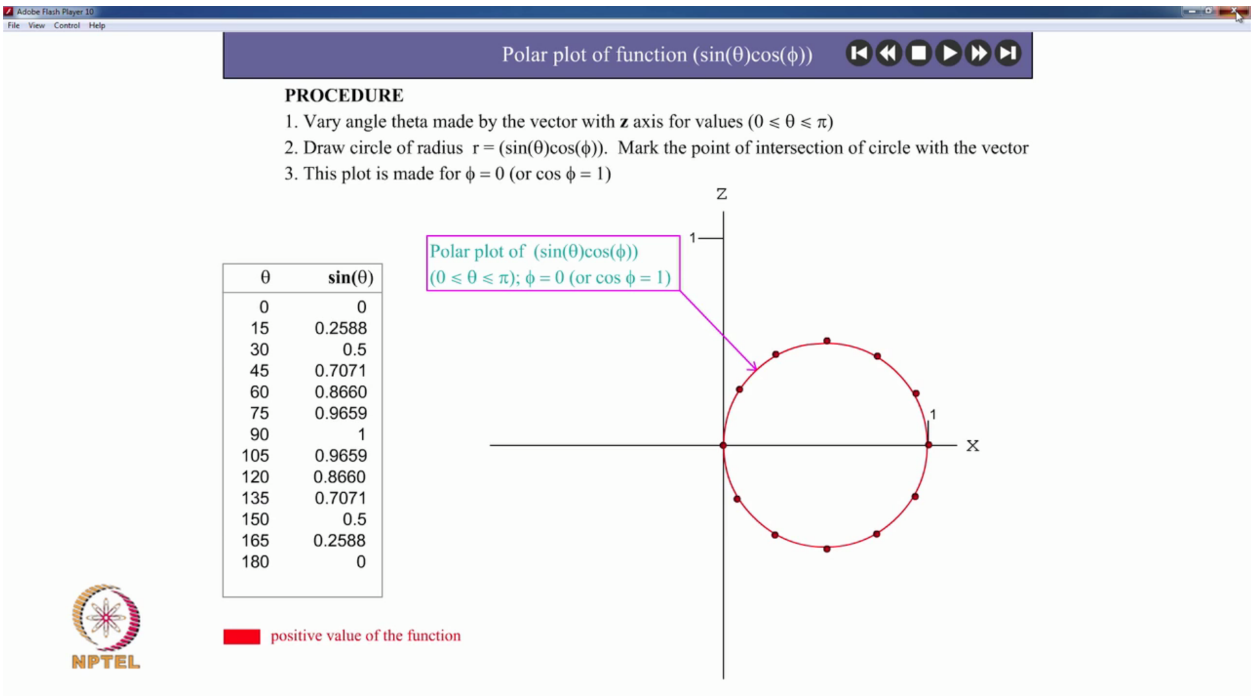


So that's the shape of cos θ in a polar coordinate system. And now in a complete sphere, how does this look like? It's the same graph for all values of φ.

