Introductory Quantum Mechanics and Spectroscopy
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Lecture – 5
Part III
The Quantum Mechanics of Hydrogen Atom

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

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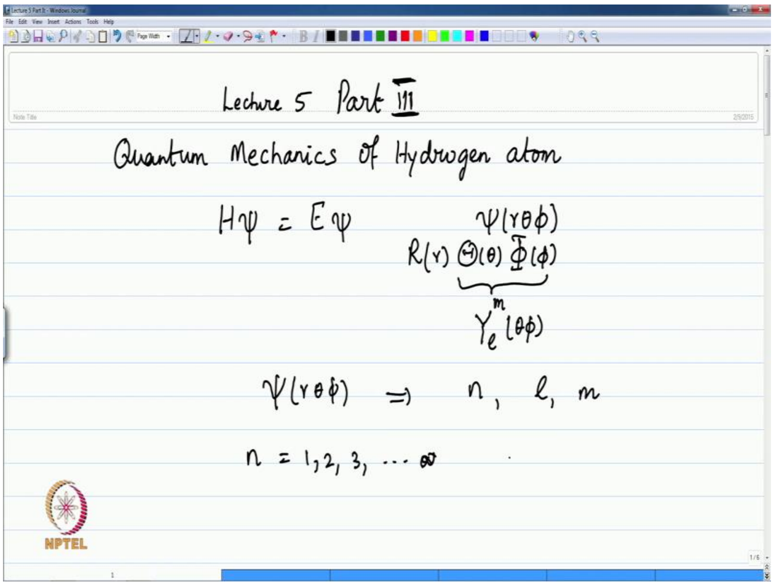

The equation being the Schrodinger equation H psi equal to E psi; psi r theta phi; and we have proposed this to be a radial part and the angular part containing theta and phi; and these two together written as a spherical harmonics of two dependents. So, this is the formal structure that we have for the solutions and the wave functions. When we solve these differential equations, the wave functions will dependent 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 infinite.

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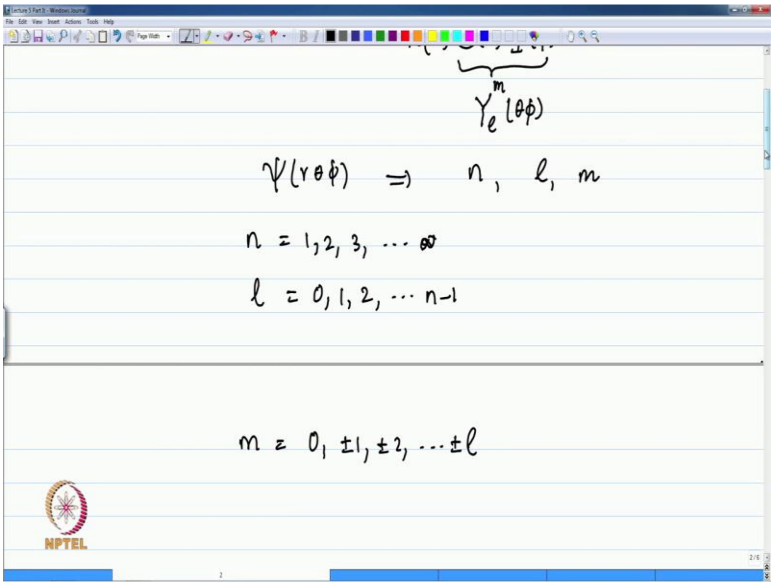

And the value of l is limited by the choice of any m; it goes from 0, 1, 2 up to n minus 1. And the value of m is also chosen by the values of l namely, 0, plus minus 1, plus minus 2 up to plus minus l.

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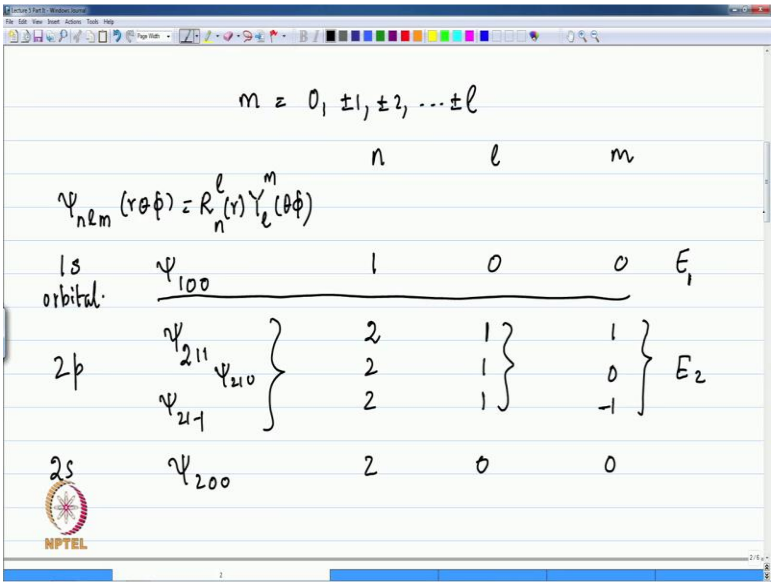

Therefore, the wave functions are given by these three quantum numbers. And if we write this psi n l m with n, l and m r theta phi as the radial function n l dependent on both the quantum numbers and the spherical harmonics Y l m theta phi. The first value is psi 1 n equal to 1. And the only choice that we have for l and 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 n is 2. And therefore, we have the wave function with the n quantum number 2; and l can be 1 or 0. And if l is 1, then m can take three possible values namely, 1, 0 and minus 1, 1, 2. And therefore, the three wave functions will have this representation – 2, 1, 1 – psi 2 1 0 and psi 2 1 minus 1 – these three. The overall energy is a solution in the radial part of the equation. Therefore, this is the E 1. The overall energy will dependent 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 psi 2 0 0 – this is 2s orbital. And the l equal to 1. They are all known as p orbitals and this is the 2p orbital.

