Engineering Chemistry - 1

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Lecture 7

Module 1 Atoms and Molecules

Hydrogen Atom: part - II (The Angular Solutions)

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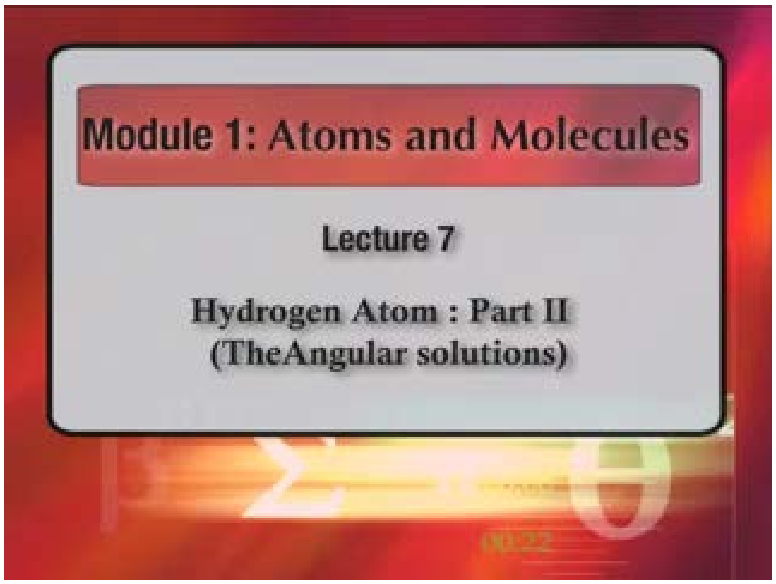

Welcome to the lectures in Engineering Chemistry. This is the series of lecture on Atoms and Molecules, molecular models and Quantum Chemistry associated with molecules. This lecture is the 7th in the series of lectures on Engineering Chemistry. Today we will continue with the solutions of hydrogen atom but one particular solution of the hydrogen atom namely the angular parts of the Schrödinger equation.

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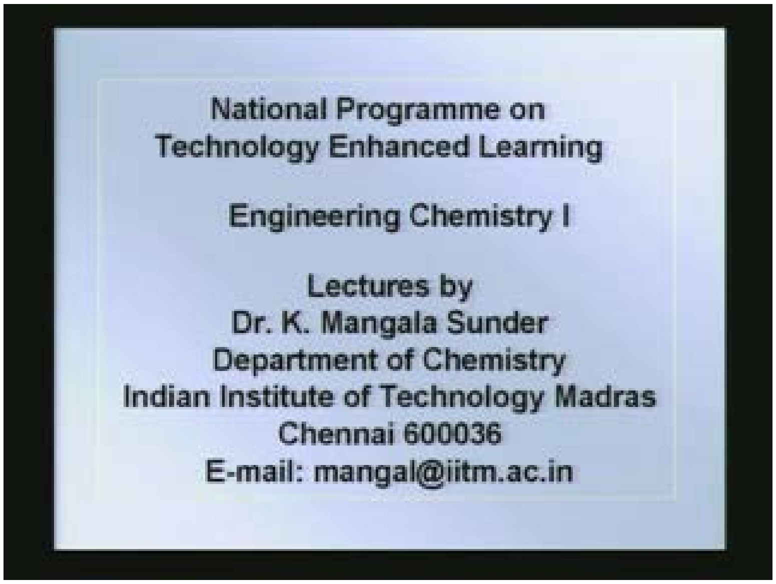

Let me give you the basic coordinates of mine that I am from the department of Chemistry and here is my email address or any contact regarding this program.

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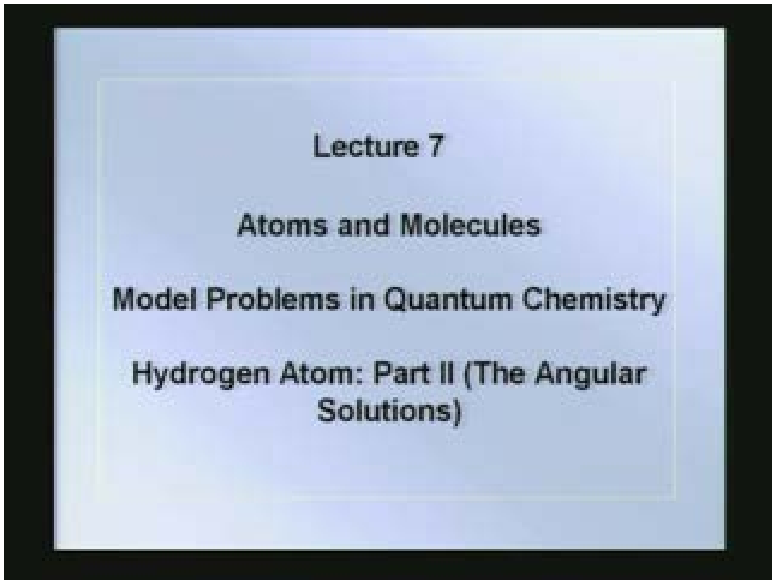

In today's lecture will look at the angular solutions we will study them we will not solve the angular equation. The objective of this series is not to provide detailed solutions to the

Schrödinger equation to the hydrogen atom but rather to look at the solutions in a meaningful way and also wherever possible to visualize them.

The detailed solutions themselves are lectures of a different kind. They are exercises in Mathematical Physics. We will not do that here like in the last lecture where I gave you the solutions of the radial part. The same way we look at the solutions of the angular part. We try to analyze, identify, pattern in them and wherever possible we shall also try to visualize them. In this process of visualization one gets the clear picture of the atomic orbital.

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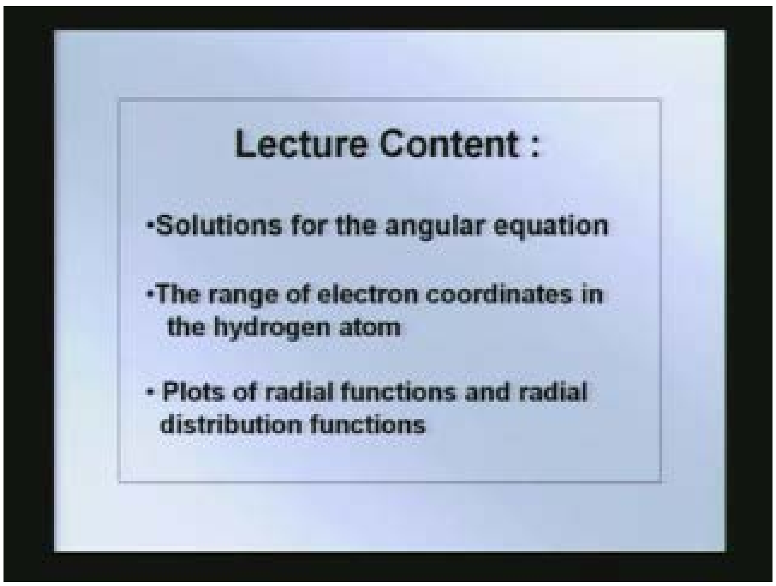

So the content is for today's lecture the solution of the angular part of the Schrödinger equation for the hydrogen atom. We shall look at the range of the electron coordinates in the hydrogen atom. We are studying the solutions using the spherical polar coordinates r, θ and ø and therefore we must know the correct range of the problem as we have looked at for the wave functions. And also we will look at the plots of both the radial distribution functions and angular functions.

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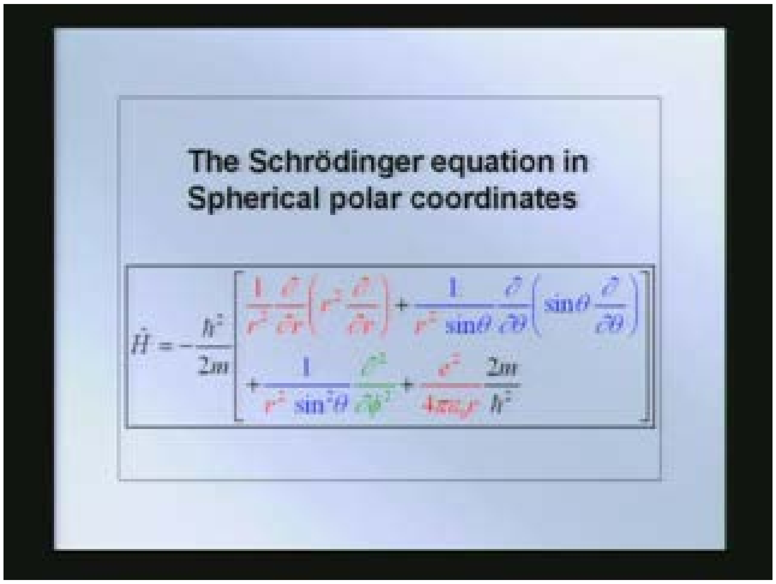

The Schrödinger equation in spherical polar coordinates let us recall the equation once again. You recall that the Hamiltonian for the Schrödinger equation for the hydrogen atom is given by $-\hbar^2/2m\{[1/r^2\ \partial/\partial r(r^2\ \partial/\partial r)]$ which is the radial part. And the angular part of this problem is given by $+[1/(r^2\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial/\partial\theta)]$ this is one of the two angles involved as the coordinates.

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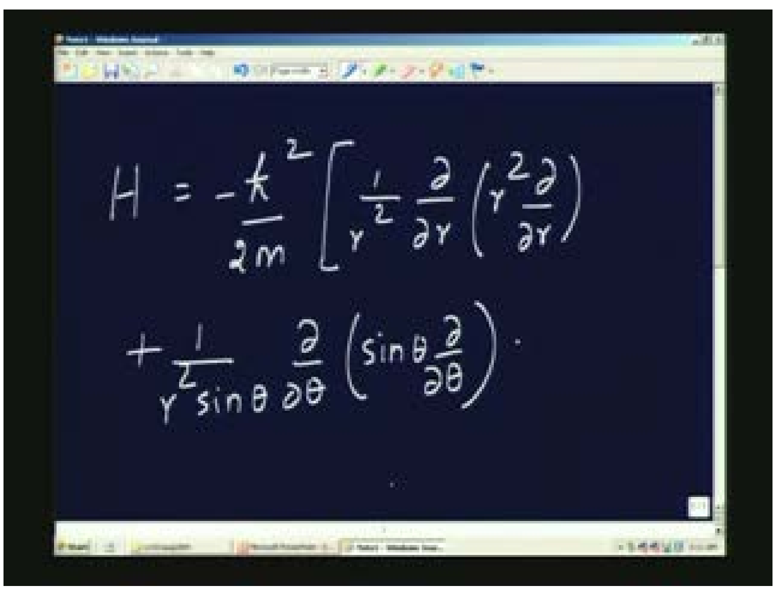

The other term is $+[^1/(r^2\sin^2\theta)\ \partial^2/\partial\phi^2]$. And of course you have the potential energy term $+e^2/4\pi\varepsilon_0 r\ (2m/\hbar^2)$,by combining all parts we get $-\hbar^2/2m\{[^1/r^2\ \partial/\partial r(r^2\ \partial/\partial r)] +[^1/(r^2\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial/\partial\theta)] +[^1/(r^2\sin^2\theta)\ \partial^2/\partial\phi^2] +[e^2/4\pi\varepsilon_0 r\ (2m/\hbar^2)]\}$, this is the Hamiltonian. And if you look at the Hamiltonian the angular parts are given by the once that I draw with the box $[^1/(r^2\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial/\partial\theta)]$ and the $[^1/(r^2\sin^2\theta)\ \partial^2/\partial\phi^2]$.

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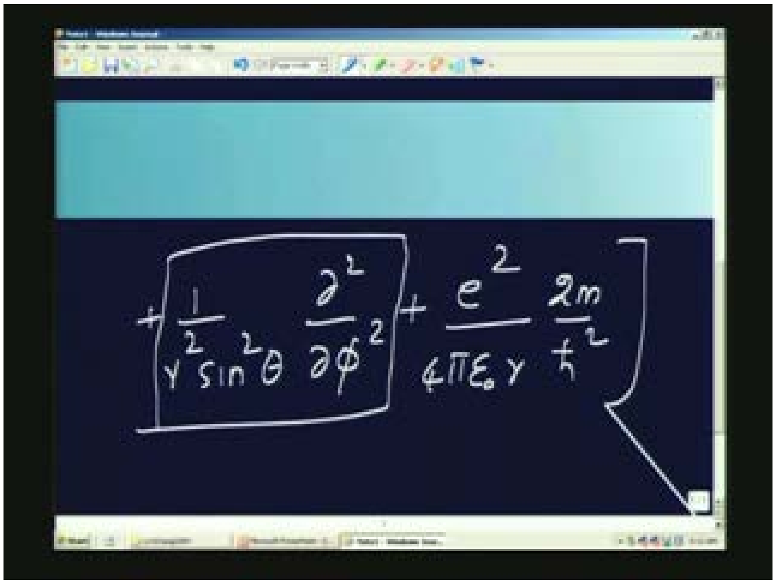

These are the terms which are solved by separating the Schrödinger equation into the radial part and the angular part. Let us go back and look at the slide. When you separate this out into a radial part and an angular part the corresponding angular equation one needs to solve is given by the (θ, ϕ) equation.

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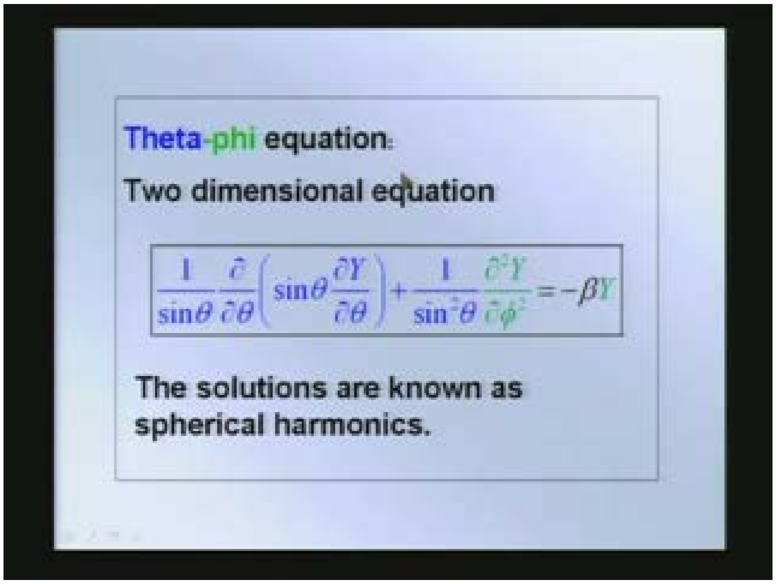

I shall leave this as an exercise for some of you to do that, the two dimensional (θ, ø) equation is now written in terms of $^1/(\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial Y/\partial\theta) + {}^1/(r^2\sin^2\theta)\ \partial^2 Y/\partial ø^2 = -\beta Y$, Y is the solution that we are looking for and it is a function of θ and ø in the same spirit as the quantum mechanics that we were trying to explain in the past few lectures namely when you have more than one variable that you try to write down the equation in such a way that the wave functions can be separated into functions of individual variable. Here it is now expressed as a radial function and an angular function and the corresponding angular function is Y. So this is the equation that we have to solve and this β is the same as the β that appeared in the radial part in the last lecture. The solutions of this equation are known in Mathematics as spherical harmonics.

Schrödinger did not solve these equations, these were well known. Schrödinger's formulations were to relate the known solutions to the solution of his equation that he proposed. The spherical harmonics have been known in various forms earlier almost 100 years or even more than that from the solutions of Lashander polynomial, Lashander differential equation and associated Lashander differential equations so these are not new.

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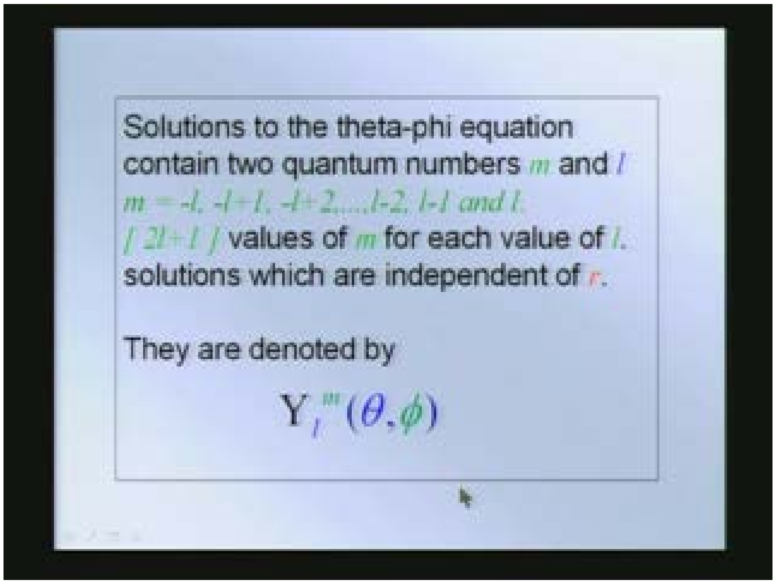

The (θ, ø) equation leads to two quantum numbers. The differential equations we tried to solve in every instance the particle in a box, the particle in two dimensional box, the harmonic oscillator, the radial functions, the radial equation for the hydrogen atom etc with a certain boundary condition lead to quantum numbers as a requirement and these are which that leads to the discretization of the energy. In the same way the angular equation with the corresponding boundary conditions that θ and ø takes certain values lead to two quantum numbers m and l. The value l was described in the previous lecture as taking the values from 0, 1, 2 up to n – 1 where n is the principle quantum number associated with the radial equation.

Now, for any given l the value of m which is the other quantum number takes the following values namely – l, – l + 1, – l + 2 all the way up to l in steps of an integer. Suppose you look at a solution corresponding to n = 1 the corresponding angular equation solution will contain only l = 0 up to n – 1 which is 0 here. Therefore l = 0 is the only possible quantum number for that particular solution. And what are the corresponding m values? So m is also from – l to + l corresponds to only 0. (Refer Slide Time: 9:23 min)

Now, extending this argument to the next case namely a radial solution with n = 2 the corresponding angular equations gives you the following possible values for the quantum numbers l and m. l can be 0, 1, 2 up to n – 1 which in this case is 0 and 1. Now, for each value of l the corresponding value of m is from – l to + l.