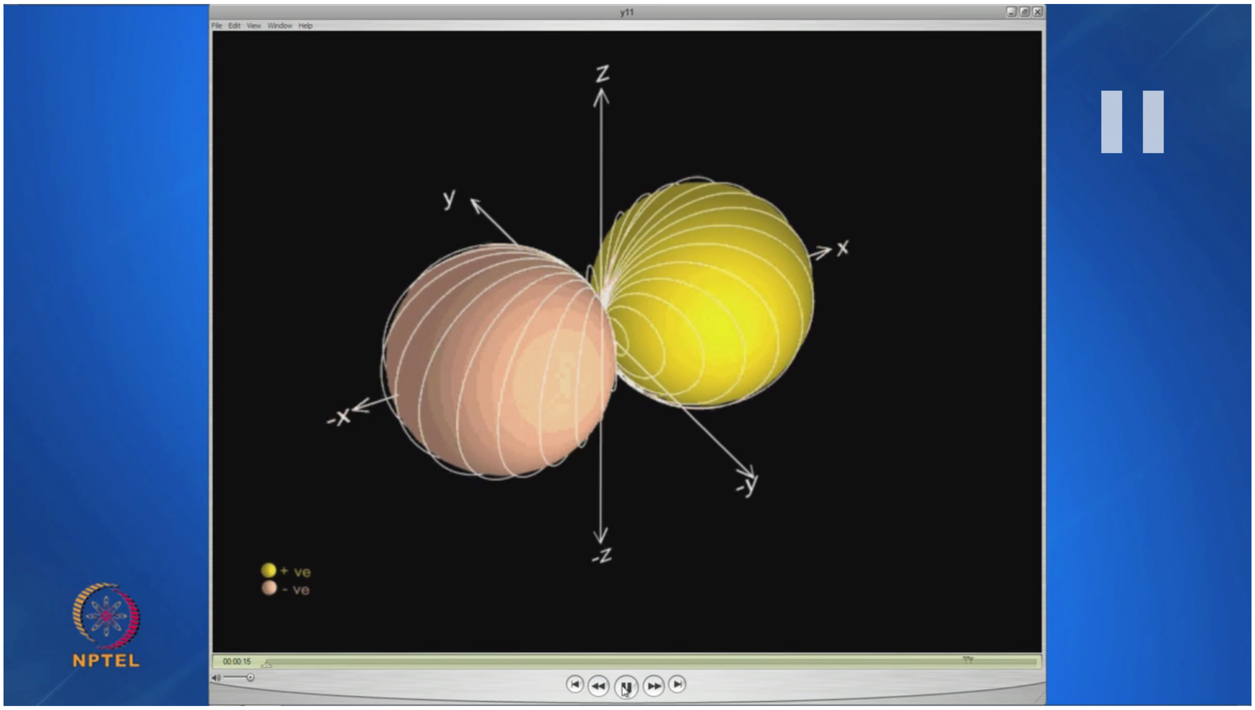


Therefore, if you plot this, okay, so here you will see Y 1,0 plotted for all values of the azimuthal angle φ and this is what you have seen for a given value of θ from 0 to π. Therefore, if you plot it for all values of φ. You will get the same graph with of course the plus and minus signs not on the either side of the X axis, because you know cosθ is negative for θ>90 and that's below the X axis and for above the X axis cosθ is positive. Therefore, this is the standard representation of the P orbital that you see ±lobe, which is nothing but the Pz orbital.

Sinθ cosφ and sinθ sinφ, which are along the other two directions. So let's first of all see sinθ plot, okay. Cosφ I've kept it as 1 by choosing P=0. So this plot is along the X axis and then this plot needs to be rotated, as you go for various values of φ while rotating it for various values of φ, you must also multiply the sinθ plot by cosφ. Therefore, it will go to 0, it will go to negative, it will become 0, it come to positive and so on.