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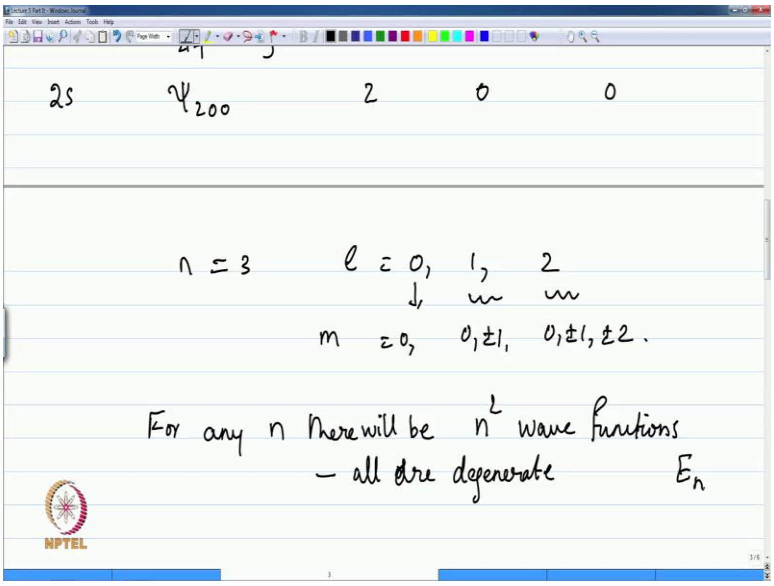

And likewise for n equal to 3, you will have l equal to 0, 1 or 2; and l equal to 0 will give you m equal to 0. This will give you three values – 0, plus minus 1; this will have five values – 0, plus minus 1, plus minus 2. Therefore, for any n, there will be n square wave functions; all of which are degenerate.

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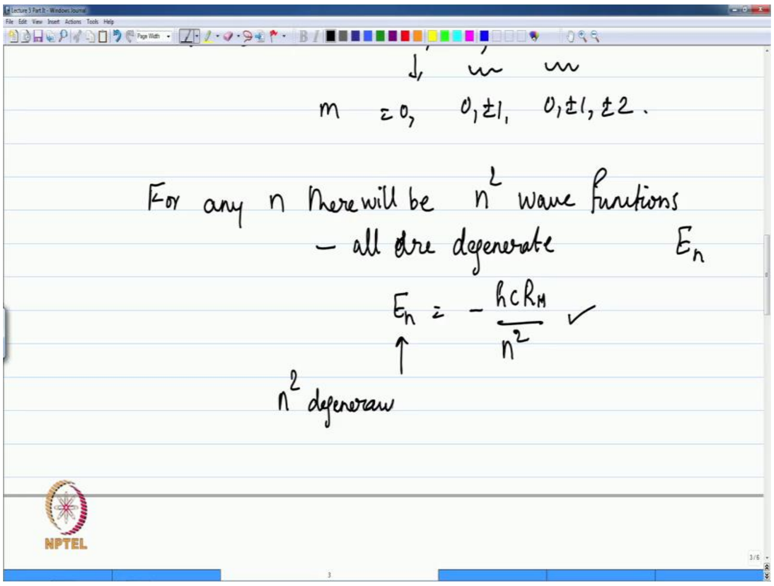

They all have the same energy according to the formula that E n given by the standard formula minus hc – the Rydberg constant by n square; where, h is a Planck’s constant; c is the speed of light. This is something that you are familiar from the Bohr’s model and also from the Schrodinger equation gives exactly this as the solution, except to that it has n square degeneracy for every n. And the wave functions are given according to this particular format.

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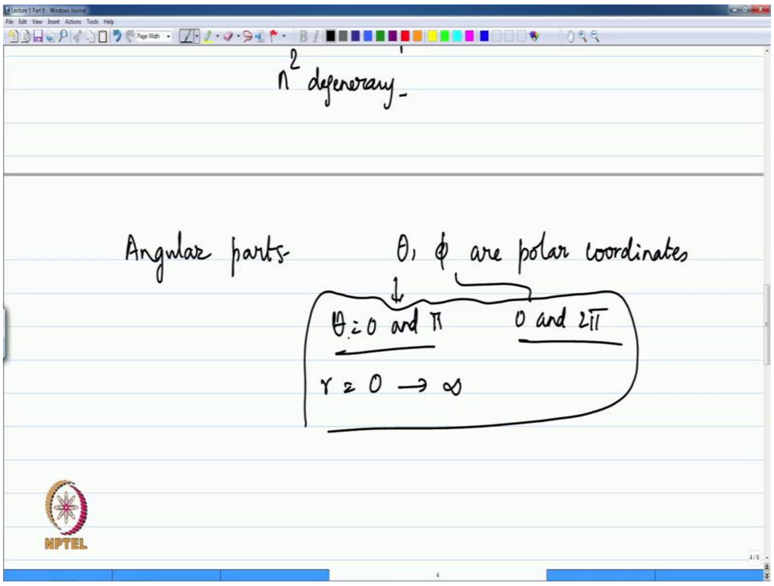

Now, what we will do is we will series wave functions in two parts; the angular part first, which brings to you the results in some familiar form to you already know namely, the orbital forms that you have seen that, the shapes of the various atomic orbitals are given by the angular parts. Now, remember theta and phi are polar coordinates. And in sphere, theta and phi have the limits of thetas equal to 0 and pi. And phi has the limits of 0 and 2pi. 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 theta and phi. The radius of course, goes from a sphere of 0 radius to infinite radius. Therefore, radius goes from 0 to infinity. So, this collection of the coordinate system that we have produces 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 3-dimensional volume is reproduced. This is seemed by a very simple animation that one can view here. So, let me show you that, these are the variations for theta and phi.