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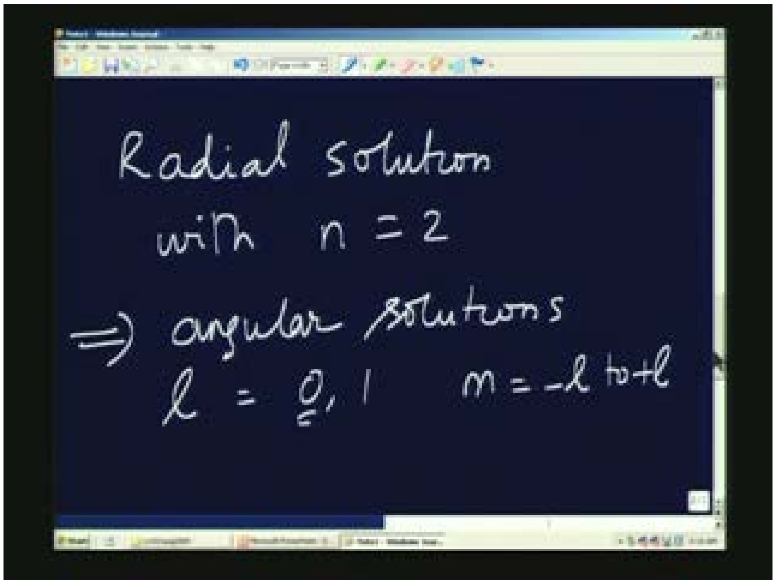

Therefore for l = 0 the only possible value for m is 0, for l = 1 the possible values are m = – l to + l which means –1, 0, +1. Please remember that these solutions are not something that you have a freedom of choice, no, they come out as a result of imposing boundary conditions on the problem as required by the nature of the wave functions that the wave functions must vanish at the boundaries of the problem and so on. Therefore the quantum numbers are natural as solutions.

These are the quantum numbers associated with the hydrogen atom and every orbital of the hydrogen atom has three quantum numbers. The result that you studied earlier comes out of the requirement of solving the Schrödinger equation very rigorously using the Mathematics as we know. Therefore the choice of m’s and l’s are not arbitrary but subject to the rules that I specified just a few minutes ago.

Let us go back and look at the slide. The solutions are therefore for a given value of l and for a given value of m, now given a principle quantum number n it is easy for you to show that for every n there are n square such solutions of Y, we will see that in a minute.

First of all because of the quantum numbers involved let us denote our solutions Y in the form of quantum numbers Y_l^m and these are obviously function of θ and ø the two variables for the angular part of the hydrogen atom and there are n square such solutions, it is easy to see that.

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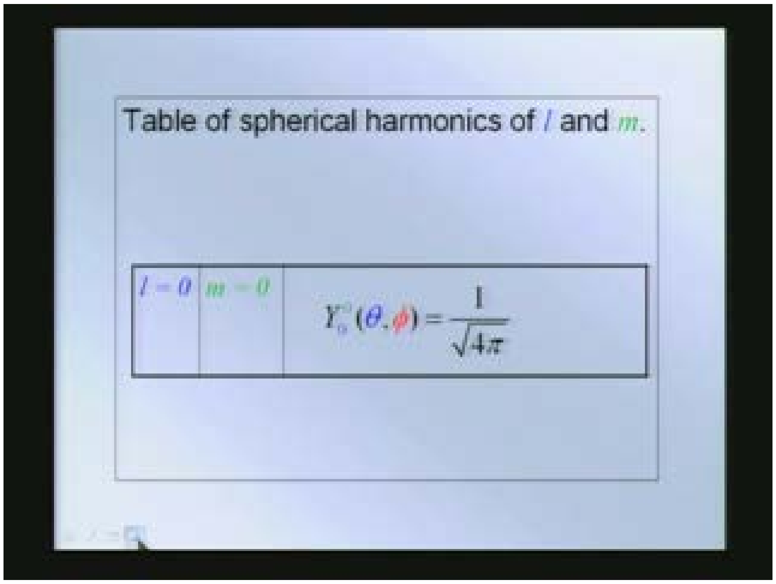

What are the functional forms of these Y_l^m? The differential equations which were solved earlier are the functional forms for the solutions Y. We can organize them in the form of a table for a given value of n and for various values of m. It so happens that for l = 0 and m = 0 this function is actually independent of θ and ø it is nothing but n constant and this $1/\sqrt{4\pi}$ is a normalization constant as we will see later. This $Y_0^0(\theta, ø)$ is $1/\sqrt{4\pi}$ independent of θ and ø.

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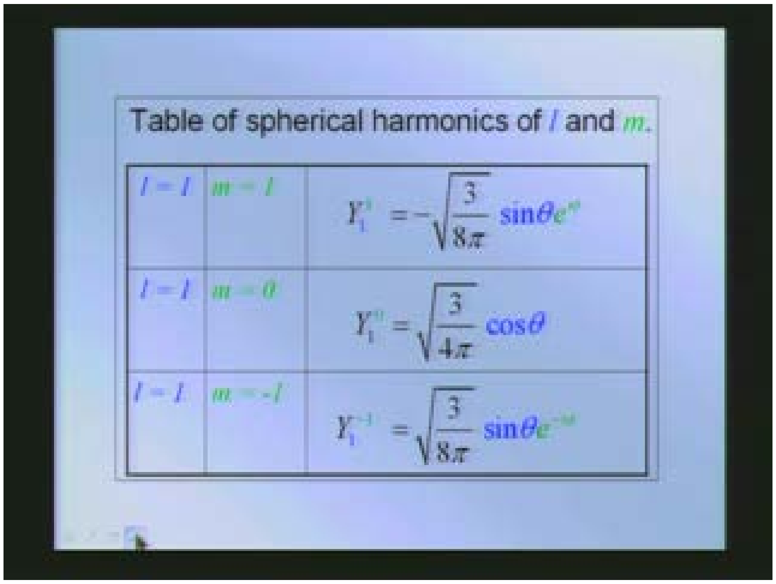

For l = 1 there are three solutions m = 1, 0 and – 1 and you notice for l = 1 the corresponding values are indicated by Y_1^1, Y_1^0, Y_1^{-1} and the solutions involved there is $-\sqrt{(3/8\pi)}\ \sin\theta e^{i\phi}$, a minus sign involved here. You see that this is a function of θ and ø. The Y_1^0 is $\sqrt{(3/8\pi)}\ \cos\theta$ and this is independent of ø. And then Y_1^{-1} is $\sqrt{(3/8\pi)}\ \sin\theta e^{-i\phi}$ and it is looks exactly like Y_1^1 except for the sign difference here as well as this one more difference $\sin\theta e^{-i\phi}$ where the Y_1^1 was into the +iø. They appear to be complex conjugates of each other with a sign difference. This is the set of solutions corresponding to l = 1. No matter what the value of n is as long as n is greater than 1 if n is 2 then l = 1 is allowed, if n is 3 then l = 1 is also allowed. (Refer Slide Time: 14:30 min). Therefore no matter what the value of n the principle quantum number is you call as the second orbital or third orbital or fourth orbital. You remember 2s, 3s, 4s, 5s etc what are those 2, 3, 4 etc? They are the quantum numbers n and no matter what the value of n is. For l = 1 these are the three possible solutions. For l = 2 which is possible only if n = 3 because n – 1 is the maximum value for l therefore n must be 3 in order for l to be 2. For l to be 2 there are five possible solutions namely m = 2, 1, 0 – 1, – 2 and again let us look at the solutions carefully.

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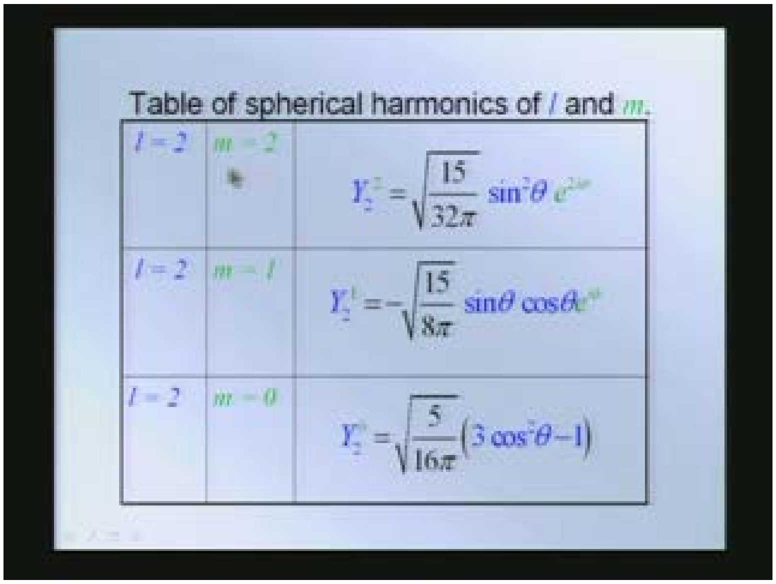

For m = 2, the ø dependents is $e^{2iø}$ and it is $Y_2{}^2$ here the lower the subscript is 2, the superscript is 2 corresponding to m value. The superscript here corresponding to m is 1, $Y_2{}^1$ corresponding to the m value the exponential here that the ø function is $e^{iø}$, and $Y_2{}^0$ does not contain any exponential ø it is independent of ø.

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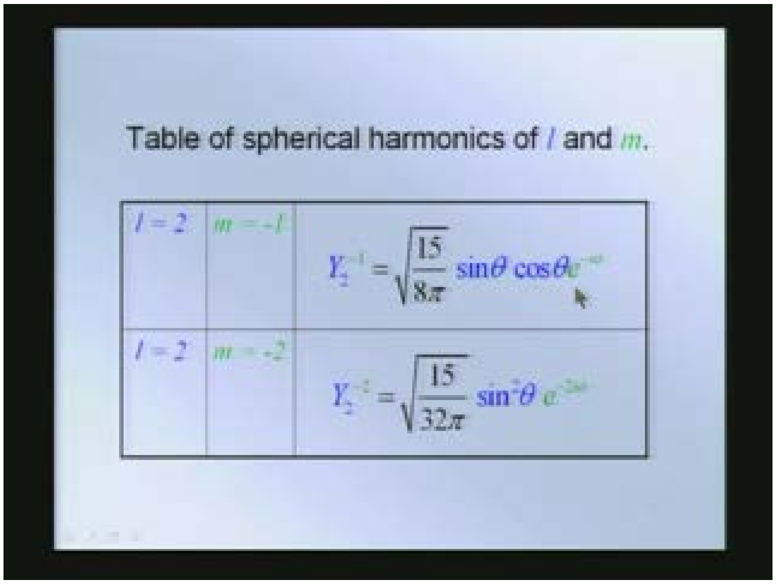

For m = –1 the ø dependents is $e^{-iø}$, for m = – 2 the ø dependents is $e^{-2iø}$.

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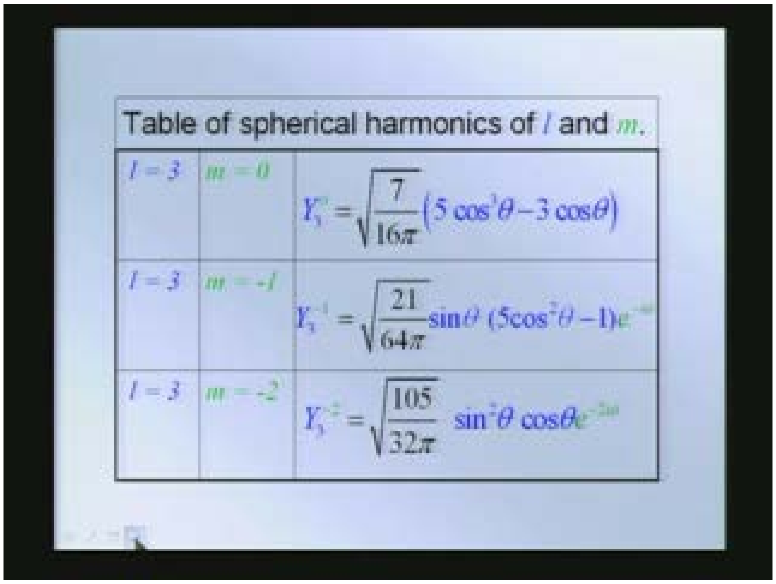

Basically what you see is that whatever is the corresponding value of m the ø part seems to be $\mathbf{e^{im\phi}}$. In fact that is a rigorous solution one can obtain by solving the angular part using Mathematics. What about the θ dependence? For m = 2 the θ dependence Y_2^{2} is $\sin^2\theta$, for m = 1 there is a $-\sin\theta\cos\theta$ and for m = 0 there is $(3\cos^2\theta - 1)$. Look at the degree of the trigonometric functions here, the degree is 2 then this is 2 the maximum here is 2 and $\sin\theta\cos\theta$ for Y_2^{-1} and Y_2^{-2} is $-\sin^2\theta$. So, the degree of the trigonometric functions for sine and cos for any particular Y_l^m is l whatever is the value of l. Here l = 2 so you have a second degree.

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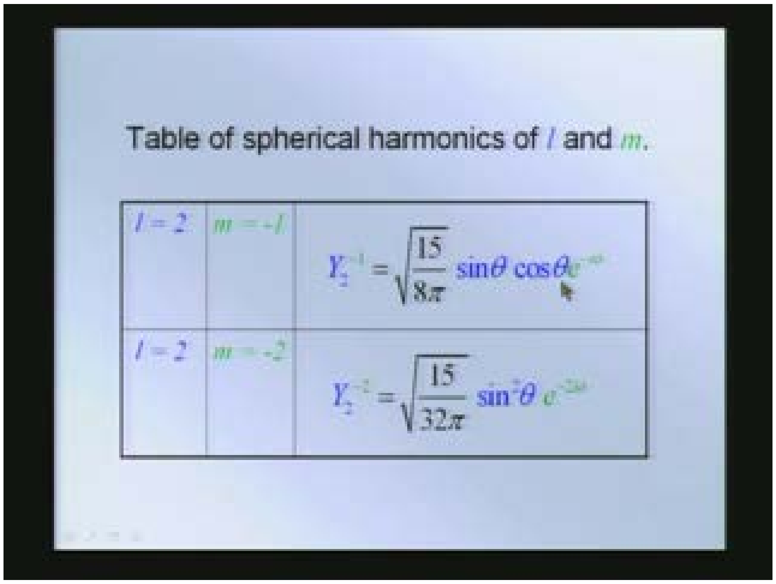

What about l = 3? Here l = 3 is possible only when n = 4. And you know, if you remember the periodic table lithium is 2, sodium is 3s in the sequence lithium, sodium and then potassium is 4s.

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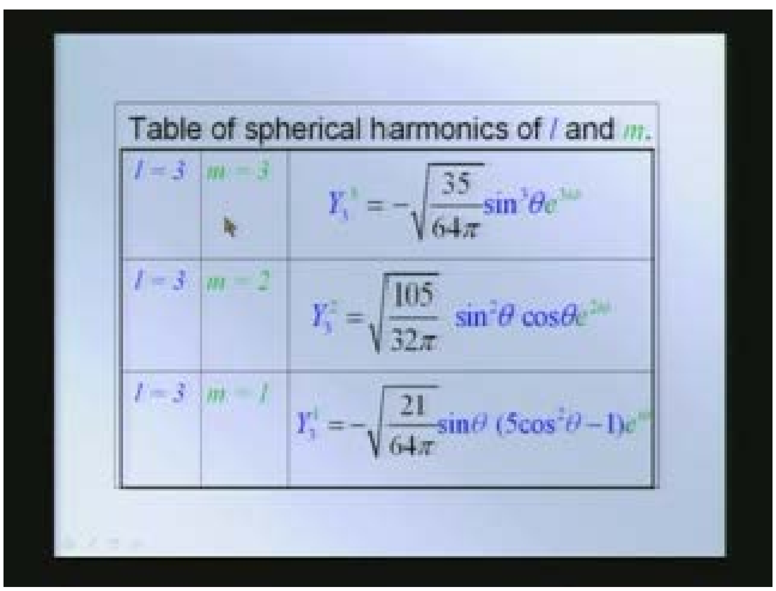

So, only when you go to the n = 4 case you have the l = 3 possibilities and for that there are seven possible values of m corresponding to 3, 2, 1, 0, – 1, – 2 and – 3. So, let us look at these functions again. For m = 3 it should be obvious that the ø dependence is $e^{im\phi}$, i is $\sqrt{-1}$ no problems we have seen this several times. For m = 2 the solution is $e^{2i\phi}$, and m = 1 it is $e^{i\phi}$ and so on. Now, what about the trigonometric part? For l = 3 we have $\sin^3\theta e^{3i\phi}$, degree is 3 and then $\sin^2\theta\cos\theta$ again degree is 3 and so on $\sin\theta(5\cos^2\theta - 1)$ the maximum degree is the highest degree is 3 again. So what you see is that for spherical harmonic of order 3, l and m the ø part is $e^{im\phi}$. The θ part is a corresponding polynomial or function of $\sin\theta\cos\theta$ such that the total degree is l.

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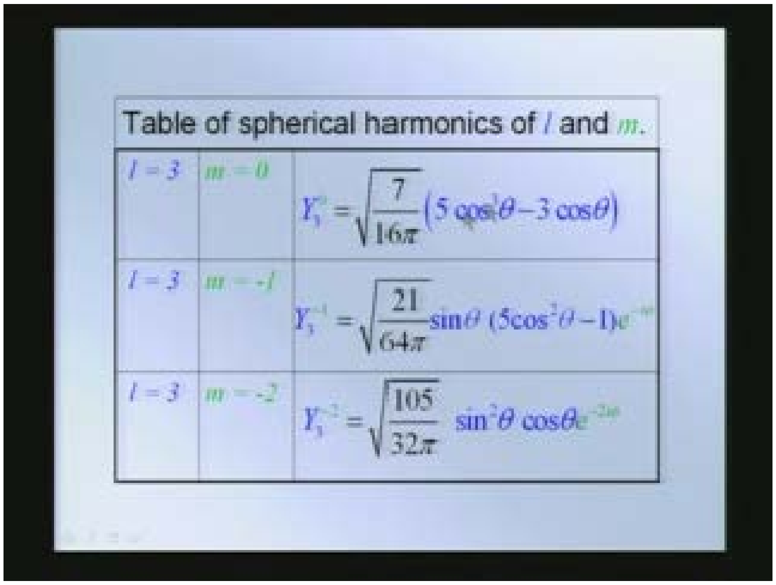

So $(5\cos^2\theta - 3\cos\theta)$, the maximum degree here is 3 and likewise $\sin^2\theta\cos\theta$ and so on. Therefore there is a pattern that one can easily remember in identifying the spherical harmonics with certain solutions corresponding to l and m.