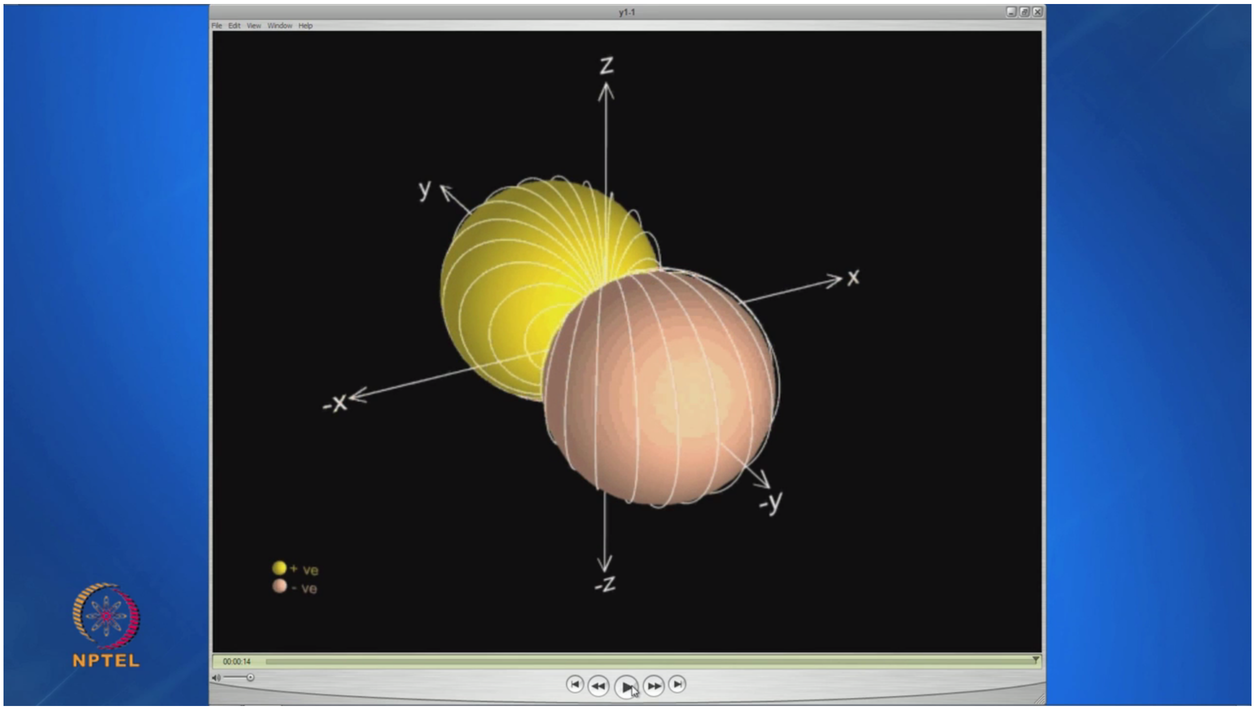


So you can see first of all the sinθ on the polar graph here, which does not have any negative values because sinθ is positive in the range 0 to 180. It starts from 0. Again, I remind you the value of sinθ is plotted along that θ direction by marking the points, and the table gives you what the value is for a few of the θs. So that's sinθ in one direction with cosφ=1 that is along the X axis.



If we plot this for all values of φ, you'll actually see that this graph is multiplied by cosφ. Therefore, it shrinks to 0 when it comes to Y, because along the Y axis φ is 0, 90 degrees. Therefore, cos90 is 0. Along the minus X axis φ is 180, therefore cosφ is -1. Therefore, from Y all the way to -Y, when the φ values are between 90 and 270, cosφ is negative. Therefore, whatever you see here will have the negative sign and whatever you see on this side will have the positive sign.

So sinθ cosφ Y 1,1 Y 1,0, these are the two plots. The third function which is the imaginary part of the Y 1,1 is sinθ sinφ. The difference between sinφ and cosφ is 90 degrees. Therefore, all you would see when you plot that function is that this is rotated by 90 degrees.



So we start with the Y axis, because sinθ sinφ, if you want to plot, you plot it on a sinφ maximum, which is along the Y axis, and then you will see that sinφ is positive between φ = 0 and 180, 0 and 180 as you see it, it's between the X and -X axis and 180 to 360 when sinφ is negative, it's along the other side namely -X to the X axis along the -Y, and therefore, you see the natural function that plot that you see here, and sinφ goes to 0 or φ = 180 and φ = 360. Therefore, this is plotted along the X axis. I mean that proves the point. The trigonometric functions look different, but the functions have the same representation, graphical representations on a sphere, because the sphere doesn't care for what is X axis or Y axis or Z axis, all three are the same. Therefore, the orbitals are symmetric about the three mutually perpendicular directions and it's your convention to choose a right-handed coordinate system and a standing up axis, because most of us see standing up. I mean it can be lying down or it can be standing down. The Z axis is as arbitrary as the sphere's direction is.

Therefore, if you go to the nuclear magnetic resonance research lab, you will see the Z axis is horizontal, because the magnets are like this and therefore this is the Z and you are XY plain is this way, right. So it's your choice. On a spherical coordinate system, when you block the spherical harmonics Y l,m, you get exactly the distributions and the shapes that you have seen in your textbooks and that's the beauty of it, and these functions are exact solutions for the hydrogen atom.

In the next part of this lecture, we will continue with the D orbitals and I will also show one F orbital. So the next lecture is purely an extension of this lecture. You don't need to see that part. If you wish, go to the web site and see all the 15 plots that we have, that I have put up, the 15 plots are for the three P orbitals, the five D orbitals, and the seven F orbitals. Chemistry and chemical systems do not require G orbitals right now, because the atomic number that we know, maximum atomic number that we know 120 still does not warrant a stable atom with a G orbital, so we don't worry about it, but spherical harmonics is fundamentally important in all of physics and all of engineering, and what you see here is nothing but the representation of a spherical harmonic, the real and imaginary part of it on a spherical coordinate system. Therefore, these pictures may be useful to anybody who wants to look at them, okay not just the chemistry part of it.

We'll continue with the D orbitals in the next lecture. Until then, thank you very much.