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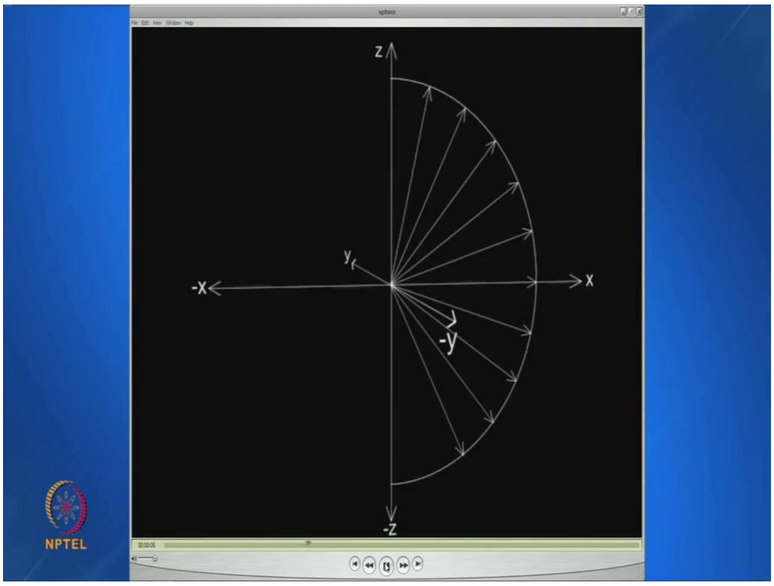

The polar coordinate has 0 to pi. So, it ranges that way.

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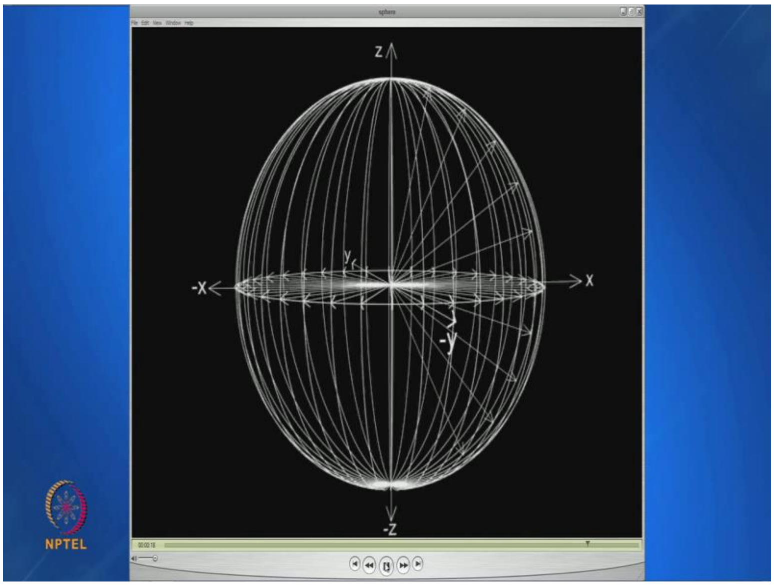

And then the phi coordinate taking the semi circle throughout – it generates the whole spherical surface. Therefore, please remember the angles are limited by this unsymmetrical or the assymetrical choice.

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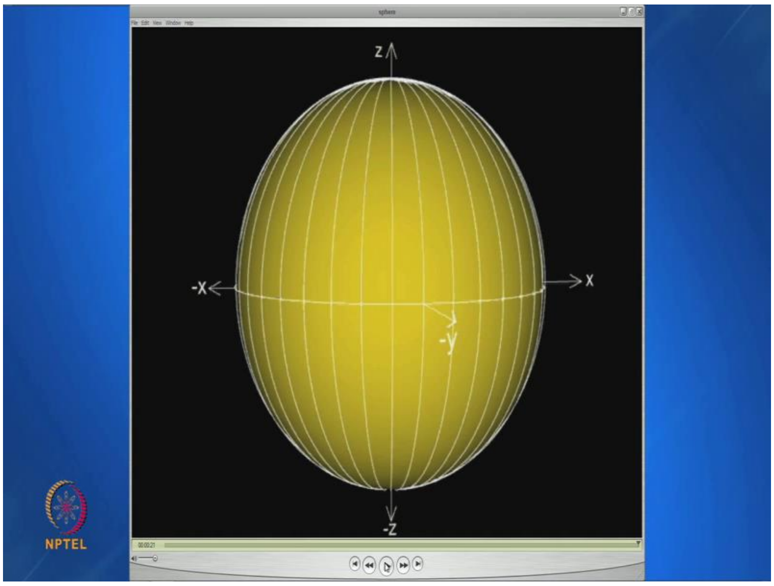

One is from 0 to pi; the other is from 0to 2pi. If you put both of them 0 to 2pi; you will generate this spherical surprise twice; you will generate the infinite volume twice. Therefore, you get the values two times that. Therefore, it is not correct. The spherical coordinates have this as the limits.