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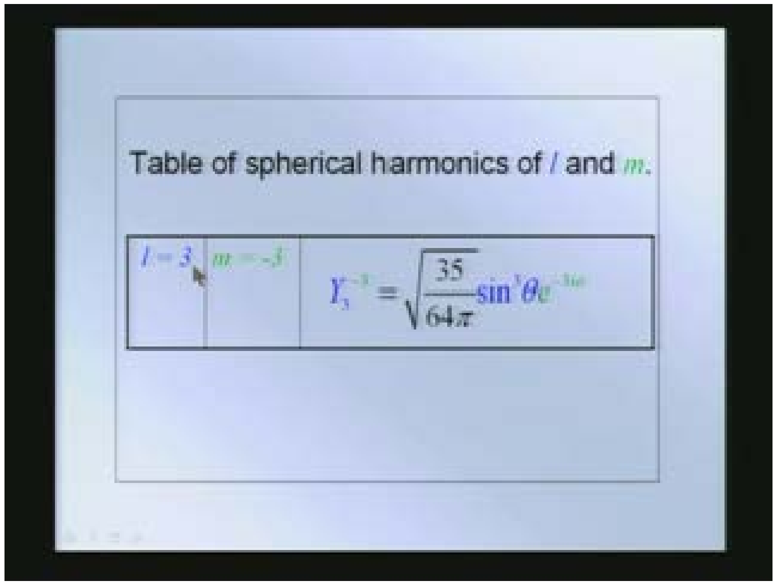

The last one of course l = 3, m = –3 is $\sin^3\theta$ and there are of course a lot of constants in front of these. You see, these seem to be random but they are not actually random they are obtained by normalizing these solutions. We will see later that these constants are obtained through basic definitions of how we write this spherical harmonics.

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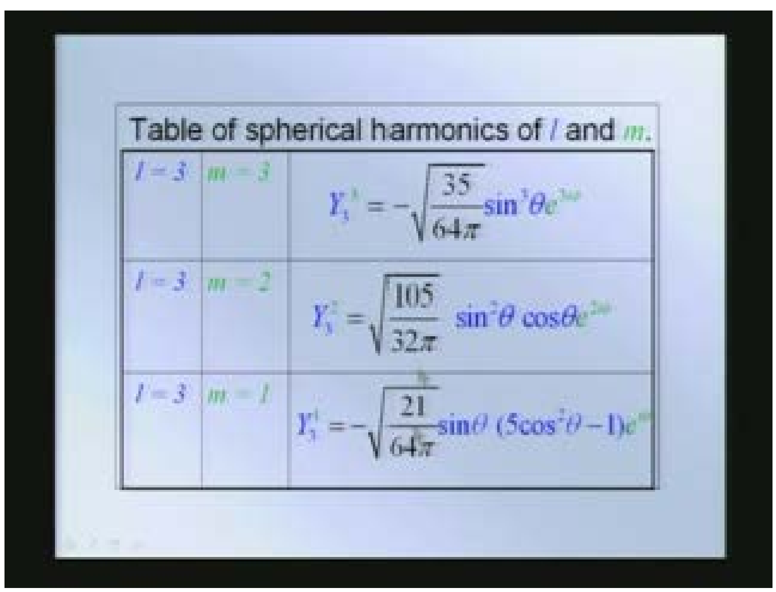

The normalization constants √35/64π, √105/32π √21/64π and so on with minus signs all over the places and that seems to be arbitrary. We do not need to remember any of these but looking at these functions one should be able to associate a corresponding l value and m value just by visual examination and that is what I am trying to do here.

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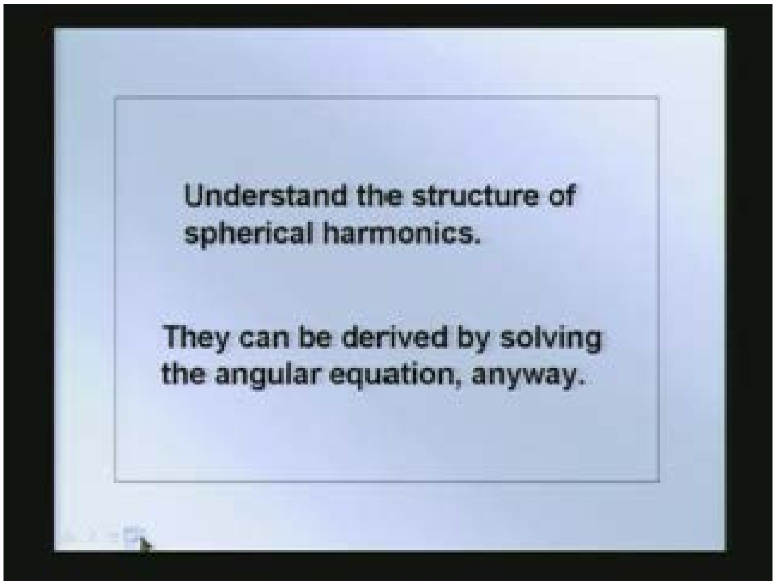

This is what I call as the structure of spherical harmonics. The whole idea of course is that spherical harmonics can be obtained by solving the associated Lysander polynomials and then the ø part and so on, that is a bit of Mathematics. Those of you are interested in Mathematics may refers to special functions and sections in differential equations and the solutions. Some of these are listed under orthogonal polynomials known as the Laguerre polynomials, Lysander polynomials, Hermite polynomials, semi-shaped polynomials, bessel functions and so on.

You can always look at the Mathematical details by solving them at your own leisure. But what is important is to understand the structure here of spherical harmonics namely corresponding l value, m value and that the fact that they can be actually derived by solving the angular equation, so these are the things to be kept in mind.

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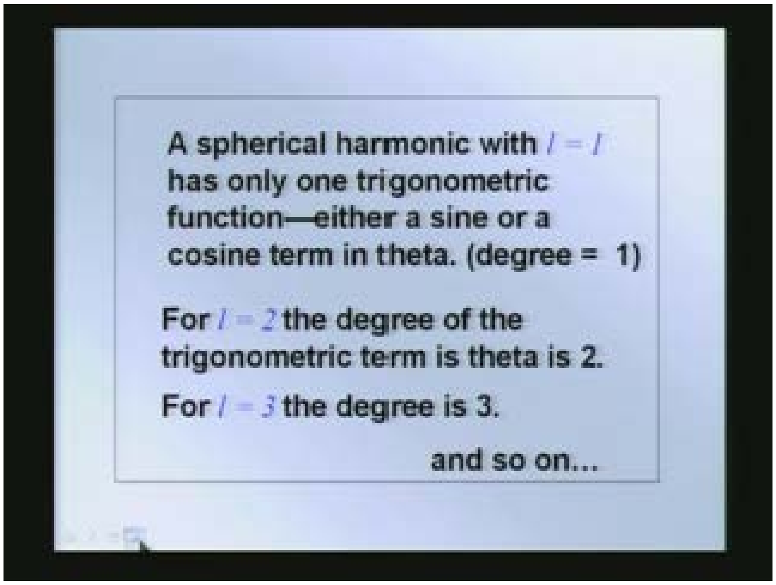

So let me summarize that part of the lecture namely a spherical harmonics with l = 1 as one trigonometric function either a sine or a cosine term in θ with degree 1. For l = 2 the degree of the trigonometric term in θ is 2. For l = 3 the degree is 3 and so on.

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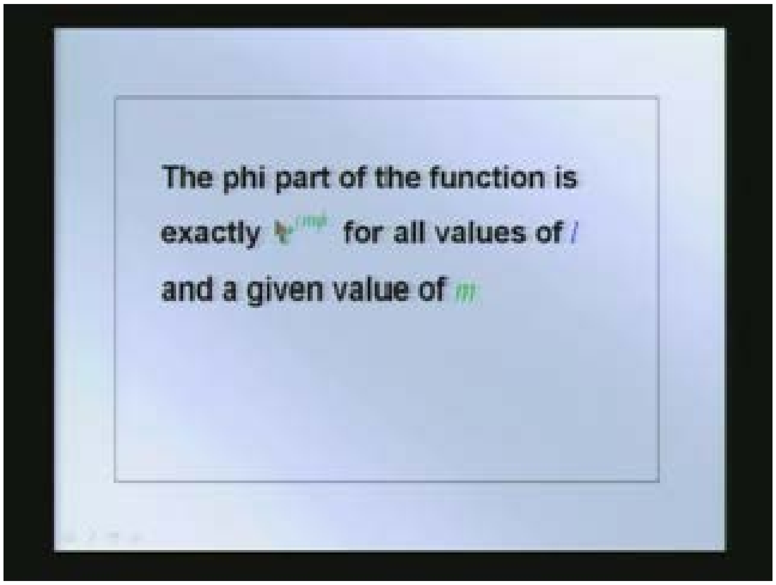

For the ø part the solution is exactly $e^{imø}$ for all values of l and a given value of m. So when m is 0 this is obviously 1 which means it does not appear. Therefore you remember $(3\cos^2\theta - 1)$ for l = 2, m = 0 and so on.

Let me give you a little about what are the values of these coordinates and how do we do the volume element integration for calculating probabilities for calculating average values in quantum mechanics etc of the hydrogen atom before we move on to visualizing these spherical harmonics.

When you plot spherical harmonics in a polar diagram you will get all the orbitals that you have seen in the text books earlier. But before that let us look at the range of the electron coordinates in the hydrogen atom and keep this in mind in doing all the possible calculations in the next lecture.

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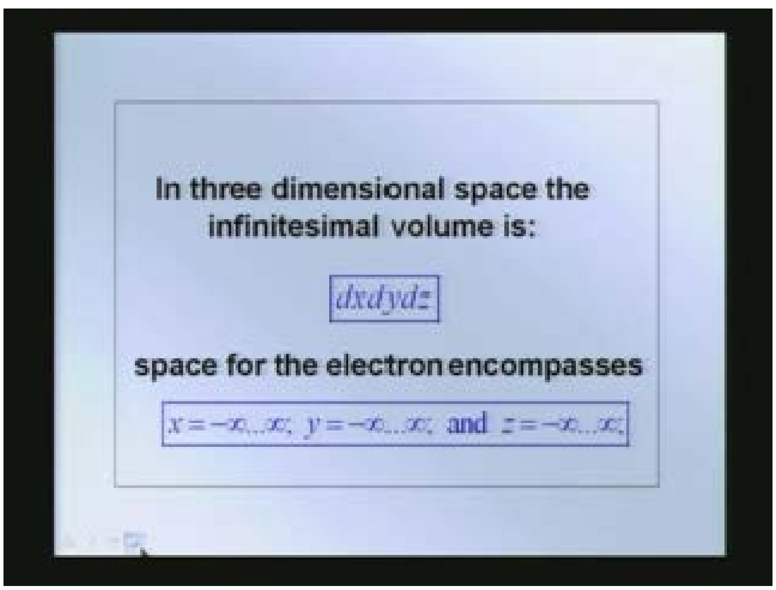

You recall that for the hydrogen atom the coordinates that we started off was x, y and z. the Schrödinger equation was written in the (x, y, z) coordinate system. And then following the conventional wisdom we transformed this (x, y, z) coordinate system into the spherical polar coordinate system of r, θ and ø. So the infinitesimal volume which you need to remember just as you did in particle in the 1D box calculation you remember doing the integrals $\int \sin^2 x \, dx$ and x ranging from 0 to l where l is the length of the box in order to calculate probabilities, in order calculate the average values in quantum mechanics. Same way if we have to do this for the hydrogen atom the infinitesimal volume element dxdydz is the volume in the Cartesian coordinate space.

And what are the available values for these coordinates for the electrons in the hydrogen atom? The whole universe, $x = -\infty$ to $+\infty$, $y = -\infty$ to $+\infty$ and so is z, it is Universe. Of course it does not make any sense to have the hydrogen atom nucleus here and the electrons sitting somewhere in Los Angeles does not make any sense. But the probability that such a situation arises and the fact that the electron belongs to the hydrogen atom the nucleus here those are all extremely small. Quantum mechanics is going to give you reasonably convincing answers that such probabilities are actually meaningless.

However, in principle the coordinates allowed for the hydrogen electron with the nucleus at the origin keeping the nucleus at the origin the coordinates available to the hydrogen atom electron is the whole Universe $-\infty$ to $+\infty$ in all the directions three dimensions and we talk about a three dimensional world this is the space available for the electron. Therefore how does this translate in the r, θ and ø coordinate system?

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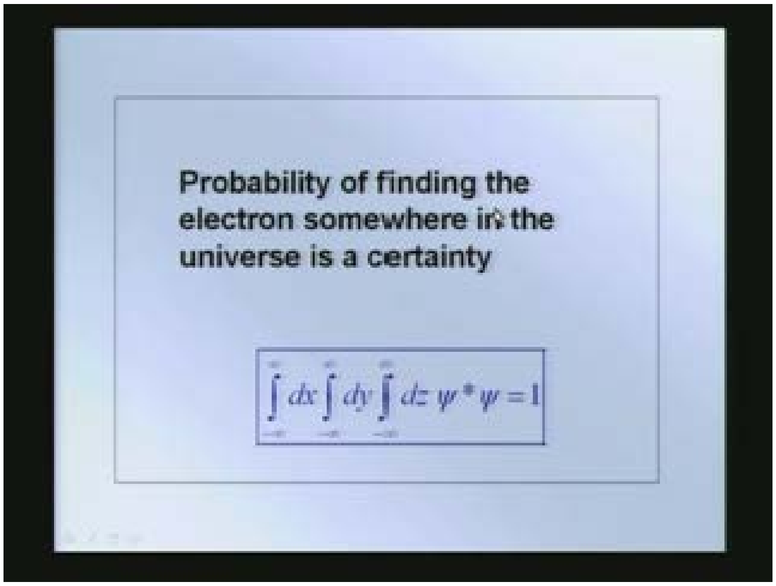

The probability of finding the electron somewhere in the Universe is obviously when you add all these probabilities, if you put the electron in the Universe it is going to be there only. Therefore the total probability of finding the electron in the Universe has to be 1. So, if you write the wave function as the $\int dx \int dy \int dz\ \psi^*\psi$ (with in the limits $-\infty$ to $+\infty$) as the probability.

If we write $\psi^*(x, y, z)\ \psi(x, y, z)\ dx\ dy\ dz$ what is the meaning of this? The meaning of this particular term is that this represents the probability of finding the electron in a volume enclosed between the range here $x \to x + dx$, $y \to y + dy$ and $z \to z + dz$ that is in the volume range $dxdydz$ centered around under the points x, y, z. This is the interpretation for the ψ, there is no other interpretation for the wave function.

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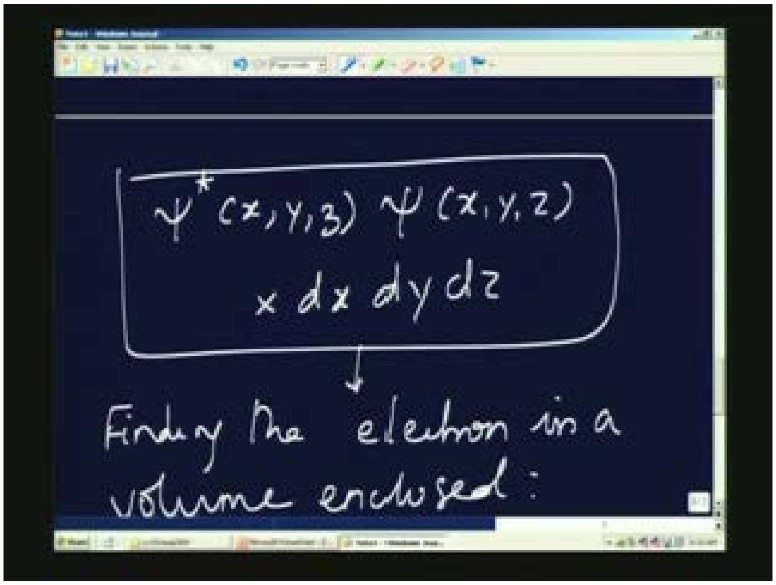

I have been telling you and so have been all my teachers telling me that the wave function itself is a meaningless quantity. The absolute square of the wave function calculated in a certain small region of space gives you the probability of finding the electron in that space. So this quantity is the only meaningful quantity that we can extract by knowing the solutions of ψ. But now instead of (x, y, z) we will write this in the form of r, θ and ϕ that is ψ is now written in terms of $\Psi(r, \theta, \phi)$. Therefore we need to translate the $dxdydz$ into $drd\theta d\phi$ in that particular space. (Refer Slide Time: 27:08 min)

Let us go back and look at the slide. If you calculate that probability and you add all these probabilities dx, dy, dz over the entire domain or entire Universe that is the integration you are adding all these probabilities then the total probability is of course 1 because the electron once it is put in it is in somewhere in the Universe.

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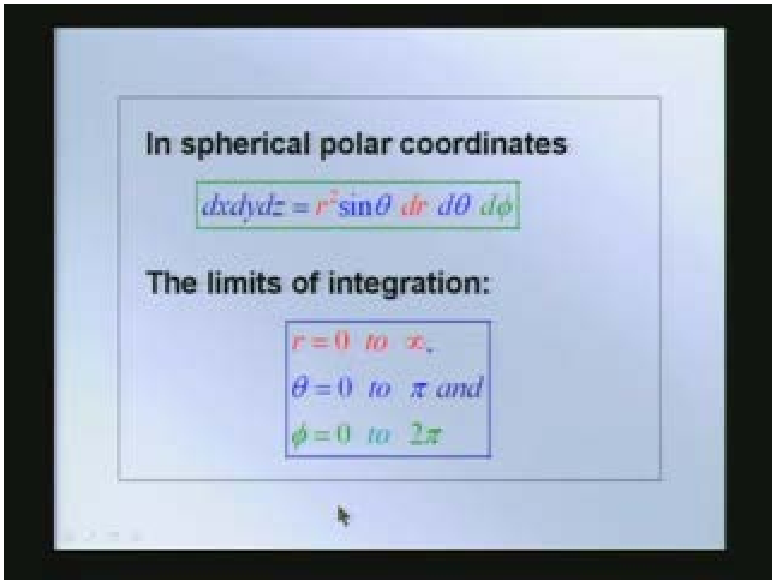

In spherical polar coordinates of course the dxdydz has to be written as r^2sinθ dr dθ dø. This again comes from simple volume element calculations using multiple integrals between different coordinate spaces. This is in fact related to what is called the Jacobian of the problem in the transformation between (x, y, z) coordinate system to r, θ and ø coordinate system. If you do not know that this is one thing worth memorizing dxdydz has to be replaced by r^2sinθ dr dθ dø. What are the ranges of the values? r is of course the radius of the sphere you recall that it is a spherical polar coordinate system where r represents any given sphere of radius r therefore the smallest sphere is the radius is a point the radius is equal to 0 and the largest sphere is equal to infinity.

So, r takes the values between 0 to ∞ representing the sphere. And θ you recall is the polar coordinate from 0 to π as it goes from the z axis the polar axis the north pole to the south pole and ø takes you around the globe in a sphere and that is 0 to 2π. This is the limit of integration that one has to keep in mind just like one has the limits for x, y, z as −∞ to +∞ for all three of them. So the limits of integration must be kept in mind in doing these calculations for probabilities and for average values. Now, with that we will come one part of the lecture.

The second part is, we have looked at angular part let us see how the angular parts look like in an appropriate coordinate system because we are referring to the angular variables θ and ø we have to represent it in the coordinate system in which θ and ø are obvious.

So, first we will look at the l = 1 case, l = 1 is possible only when n = 2 that corresponds to this 2 in 2p and l = 1 is referred to as p. Remember, Sharp Principle Diffuse and Fundamental SPDF the s is for l = 0 it is also spherical but it is always known as the sharp line and the p is for principle corresponding to l = 1. So here when we talk about 2p we are looking at the n = 2, l = 1 the corresponding angular parts of the functions let us visualize.