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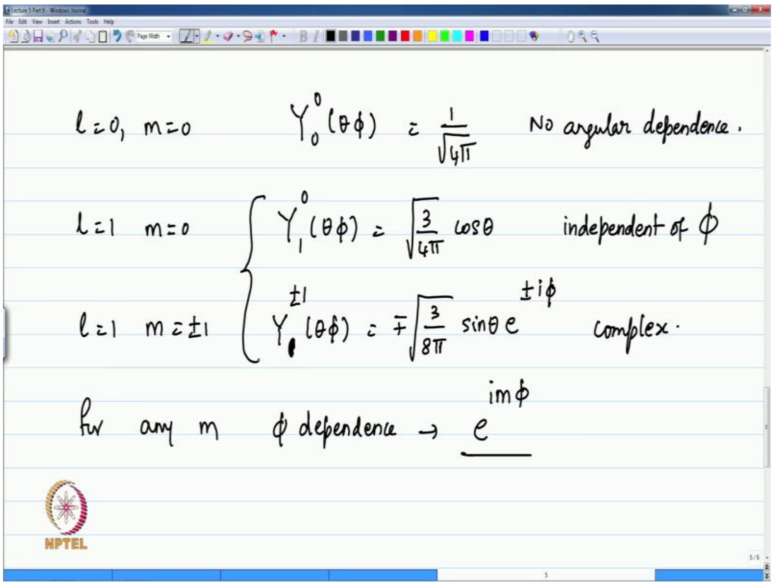

Now, let us look at the series of functions that we wanted to see pictorially. So, let me write some of the spherical harmonic solutions. When l is 0 and m is 0, the spherical harmonics Y 0 0 is not dependent on any angle and it has a value 1 by root 4 pi; no angular dependents. When l is 0; then l is 1. When l is 1 and m is 0; the spherical harmonic is Y l m is 1 0 theta phi. And it has the value that root 3 by 4 pi cos theta independent of phi. When l is 1 and m is equal to plus or minus 1, the spherical harmonics is Y 1 plus or minus 1 theta phi. And it has the form minus or plus root three by 8 pi sin theta to the plus or minus i phi. This is pi; this is phi –complex functions. And in general, for any m, the phi dependence is given by this function e to the i m phi. And you can see that, here is plus or minus 1 phi, which is plus or minus 0 phi, which is of course, 1. Therefore, these are what are called the spherical harmonics for the p orbital.

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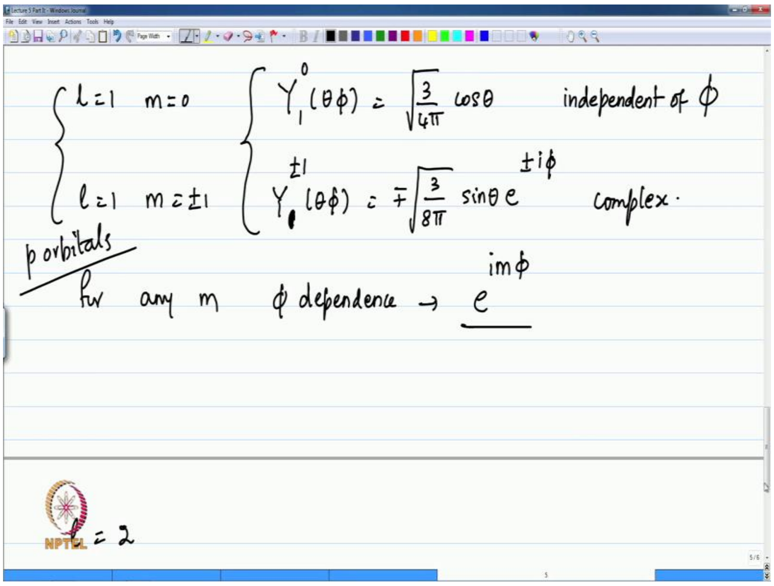

And what are the values for the l equal to 2, which are known as the d orbitals. All three of these are p orbitals.

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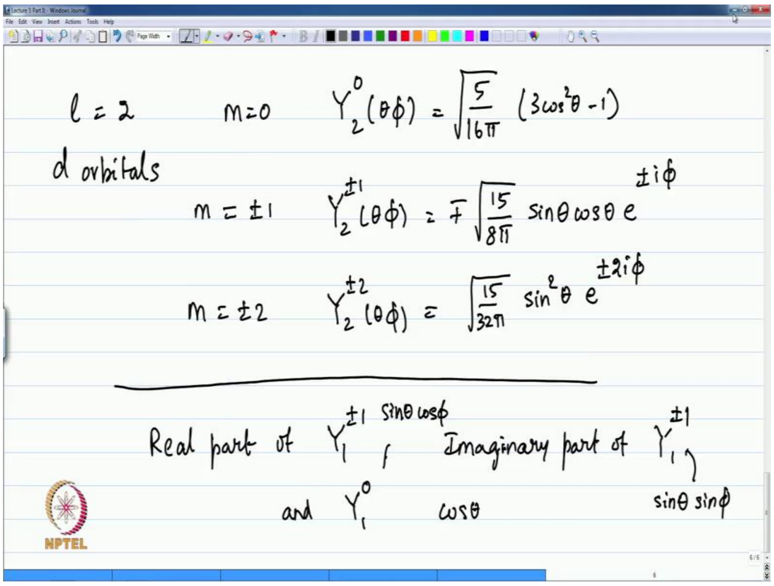

And these are the phi d orbitals. You have l equal to 2. If m is 0, you have the spherical harmonics Y 2 0 theta phi. And the value is given by root 5 by 16 pi times 3 cos square theta minus 1. And when m is plus or minus 1, Y 2 plus or minus 1 theta phi has a minus plus and square root of 15 by 8 pi sin theta cos theta e to the plus or minus i phi. And when m is plus minus 2; the spherical harmonic is Y 2 plus minus 2 theta phi; and that is given by root 15 by 32 pi sin square theta e to the plus minus 2 i phi. So, you can see that, the p orbitals are all functions of cos theta or sin theta raised to power 1; that is, it is a monomial. If l is equal to 2, you can see that, it is 3 cos square theta; but, 1 is nothing but sin square theta plus cos square theta. Therefore, it is 2 cos square theta minus sin square theta. So, it is a function of cos theta sin theta; but, degree 2 – polynomial of degree 2; and likewise, for sin theta cos theta sin square theta.

So, all the l's – the spherical harmonics for each and every l, you will have the theta-dependent part as the l-th degree polynomial homogenous. It will involve sin theta and cos theta; but, the total power of sin and cos theta will be l. The phi part is Y l m; the phi part is e to the i m phi; that is 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 plus minus signs, etcetera? That is more mathematics ((Refer Time: 12:45)) through the normalization of the spherical harmonics to unity over this fear. And therefore, these constants should be shown in the next part as the actual numbers that come out when you normalize these spherical harmonics like the way you normalize the wave functions by taking psi star psi d tau – the integral as 1. Here you would take the spherical harmonics Y l m star, Y l m. And taking through the spherical volume elements namely, theta’s equal to 0 to pi and phi is equal to 0 to 2 pi; and the spherical differential element sin theta d theta d phi. When you do that, you will get all these constants clearly.

Now, let us see the pictorial representations for the real part of Y 1 plus or minus 1 and the imaginary part of Y 1 plus or minus 1; and the function Y 1 0, which is real anyway. It is a function of cos theta. And here this will contain sin theta; the real part will contain sin theta cos phi; and the imaginary part will contain sin theta sin phi. So, we shall see this in the spherical coordinate pictures representations.

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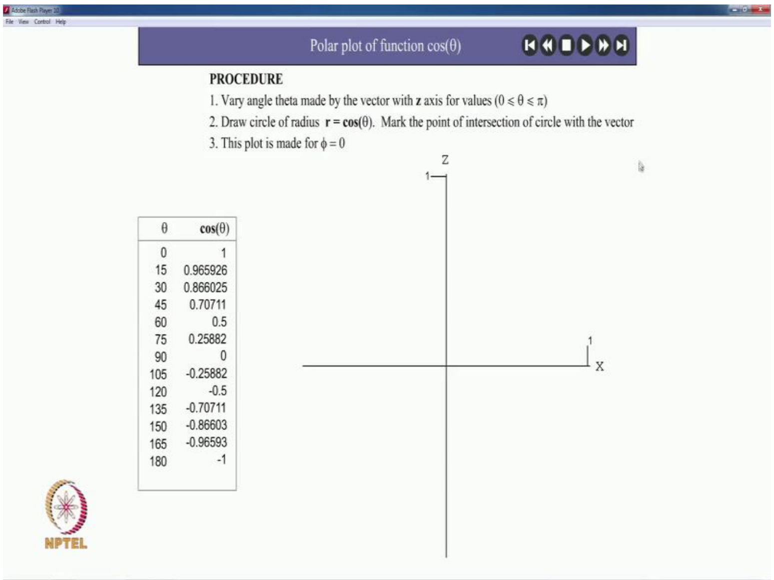

Let us look at the Y 1 1. So, first, let me see Y 1 0. Here I am plotting Y 1 0 on one value of phi; but, this function you know is cos theta Y 1 0. Therefore, it is the same for all values of phi. So, if we know the shape of this function for theta; then we can reproduce that shape for all the values of phi. And what is done here is cos theta is plotted on the theta coordinate. Remember – the theta coordinate for the polar access system starts with some z-direction, where theta is 0. And then theta is some value, some value; then it is 90 and then it is 180. So, the value of cos theta is plotted on that value of theta radius. And then you connect them.

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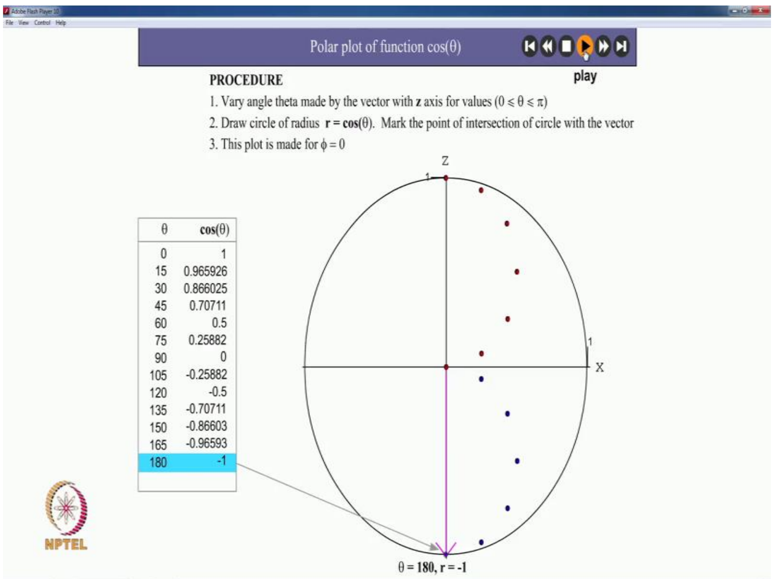

So, this is theta's equal to 0; cos theta is 1; 15 cos theta is 0.9. You mark it on the radius that the entire length. And then you connect all these points to get a representation for cos theta on a polar system – spherical polar system. This is polar. Once you do it for all values of phi, you will get it for spherical polar.