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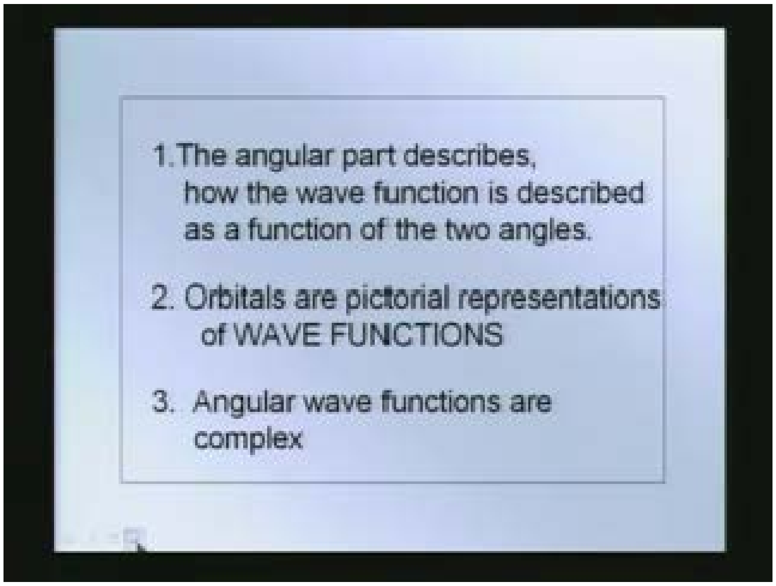

Now, one thing that you have to keep in mind is that the angular part is not the whole wave function. The angular part describes only how the wave function is expressed as a function of two angles. The overall wave function is the angular part multiplied by the radial part. And orbitals are in principles pictorial representation of the overall wave functions. But here we are going to look at only the angular part and we are going to call them as orbitals but we have to be careful that the shapes and sizes of these orbitals will be different for different p orbitals namely 2p orbital will have certain shape, 3p orbital will not have the same shape because 3p orbital corresponds to n = 3 the radial part associated with that is different. We will do the simple pictorial representation and the also the angular wave functions are complex that is there is an

$e^{im\phi}$ in them i is the $\sqrt{-1}$. Therefore we are talking about a function which has a real and an imaginary part so what we have to do is to plot the real part and the imaginary parts separately both of which are functions of real variable θ or ø.

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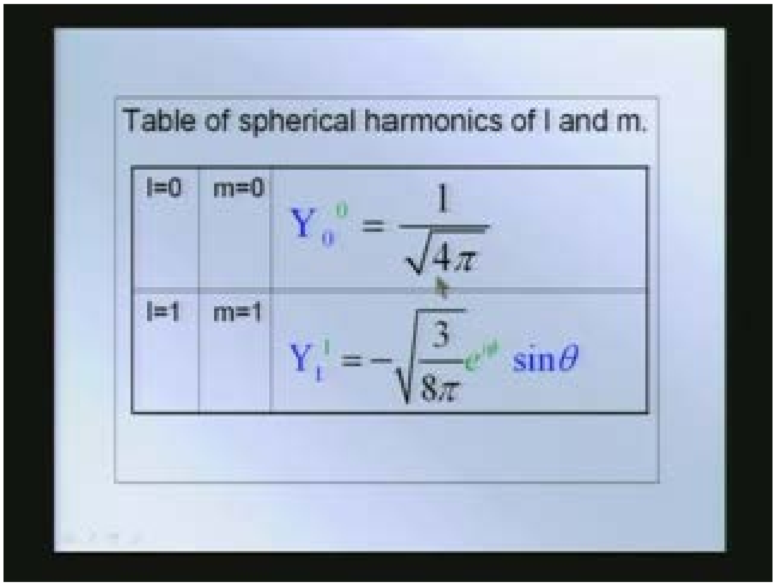

So there is no fun in plotting the first function $Y_0^0 = 1/\sqrt{4\pi}$ as a function of θ and ø is independent therefore it is uniformly the same everywhere. But the first interesting function to plot is of course not Y_1^1 itself but the real part and the imaginary parts of Y_1^1. You recall $e^{i\phi}$ sinθ, let us go back and do that. You recall that Y_1^1 is proportional to –sinθ $e^{i\phi}$. And Y_1^{-1} is again proportional same constant that sinθ but with the + sign and $e^{-i\phi}$.

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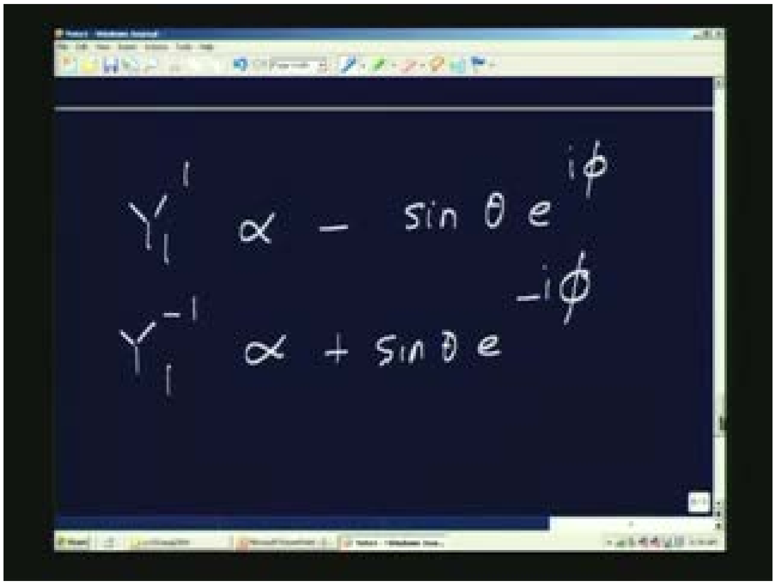

Therefore the real and the imaginary parts of these functions can be obtained by adding and subtracting these quantities. In this case because there is sign difference the real part is obtained by subtracting one from the other the imaginary part is obtained by adding one with the other. Let us do this namely $Y_1^{-1}+Y_1^{1}$. If you do that it gives you $\sin\theta\ [e^{-i\phi} - e^{+i\phi}]$ this is addition because this Y_1^{1} has a negative sign with the spherical harmonics, this $e^{-i\phi} - e^{+i\phi}$ is $\sin\phi$, leave the constants aside and the functional dependence is something like $\sin\theta \sin\phi$, that is by saying this is still there, you can do the exact algebra arithmetic yourself but the θ ø dependence is $\sin\theta \sin\phi$.

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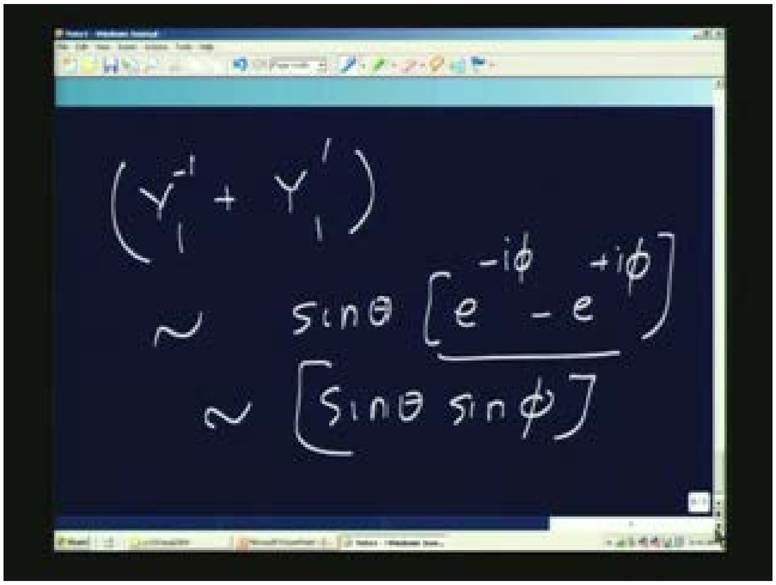

Now, the same thing if you do $[Y_1^{-1} - Y_1^{1}]$ you will get something like sinθ cosø, the cosø comes because you are adding the $[e^{-i\phi} + e^{+i\phi}]$. So what you have is one linear combination gives you sinθ cosø and the other linear combination gives you sinθ sinø.

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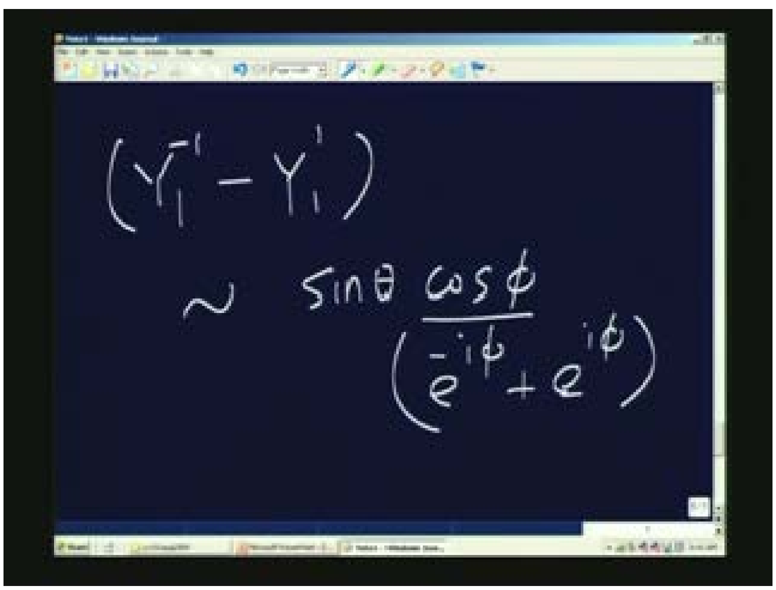

I think that should be obvious because if you recall the definition of (x, y, z) in spherical polar coordinate system x is r sinθ cosø, y is r sinθ sinø and z is r cosθ. Right now since we are only taking the θ, ø dependence let us limit ourselves to a particular sphere of certain radius r which is a constant so we do not have to worry about this. So sinθ cosø looks like the x variable, sinθ sinø looks like the y variable and cosθ looks like the z variable.

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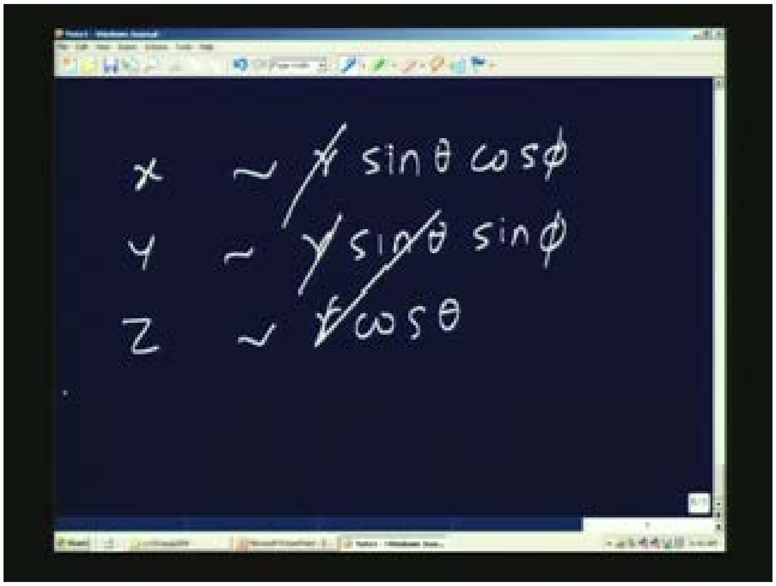

Therefore this particular combination namely sinθ cosø which is the real part of Y_1^1 is called the p_x orbital in relation to the fact that x is like sinθ cosø. (Refer Slide Time: 35:35 min)

The quantity sinθ sinø which is a linear combination of Y_1^{-1} and Y_1^1 another linear combination is called the p_y orbital and cosθ which is Y_1^0 you remember that it did not have any exponential ø dependence because the m value is 0 therefore $e^{im\o}$ is 1 that means 0 therefore the cosθ is Y_1^0 that is like the p_z orbital.

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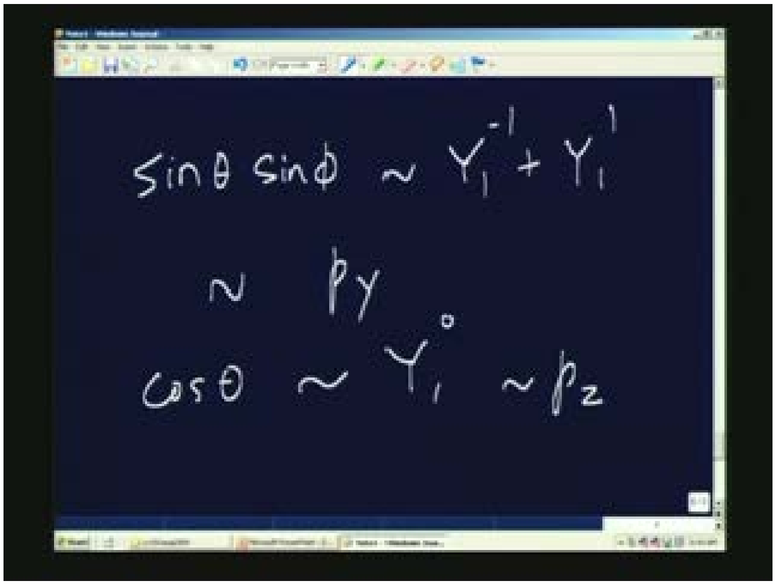

So the origin of the terms p_x, p_y, p_z orbitals basically come from the spherical harmonics which are exact solutions to the angular part of the hydrogen atom. And the labels x, y and z which are associated with Cartesian quantities Cartesian coordinate systems in the spherical polar case lead to linear combinations of the spherical harmonics. Now, let us try and plot the p_z and then we will plot the p_x and p_y.

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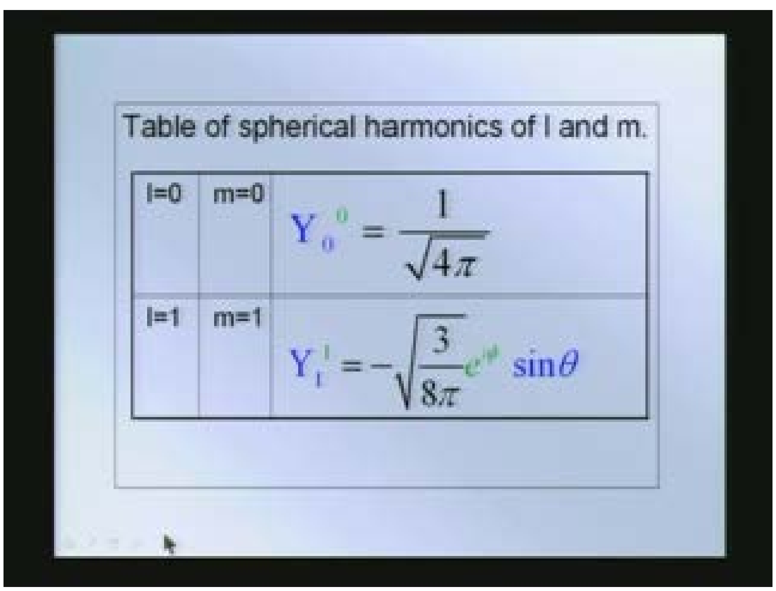

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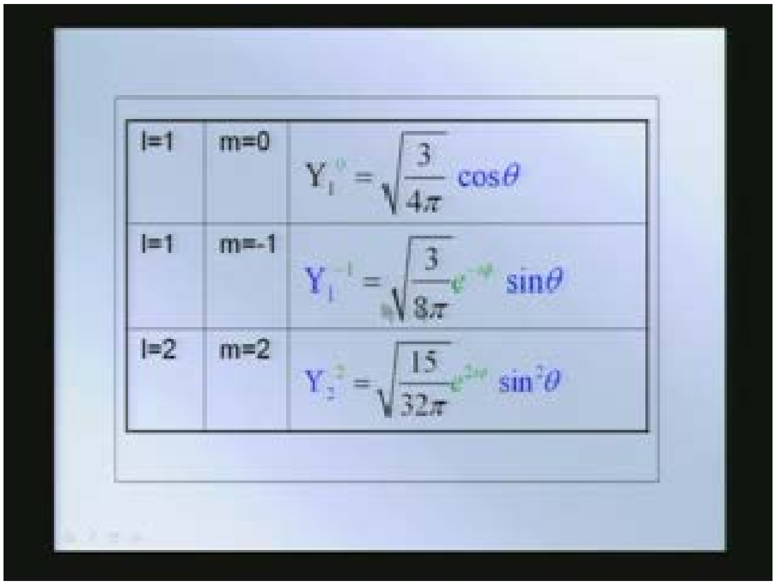

So having kept this in mind namely Y_1^1 and Y_1^0 is $\cos\theta$ this is like the p_z and this is $e^{-i\phi}\sin\theta$ and so on.

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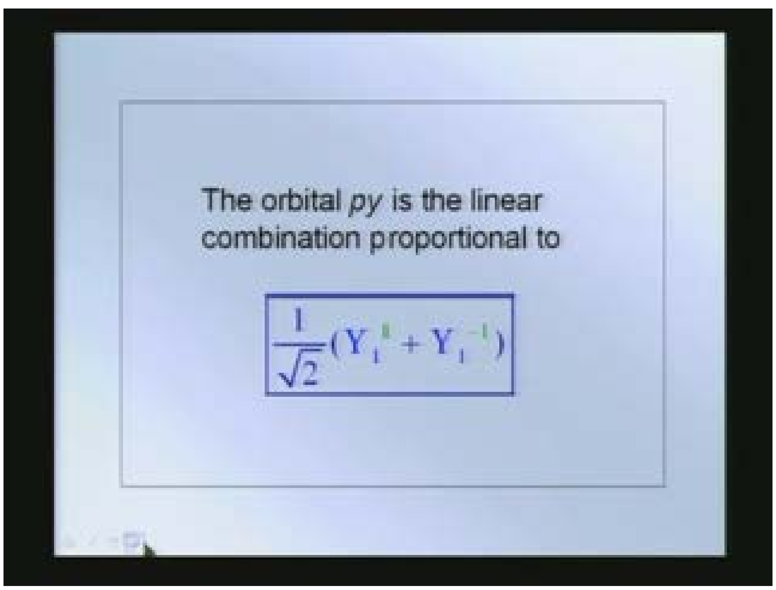

I have just now said that the linear combination $Y_1^1+Y_1^{-1}$ gives you something like p_y.