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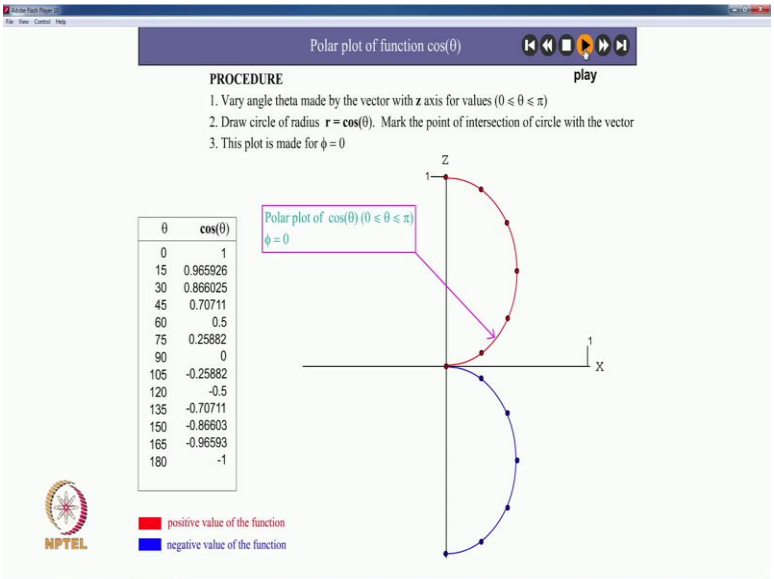

I have given a different color, because cos theta is negative for theta greater than 90 degrees; but, the values are symmetrical on either side of the x-axis. So, that is the shape of cos theta in a polar coordinate system. And now, in a complete sphere, how does this look like? It is a same graph for all values of phi.

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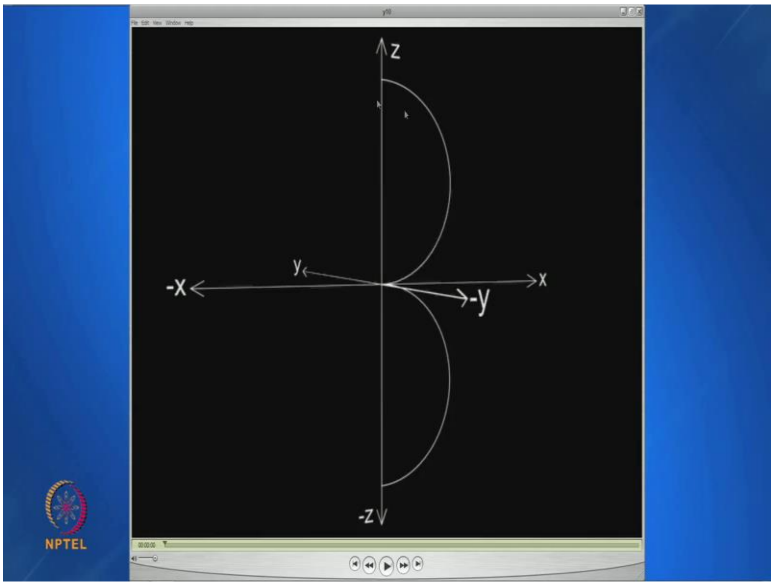

Therefore, if you plot this; so here you will see Y 1 0 plotted for all values of the azimuthal angle phi. And this is what you have seen for a given value of theta from 0 to pi.

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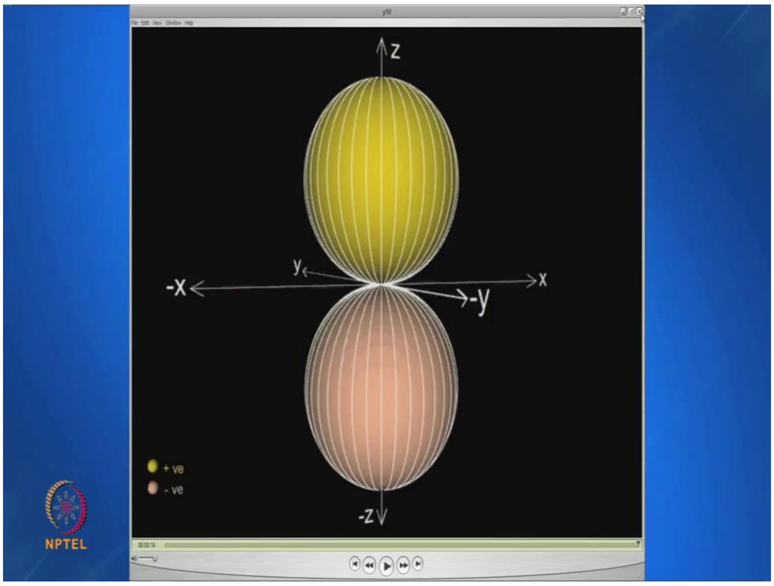

Therefore, if you plot it for all values of phi, you will get the same graph with of course the plus and minus signs have not on the either side of the x-axis, because you know cos theta is negative for theta greater than 90. And that is below the x-axis and above the x-axis cos theta is positive. Therefore, this is the standard representation of the p orbital that you see – plus minus low; which is nothing but the p, z orbital.