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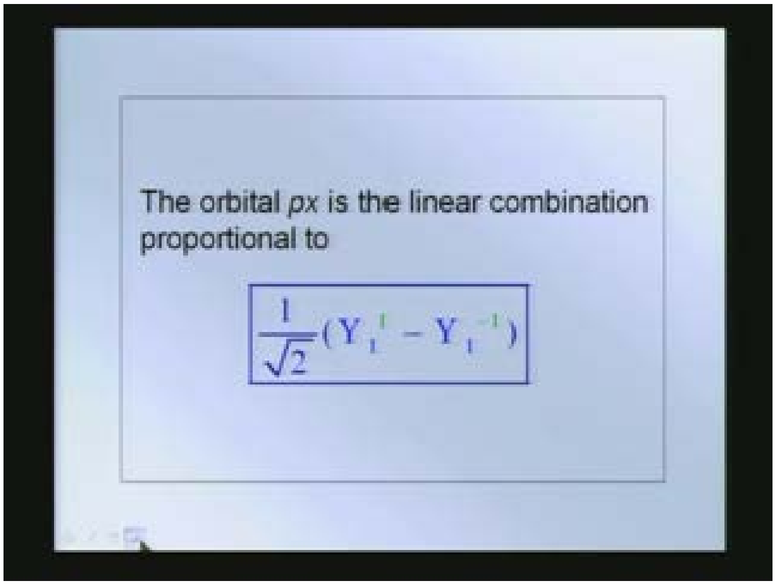

$Y_1^{1} - Y_1^{-1}$ gives you something like p_x.

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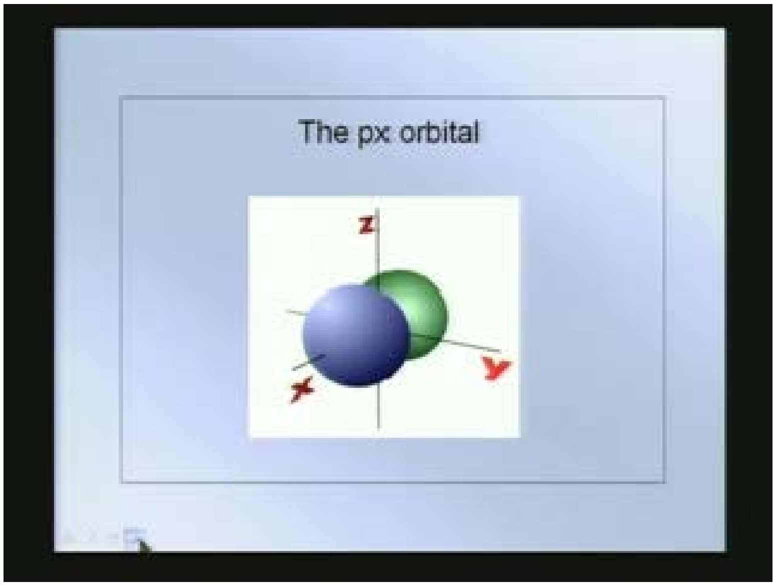

First let us look at the final form and how to get the final form from the Mathematical functions. So this the p_x orbital as we have here, how does it look like in all the directions? In all the directions you have got two lobes pointing along the x-axis and the –x-axis with two different colors. The color indicates that the function has a negative value on one side of the y-axis and positive value on the other side of the y-axis. The p_x orbital comes from rigorous solution of the hydrogen atom. Then what about the p_y?

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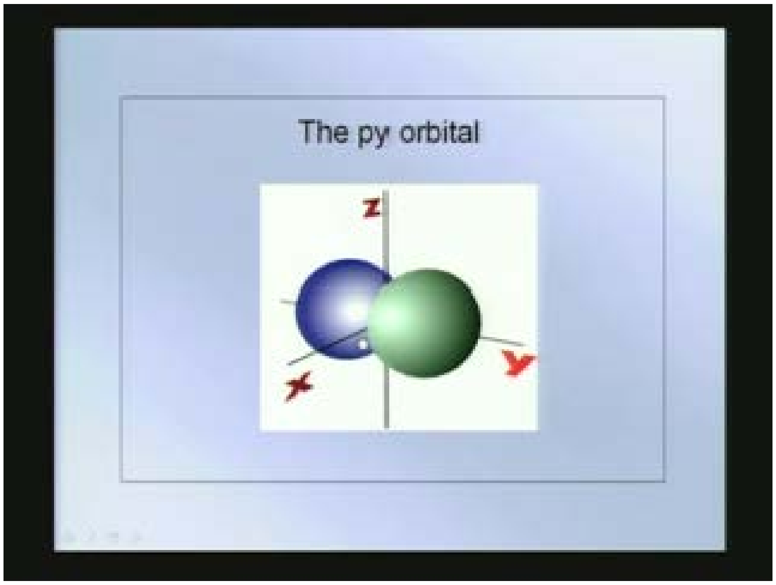

Looks exactly same as the p_x except that the two lobes are pointing along the y-axis. Again there is a plus and minus, there is a positive part and there is a negative part to this. Remember these are not the wave functions themselves but these are pictorial representations of the angular part of the overall wave function. A correct representation must involve the angular parts as well. But we call them as orbital anyway, you have to remember that it is somewhat inaccurate but it is done for convenience, and then p_z.

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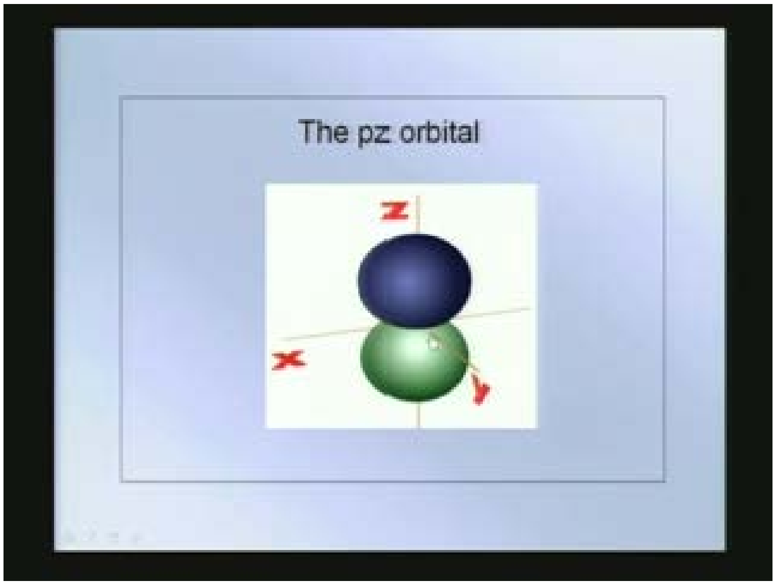

Again there is no difference between x, y and z except that the lobe this time point along the z-axis with positive and negative parts again. So it looks like there is symmetry. But you remember the functions do not appear to give any of this if you look at these functions. One is sinθ cosø, these functions are very different sinθ sinø and the third is cosθ and when you plot them in a certain coordinate system they look exactly the same except that they seem to be in three different axis system. The pictures that you saw were plots of these in polar coordinate system it is a polar diagram it is not a Cartesian diagram. How does a sinθ look like in a Cartesian space? The sine function looks like that, a cosine function starts from 1 to 0 to – 1 then back to 1, a polar diagram is slightly more certain. If you plot these functions in a polar diagram you get exactly those plots the rest of this lecture is only to illustrate that for these three functions.

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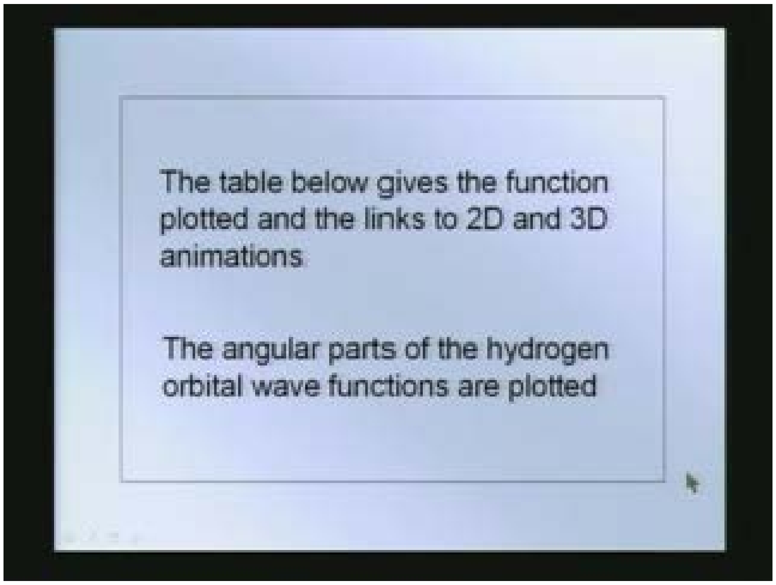

So let us list these functions and see how the polar diagrams are drawn. What we are going to do is only plot the angular part of the hydrogen orbital wave functions we are going to develop that full plot of the two spheres that you saw from the scratch.

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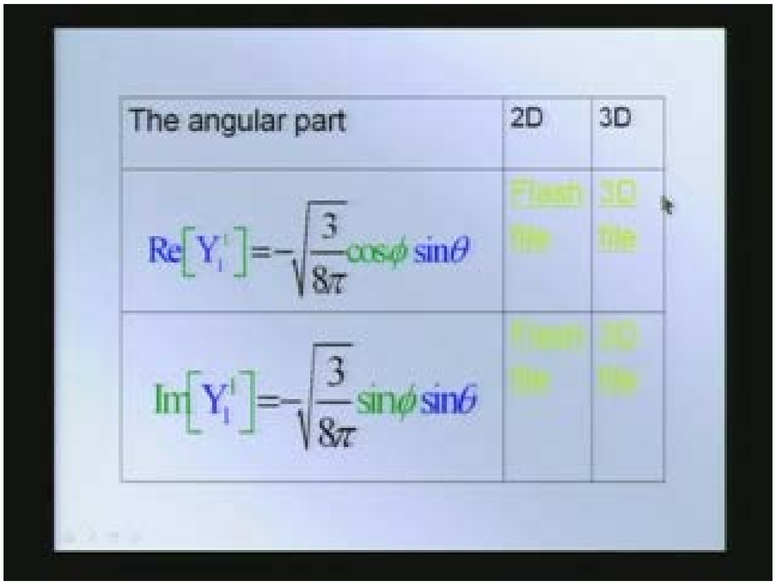

There are two files here; one is called the 2D meaning is a two dimensional picture and the other is a three dimensional picture. First we are going to look at the function cosø sinθ term, you know these factors are not relevant right now.

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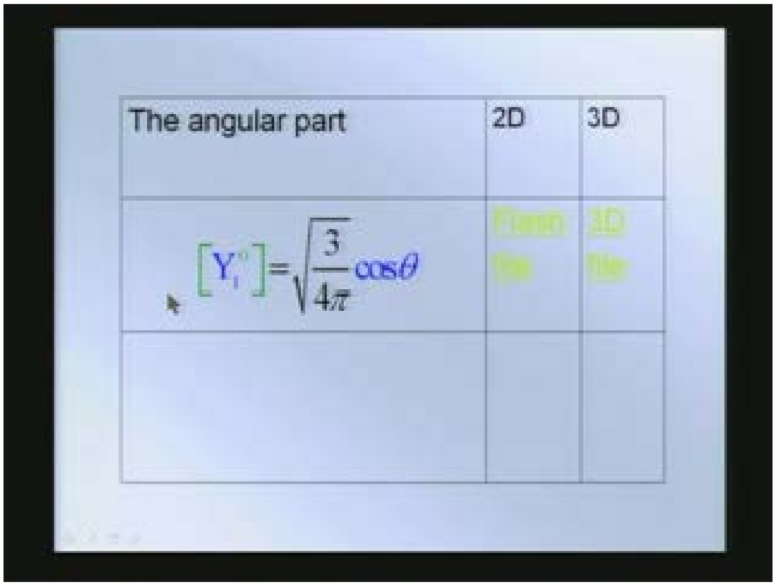

It is a real part of Y_1^1 is cosø sinθ the other is imaginary part. Let us look at what is meant by cosø sinθ in a two dimensional plot.

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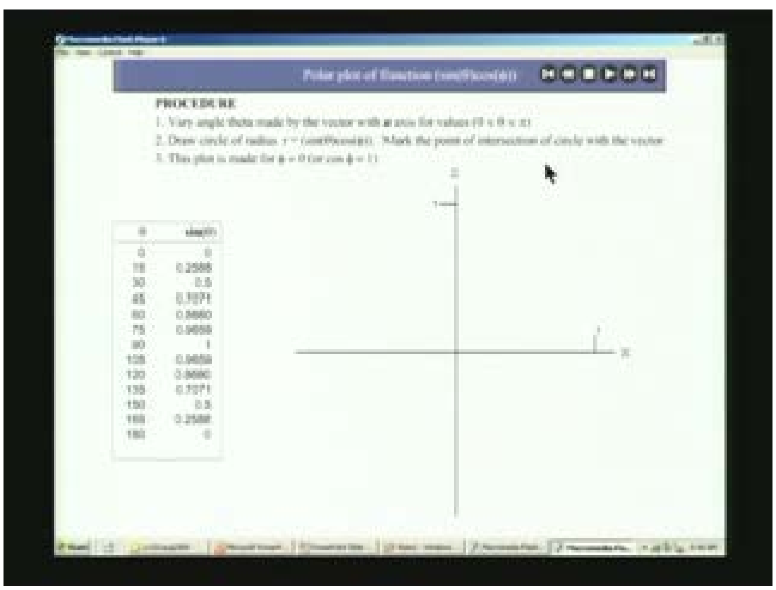

What is being done here is, since we are plotting a function which is a function of two variables θ and ø, first let us choose one variable, plot this as a function of that variable by keeping the other variable a constant and then we will vary that variable. So what you look at here is a plot of sinθ cosø by keeping ø as a constant value, ø is 0 here. You remember that the θ variable is something like a z axis in a sphere so the θ goes from 0 to π. And if you recall the ø variable goes around 0 to 2π. So let us keep the ø at one value namely along the x axis as a constant ø is 0 and we are going to plot for ø = 0 so that cosø is 1 it has the maximum value. So let us plot sinθ as function of θ for various values of θ as θ goes from 0 to π. Here are the values of θ a few of them. You remember that when you plot a function you plot a few points and then you draw the line to make it continuous. So, for θ = 0, sinθ is 0 values are given from an excel spread sheet sinθ = 15, 30, 60, 90 all the way up to 180 all the possible values.

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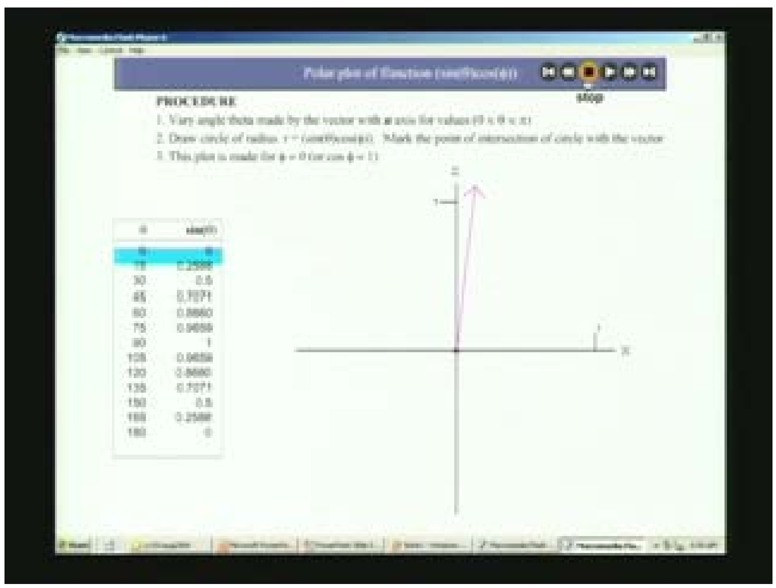

So how do you plot this? You mark the value of θ by the radius, the radius makes the angle θ with respect to this axis. So if you go back this radius right now makes an angle θ = 0.

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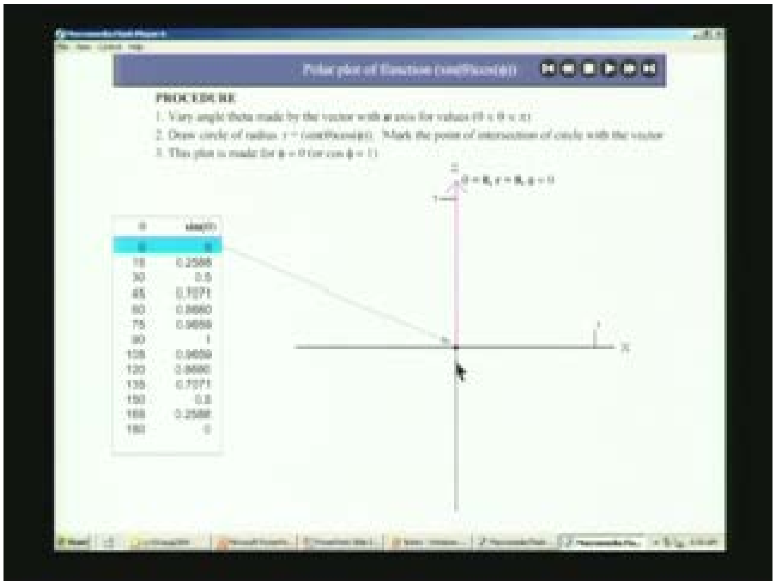

What is the value of sinθ, you mark that as a length along the radius since sinθ = 0 it is right in the beginning and right at the origin. The next is sinθ = 0.25 at θ = 15°.

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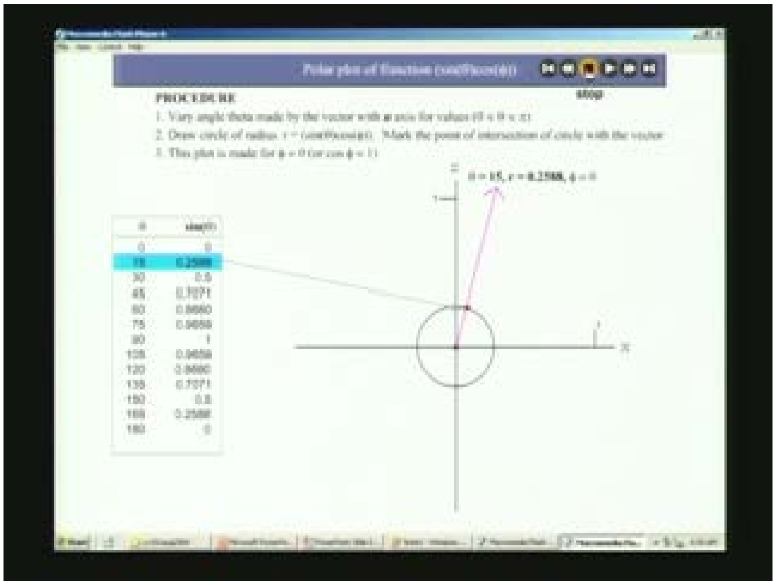

So what you have done here is this is the angle θ = 15° that is the radius makes the z axis and the value 0.25 is because you draw a sphere of radius 1 you can mark the length 0.25 as the value sinθ corresponding to θ = 15°. What is the next value? You see that for θ = 30° and if you look at the circle it tells you that this is half the value since it is the radius and the corresponding half value is here and that is the point

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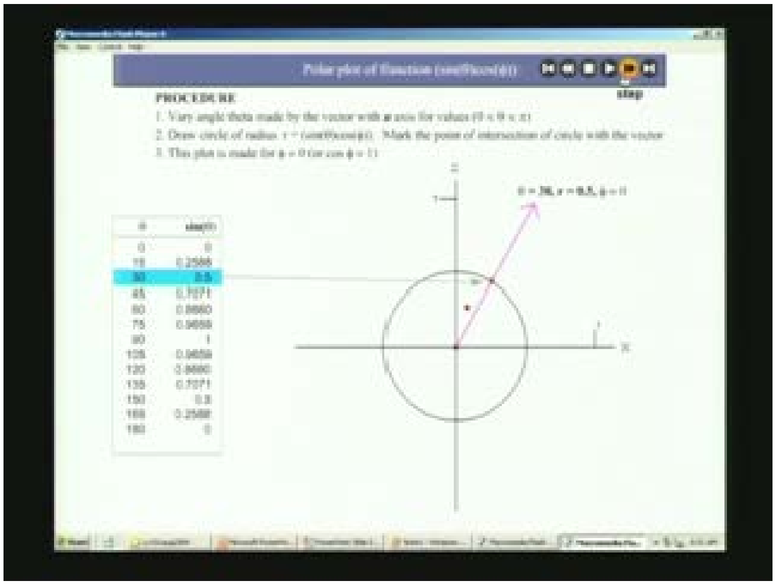

and then you draw correspondingly all the points for this particular graph for theta is = 15°, 30°, 45°, 75°and 90° and so on.

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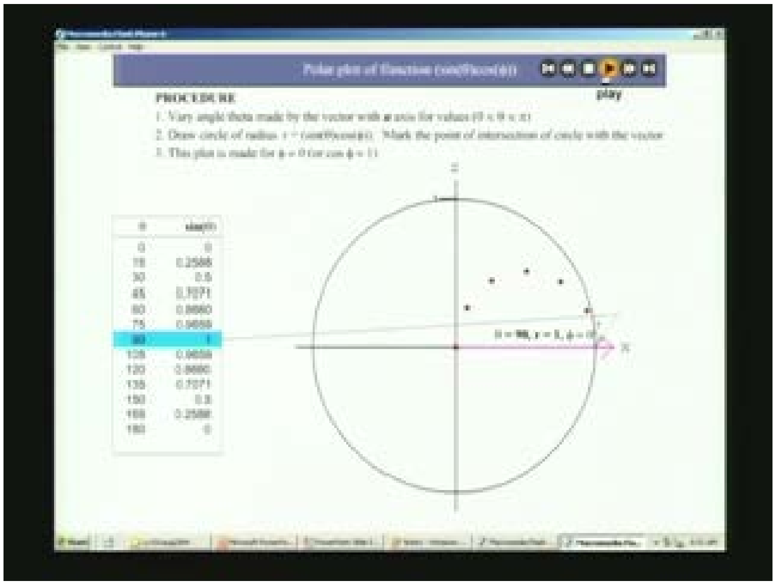

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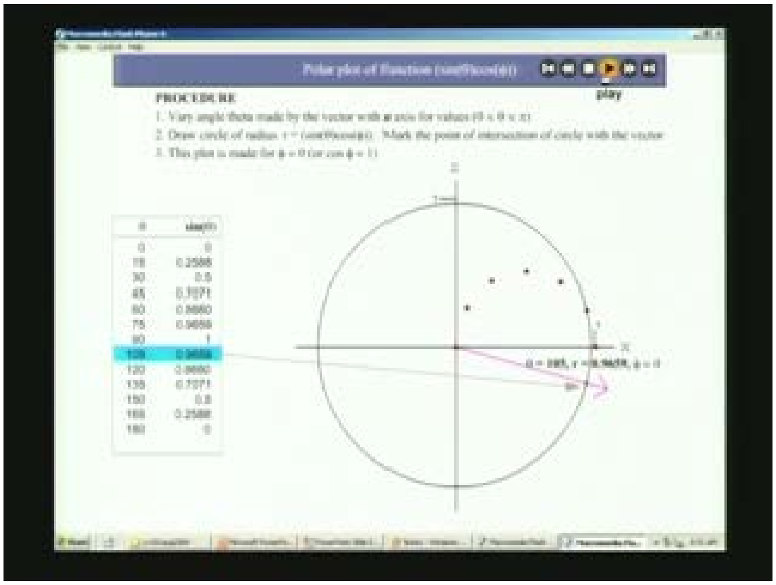

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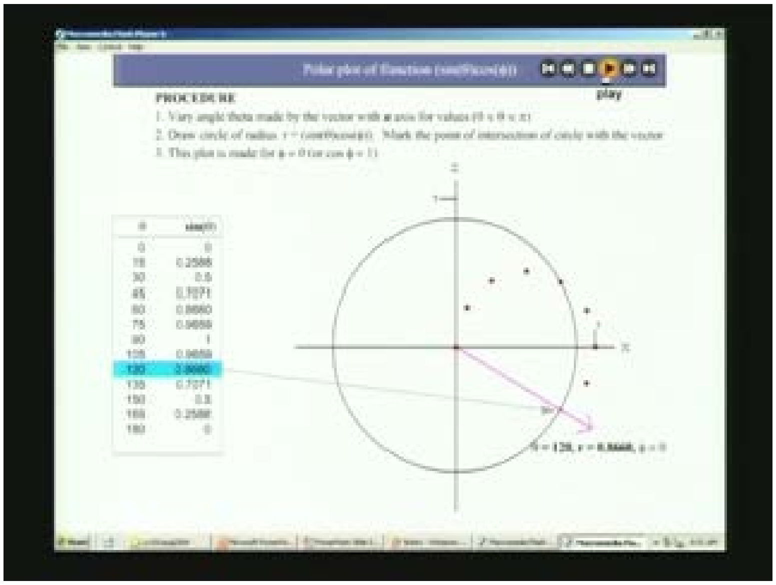

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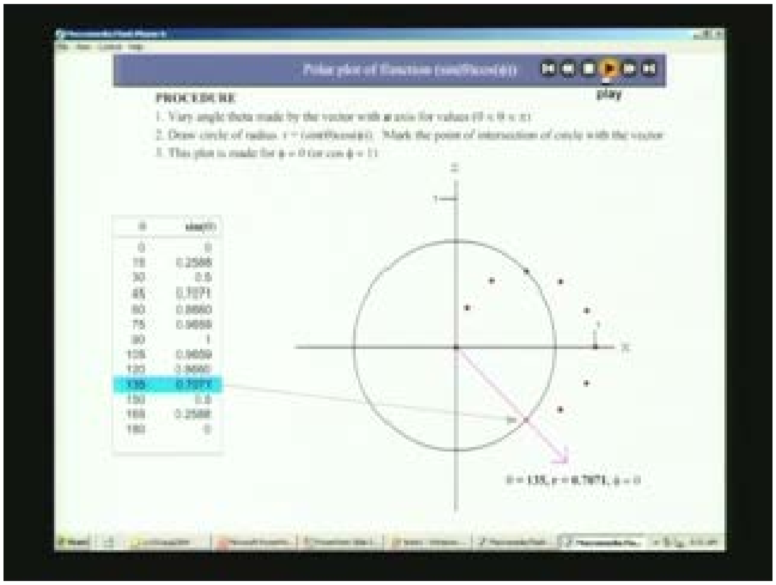

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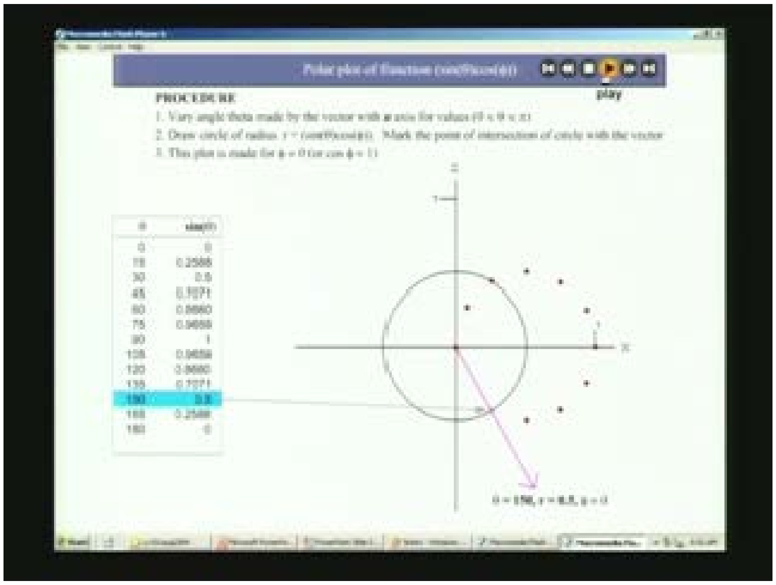

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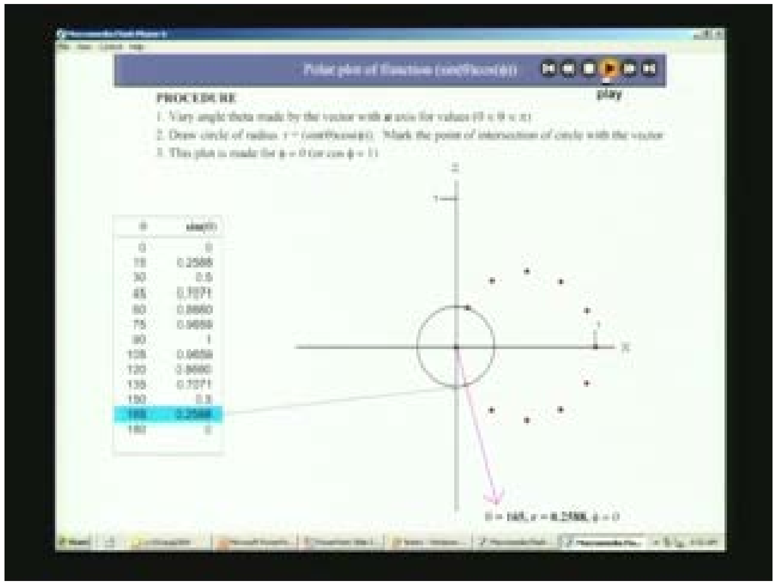

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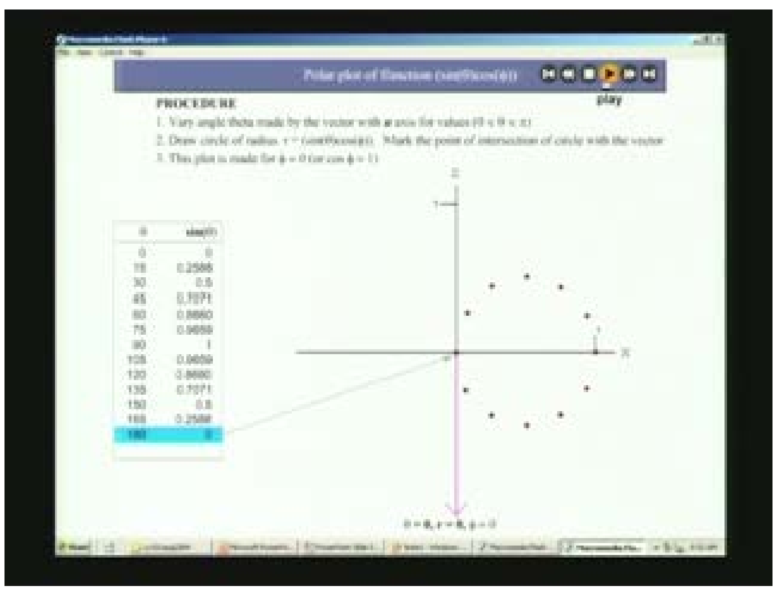

Now if you join all these points it looks like a perfect circle, it is a perfect circle. Now, this is for a given value of ø namely ø = 0. Since you want to sinθ cosø in a polar coordinate system in which you remember in a sphere θ is this variable, ø is this variable (Refer Slide Time: 44:49 min) now we have got θ plot for this variable and now we have to simulate this for all the values of ø. That is, we have to draw the circle for every value of ø, how do we do this? We have to multiply each one of this by cosø, let us do that in the three dimensions.

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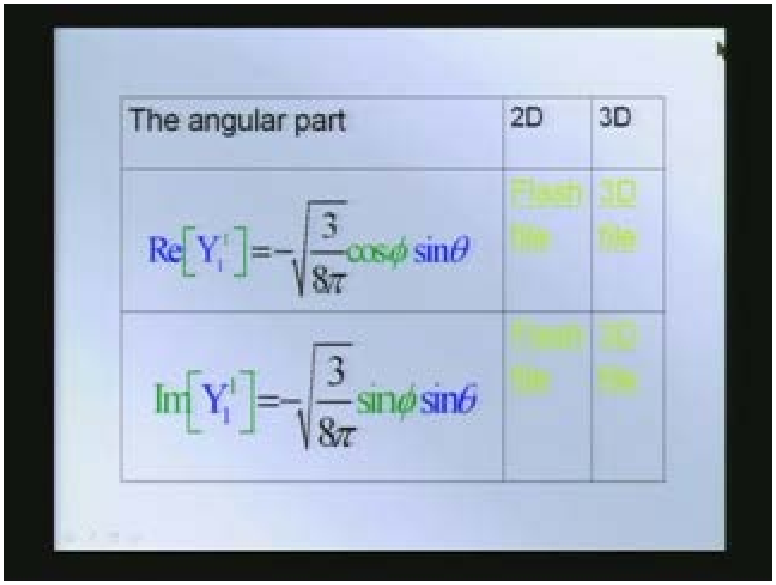

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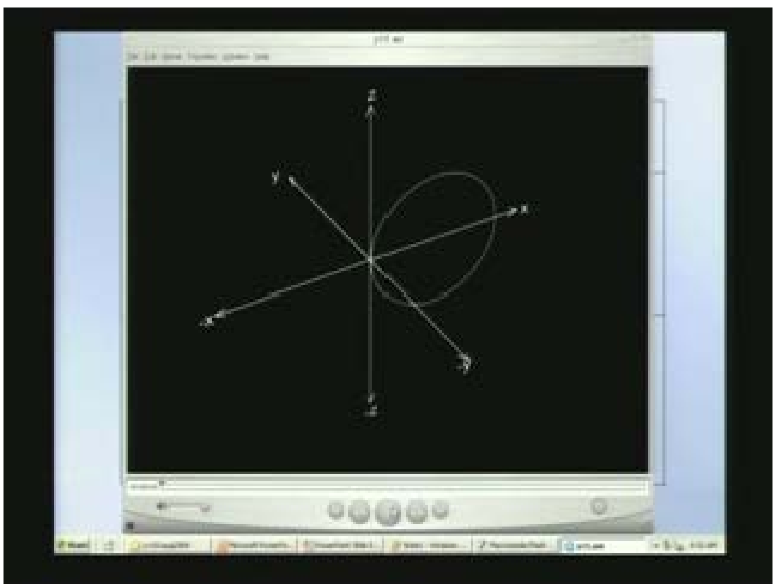

Let me go back to the picture, so the first one is along the x axis ø is 0 so what you have is the plot sinθ here cosø is 1. Now, as you go from the x axis to the y axis to the – x to the – y and back to the x axis you are going to go from ø = 0° to 90° to 180° to 270° and then to 360°. Therefore you are going to multiply this function by cos ø for every value, when you do that what you get?

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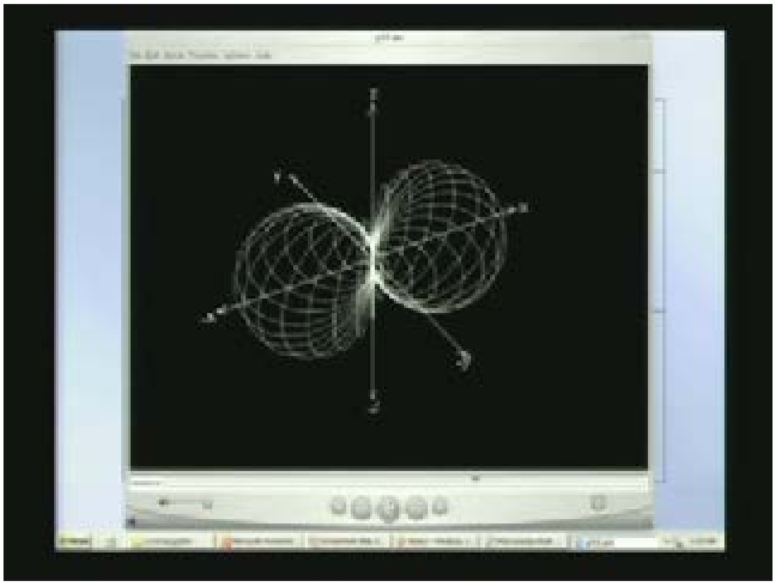

Now this is the plot you will get.

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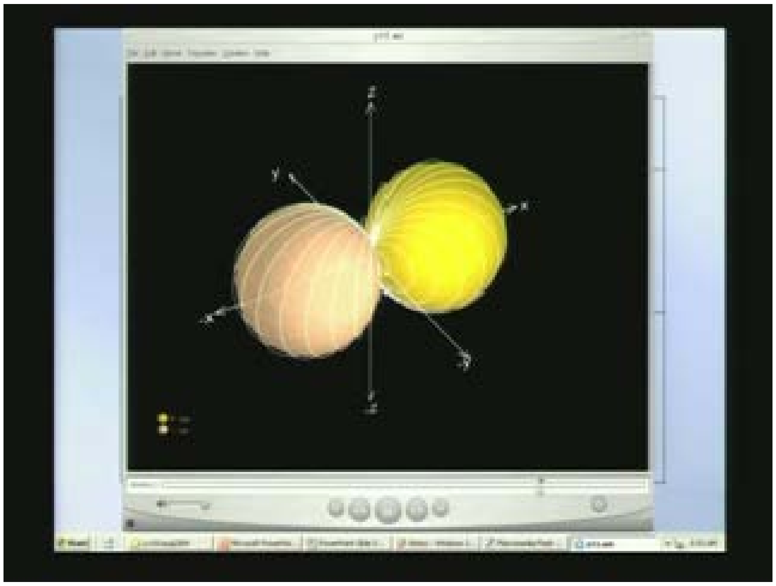

Let us go back and see that. you see that the circle shrinks in size because of the value of cosø < 1, the circle becomes 0 absolutely vanishing at ø = 90° along the y axis and then for ø > 90° the value cosø is negative you see that it keeps increasing but the function is now negative that is

180° and then it goes down again in value at 270° it goes to 0 and then it starts increasing again from 270° to 360° because cosø increases.