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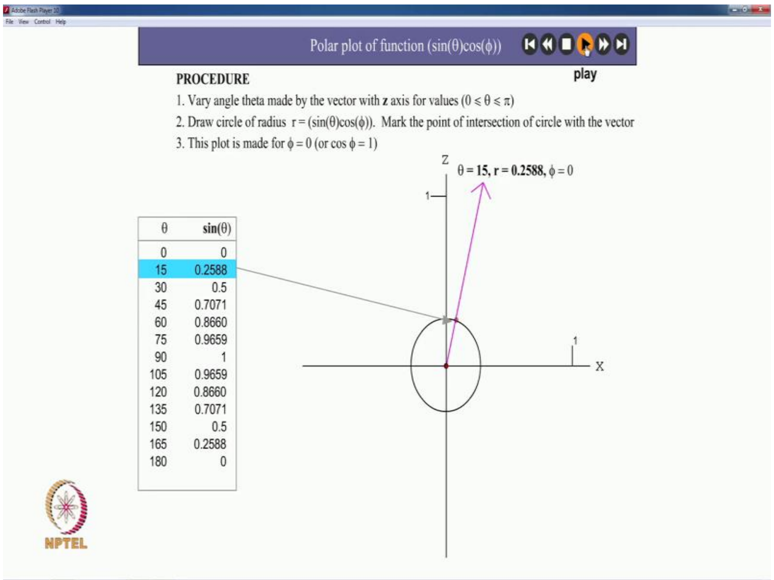

Sin theta cos phi and sin theta sin phi, which are along the other two directions; so, let us first of all see sin theta plot; cos phi – I have kept it as 1 by choosing p is equal to 0. So, this plot is along the x-axis. And then this plot needs to be rotated. As you go for various values of phi; while rotating it for various values of pi, you must also multiply the sin theta plot by cos phi. Therefore, it will go to 0; it will go to negative; it will become 0; and it will come to positive and so on. So, you can see first of all the sin theta on the polar graph here; which does not have any negative values, because sin theta is positive in the range 0 to 180.

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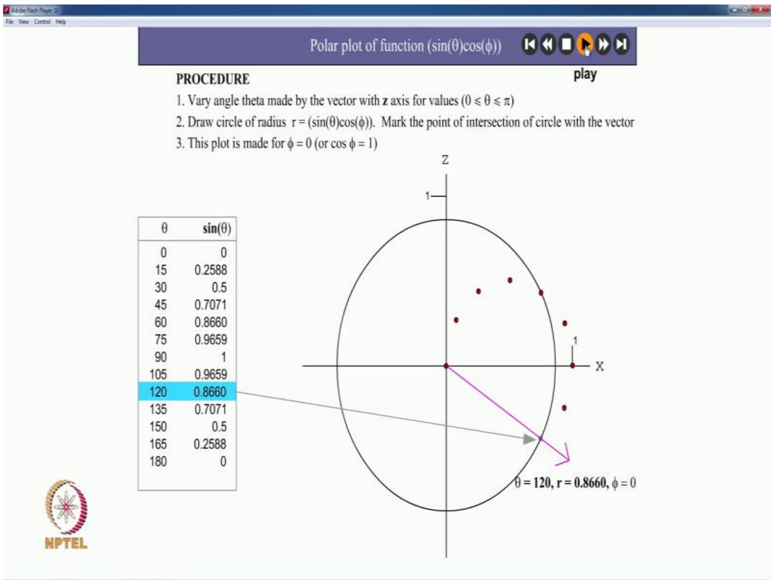

It starts from 0. Again I remind you the value of sin theta is plotted along that theta direction by marking the point. And the table gives you what the value is for a few of the thetas.

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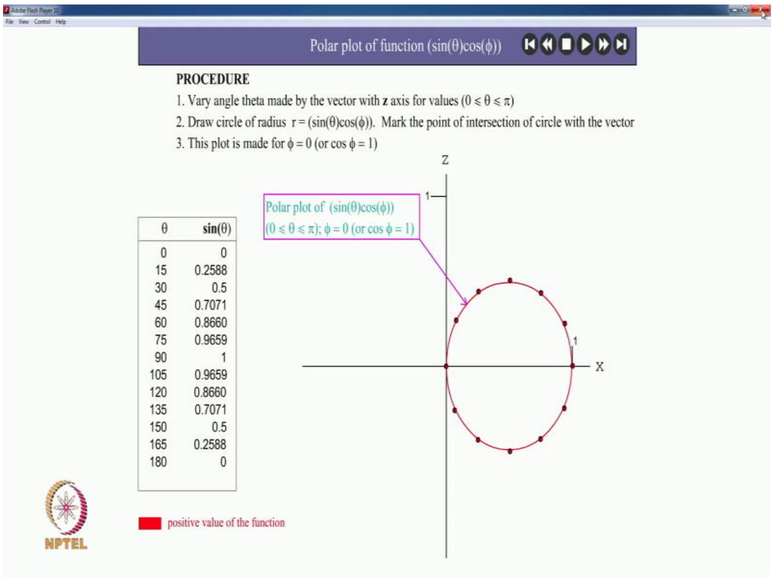

So, that sin theta in one direction with cos phi is equal to 1. That is along the x-axis.