Now cosø is positive in the 1st and 4th quadrant therefore the function as a whole is positive here whatever the plot that you see here represents the positive plot and whatever you see in the second and third quadrant gives you the negative part and when you draw the continuous plot by keeping all the contours you see a positive part of the function and a negative part of the function, this is cosø sinθ. Now what is the corresponding plot for sinø sinθ. Here cosø started with the x axis because the value of ø is 0 so cosø is 1. If we start with sinø sinθ the value of ø is 90°corresponding to sinø = 1. sinø sinθ if you look at the corresponding plot

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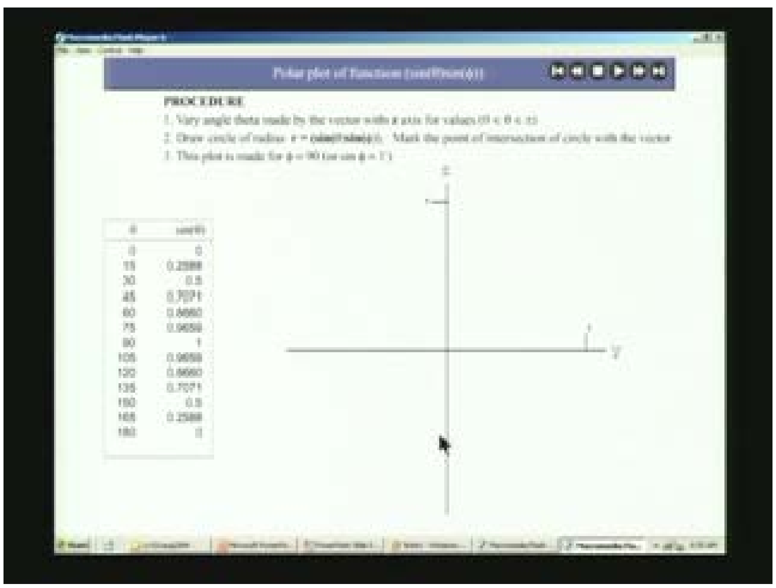

the plot is again sinθ only in two dimensions but we are going to draw this plot for ø = 90° because that is where sinø is maximum therefore what you get out of this when you draw it is again the same plot like what you had sinθ, no problems it is easy to go through the whole and see that the end results is exactly sinθ except that now it is along the y axis not along the x axis.

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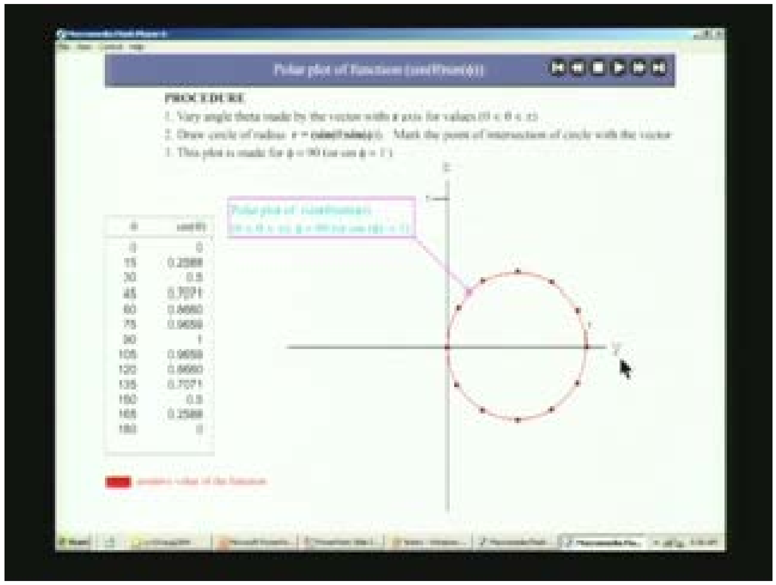

Therefore the corresponding 3D plot starts with the maximum along the y axis, this is sinθ for ø = 90°, sinø sinθ and it goes down as ø increases goes to 0 and becomes – 1 here goes to 0 and increases. . (Refer Slide Time: 48:51 min). And you remember the value of ø from 0 to 180, sinø is positive that is sin is positive in the first and second quadrant and it is negative in the third and the fourth quadrant.

Therefore the function sinø sinθ looks exactly like the previous one except to that it is rotated by 90°. So it is obvious to see that the p_x and p_y are two orbitals which are identical except that they are centered about one about the x axis and the other about y axis. What about the p_z? That is interesting, it is cosθ it is not sinθ. Let us look at cosθ and with that we come to the end of today's lecture. Let us plot cosθ in the polar coordinate system.

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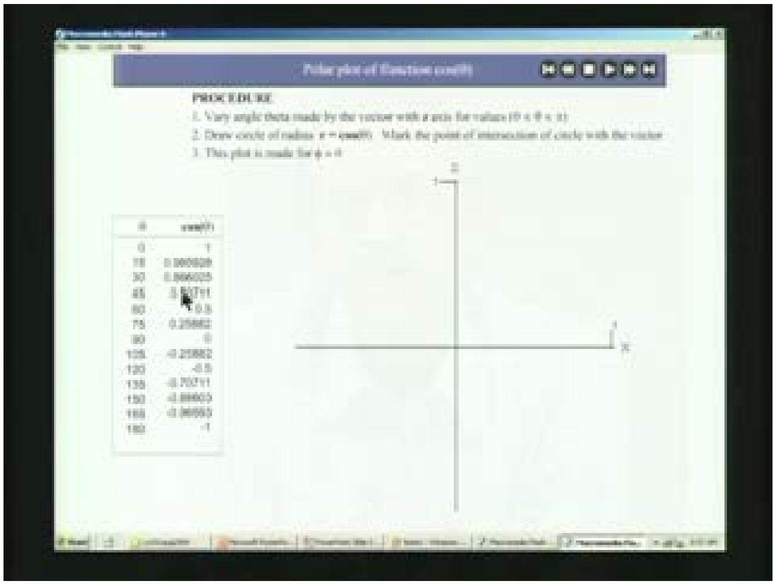

We have no difficulty with ø because the function is independent of ø, it is cosθ only that is the z axis. You remember, z corresponds to cosθ $e^{im\phi}$ for m = 0, there is no ø dependence, cosθ is of course 1 for θ = 0. There is a table which gives you the values up to 180° for cosθ is – 1 so let us plot that here. It starts with 1 the maximum value θ = 0.

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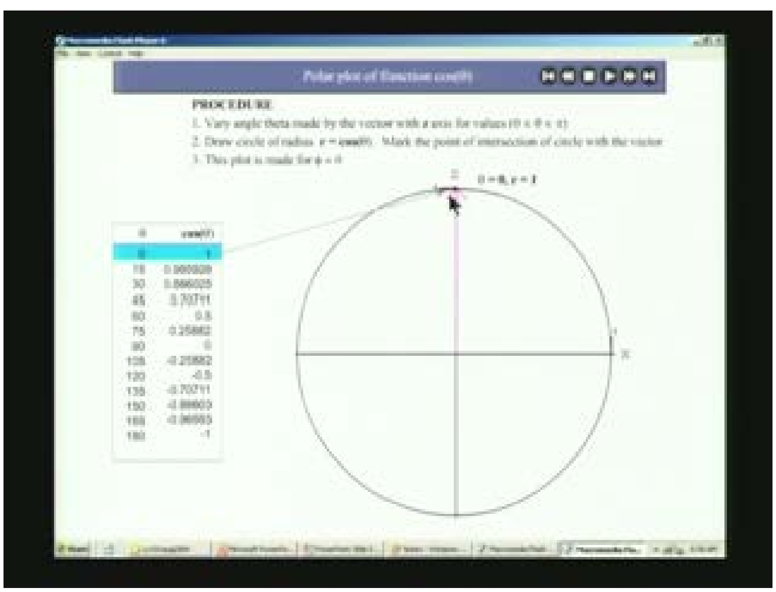

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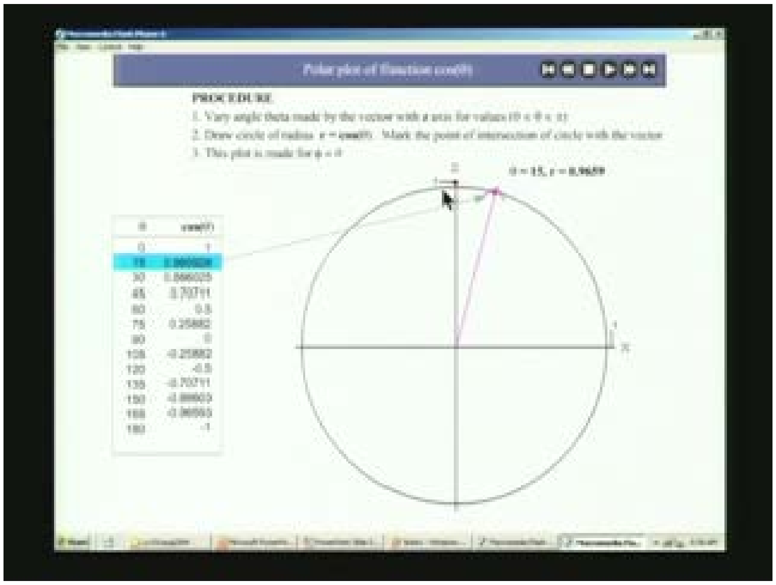

Then progressively it decreases, the cosθ value decreases.

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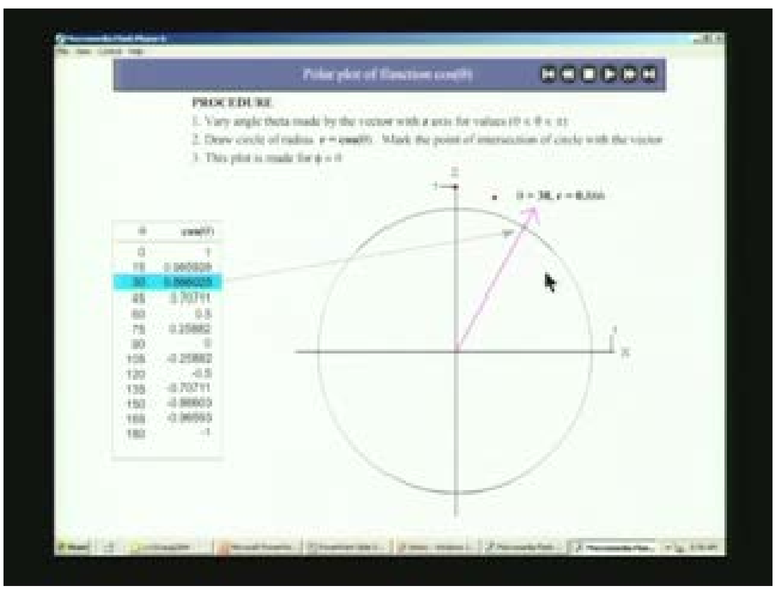

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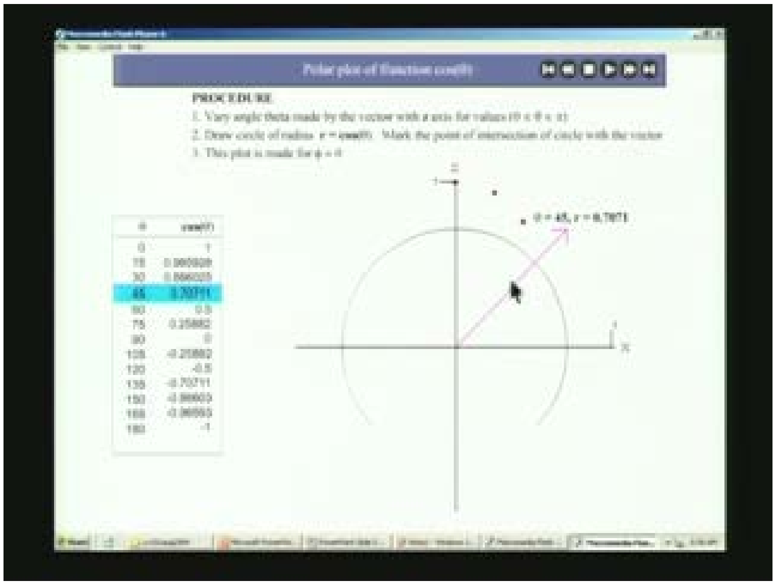

Remember, the length tells you the value and the angle tells you the θ.

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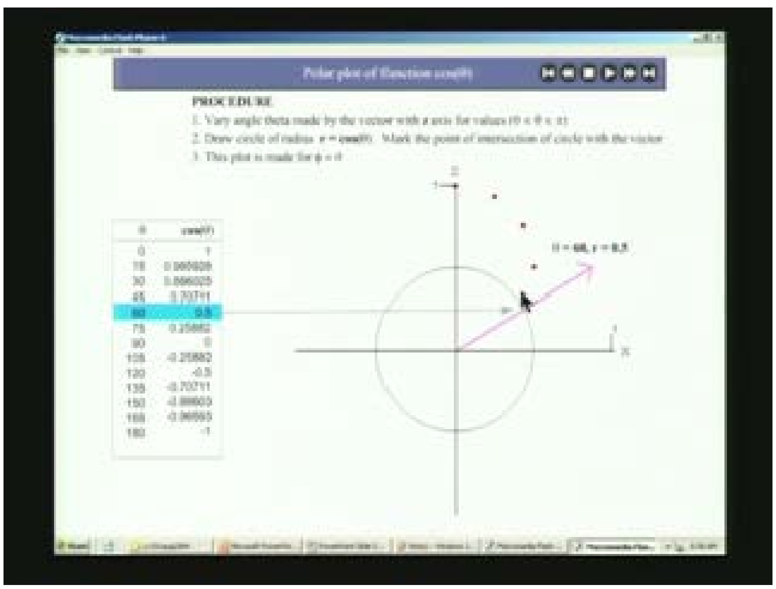

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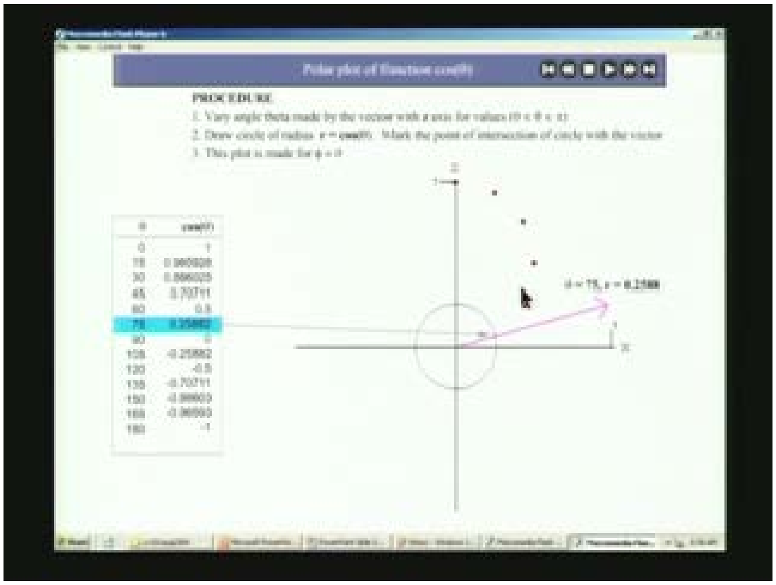

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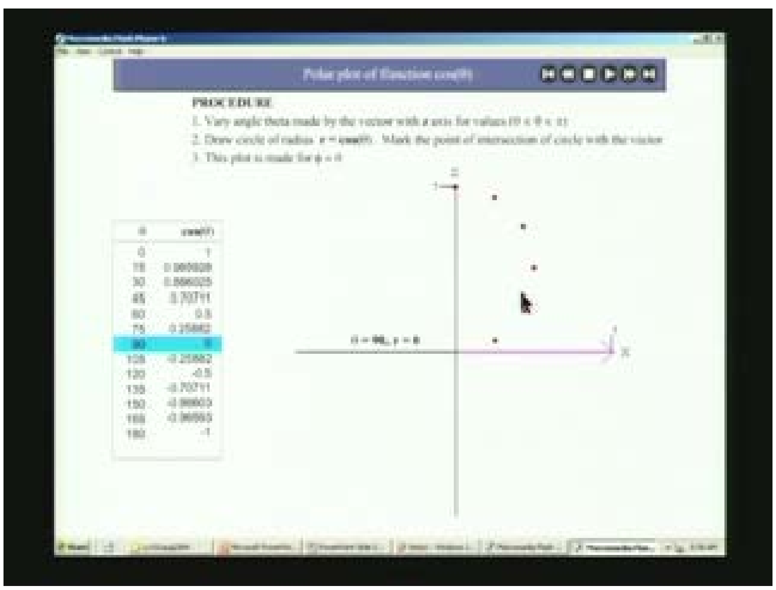

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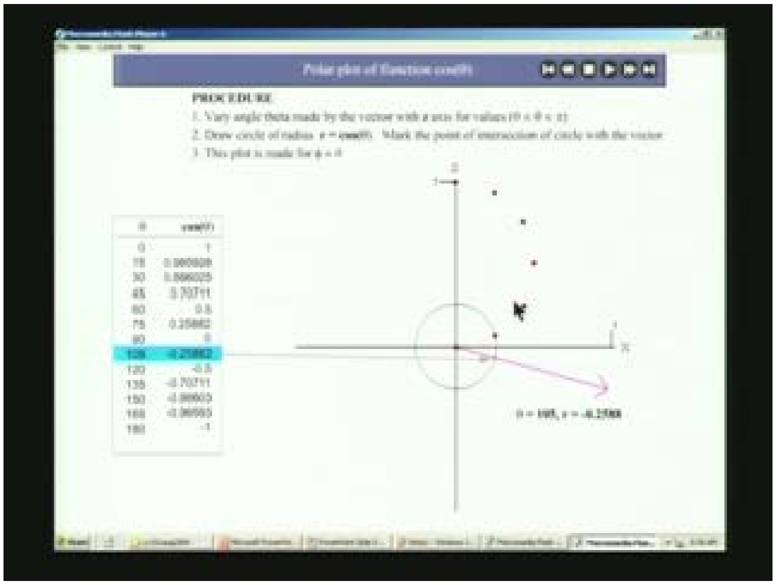