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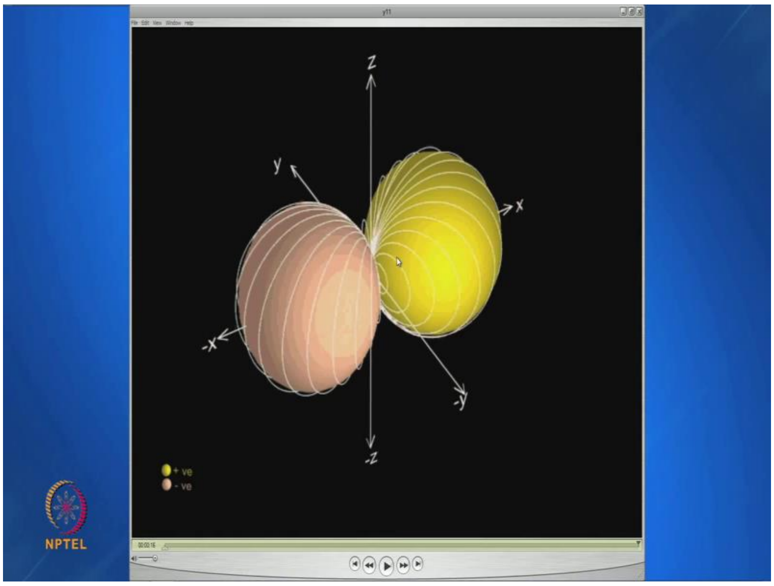

If we plot this for all values of phi, you will actually see that, this graph is multiplied by cos phi. Therefore, it shrinks to 0 when it comes to y, because along the y-axis, phi is 0 – 90 degrees. Therefore, cos 90 is 0. Along the minus x-axis, phi is 180. Therefore, cos phi is minus 1. Therefore, from y all the way to minus y; when the phi values are between 90 and 270, cos phi 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, sin theta cos phi – 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 sin theta sin phi; the difference between sin phi and cos phi is 90 degrees. Therefore, all you would see when you plot that function is that, this is rotated by 90 degrees.

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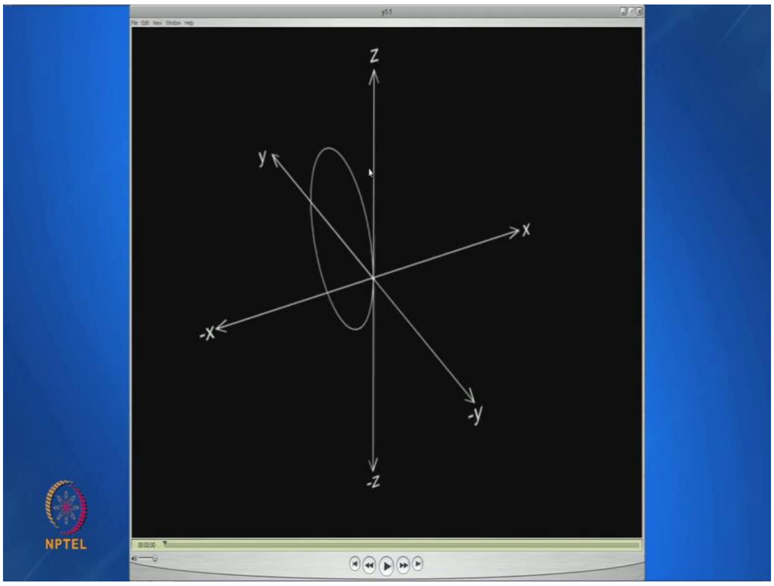

So, we start with the y-axis because sin theta sin phi if you want to plot; you plot it on a sin phi maximum, which is along the y-axis. And then you will see that, sin phi is positive between phi is equal to 0 and 180. 0 and 180 – as you see, it is between x and minus x-axis. And 180 to 360; when sin phi is negative, it is along the other sign namely minus x to the plus x-axis along the minus y.

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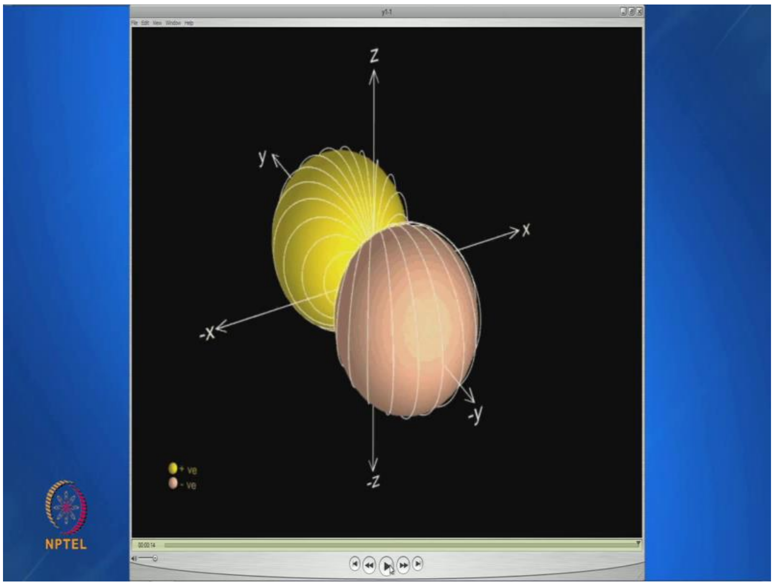

And therefore, you see the natural function – that plot that you see here. And sin theta goes to… Sin phi goes to 0 or phi is equal to 180 and phi is equal to 360. Therefore, this is plotted along the x-axis. I mean that proves the point. This trigonometric function look different; but, the functions are the same representation – graphical representations on a sphere, because this sphere does not 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 is 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 this 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 set and the xy-plane is this way. It is your choice on a spherical coordinate system. When you plot the spherical harmonics Y l m, you get exactly the distributions and the shapes that you have seen in your text books. And that is a 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 do not need to see that part. If you wish, go to the website and see all the 15 plots that we have; that I have put up. The 15 plots are for the three p orbitals; the 5 d orbitals and the 7 f orbitals. Chemistry and chemical system do not required 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 the g orbital. So, we do not 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; not just the chemistry part of it. We will continue with the d orbitals in the next lecture.

Thank you very much.