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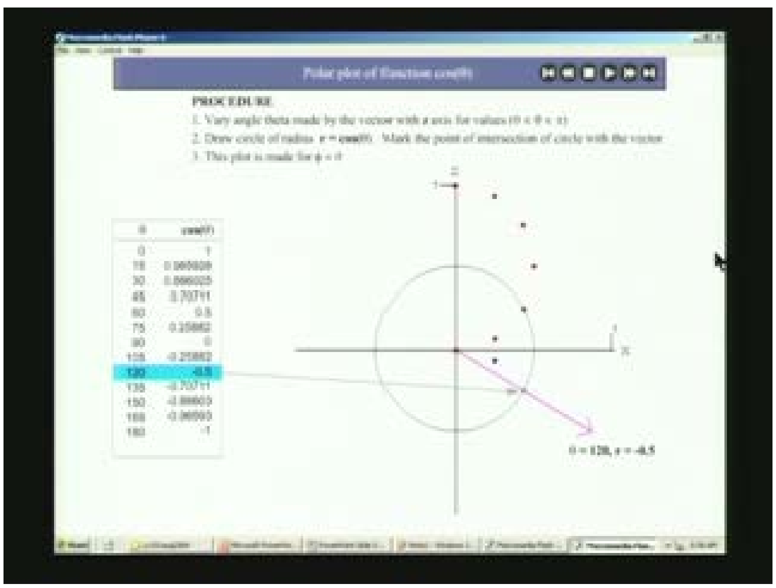

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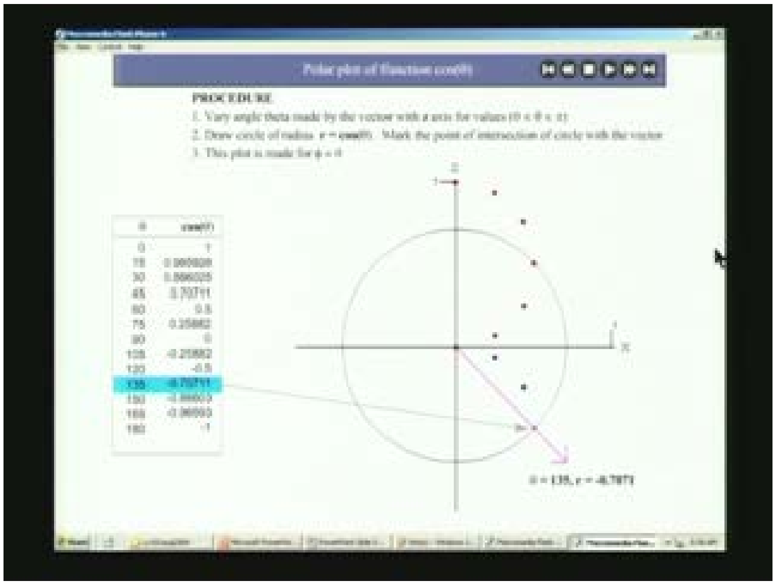

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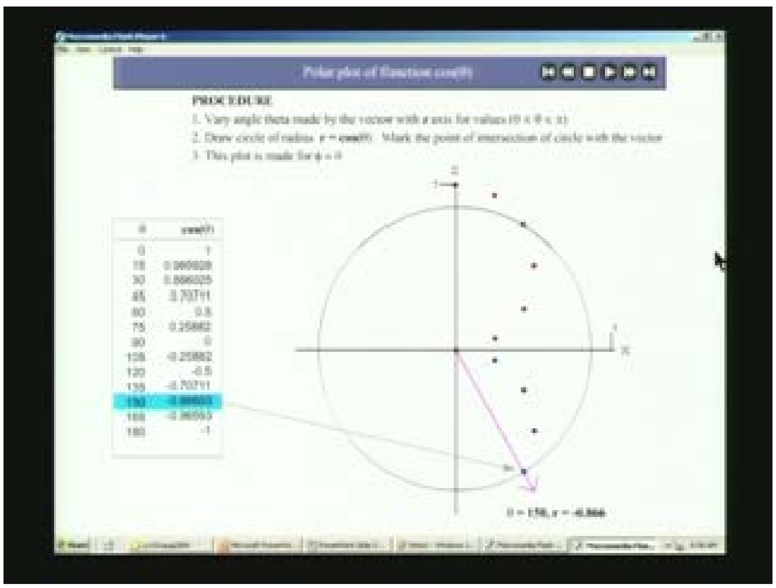

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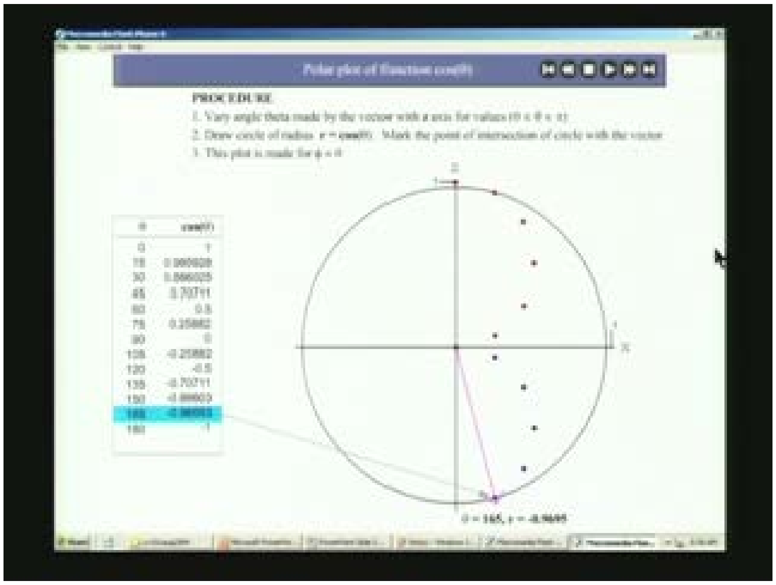

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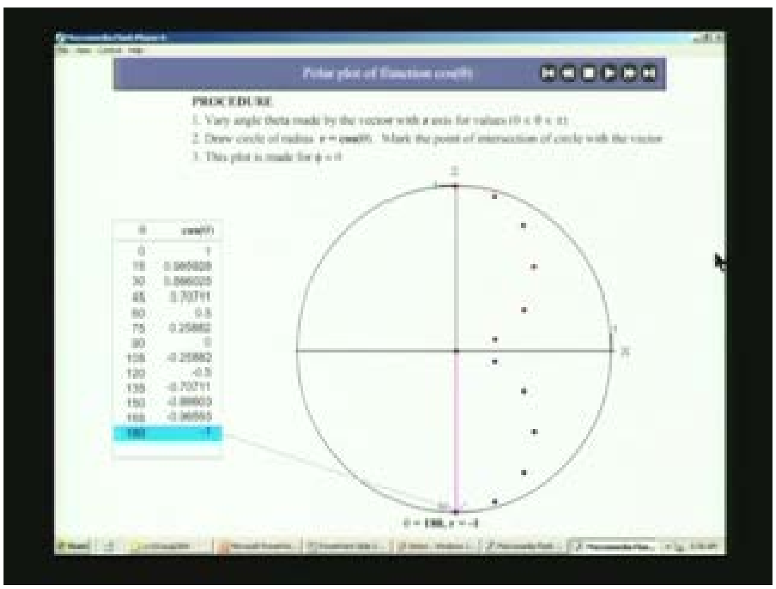

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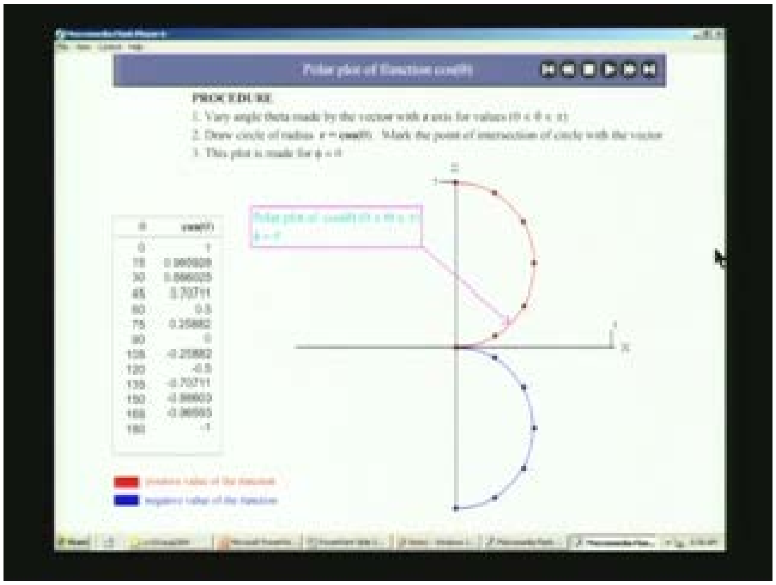

So you see that the cosθ looks like two half circles now instead of one whole circle as it was in the case of sinθ. But remember there are now two graphs; there is a red graph and there is a blue graph because you know that θ if it is greater than 90° then cosθ is negative. Therefore the function cosθ is positive in the first half of the θ = 0° to 180°, i.e. θ = 0° to 90° then it is negative and that is the blue graph. Now, since this is independent of ø when you plot this in three dimensions involving the ø variable how does it look like?

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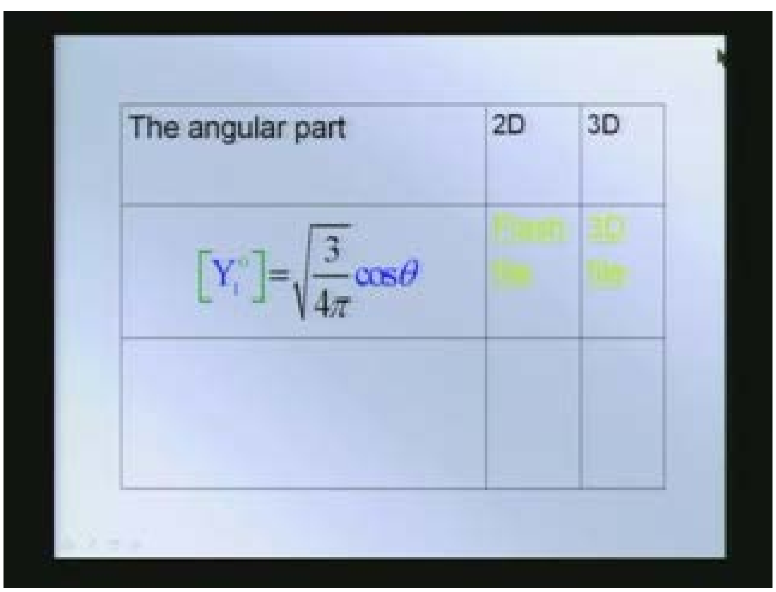

There is no ø dependence and therefore there should not be any change in the shape of this function.

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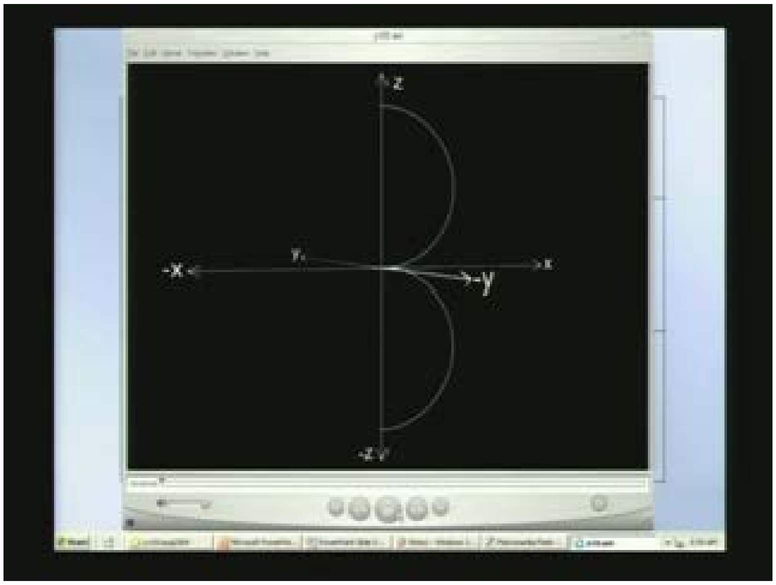

It is the same for all values of ø.

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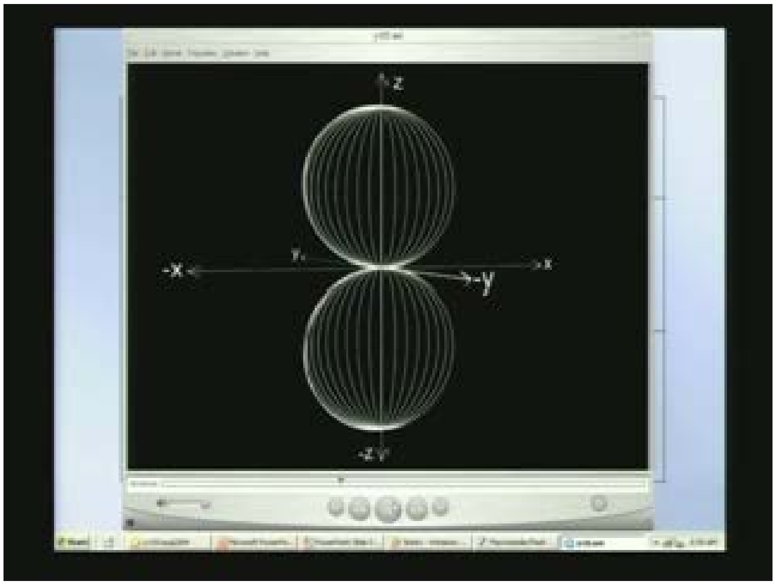

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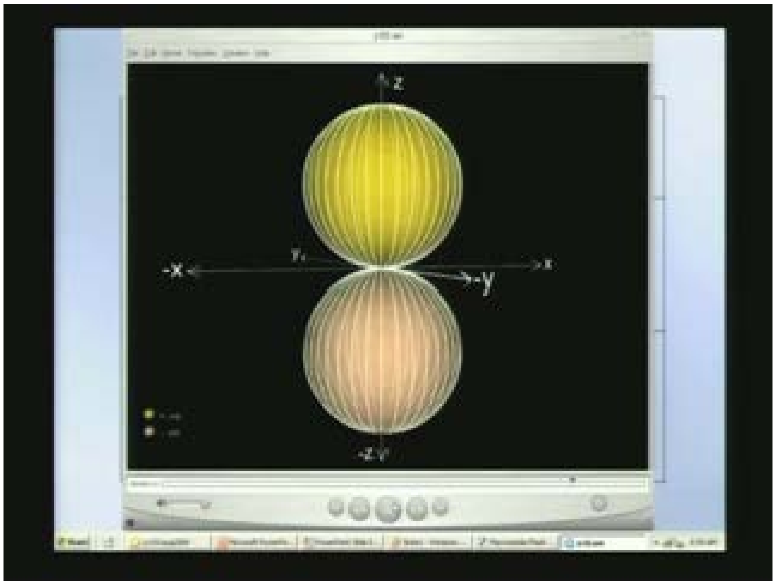

So there is no problem now, cosθ leads to an orbital which looks like exactly like the p_x orbital or the p_y orbital except that now it is along the z axis. The positive quadrant because you remember since it is independent of ø the cosθ, θ = 0 to 90 keeps it as a positive lobe and θ = 91 to 180 this is the negative lobe so again two lobes are there plus and minus and the p_z orbital looks identical to the p_x orbital or the p_y orbital except to that now it is along the z axis. You know there is no mystery associated with the p orbitals that you saw earlier.

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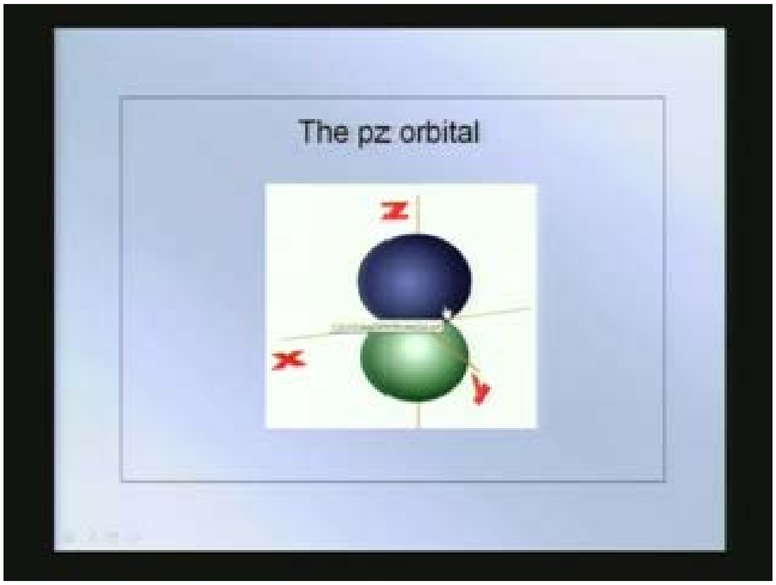

There is no mystery associated with it when somebody tells you that this is how the orbitals look like. If you understood how to plot simple trigonometric functions which are the solutions of the Schrödinger equation for the angular part then there is no problem in plotting these, these are nothing but polar representations in the three dimensional spherical coordinate system in the (θ ϕ) representation. If you plot trigonometric functions you get everything that you think about.

In the next lecture we will see the same thing for the d orbitals. The d orbitals correspond to l = 2 and the d orbitals are possible only when the principle quantum number n is 3 or more. So that is 3d orbitals, 4d orbitals, 5d orbitals are possible but not 2d. So, when the d orbitals are present how do we represent the corresponding spherical harmonics? It is exactly by the same procedure that I described here except that you have more lobes multiple points where the functions go to 0 and so on because the trigonometric function for the d orbitals are of degree 2, l = 2 means that the trigonometric function contain cosθ and the sin θ or $\sin^2\theta$ of degree 2 therefore there is going to be some 0's in between in the functions.

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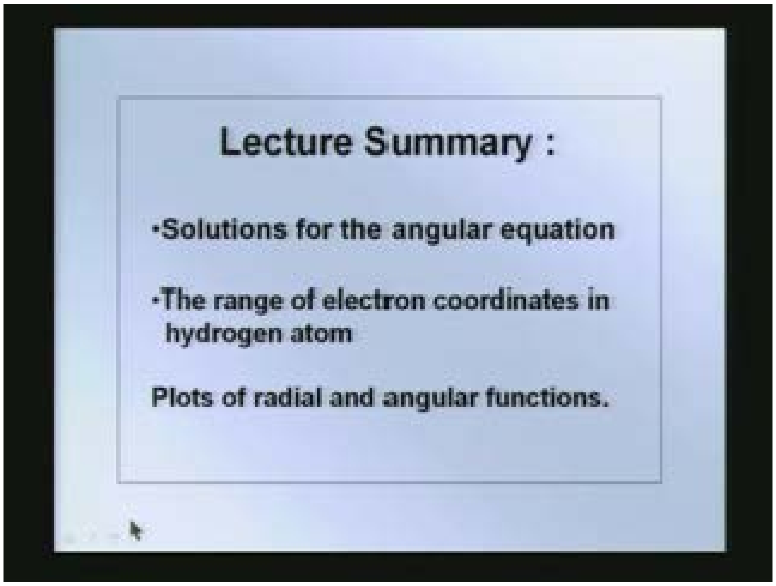

Before I conclude this let me recall that what we try to do in today's lecture was to look at the solutions of the angular part examine the solutions not derive the solutions and understand that what are the possible ranges for the electrons coordinate for the hydrogen atoms in the spherical coordinate system and also try and understand the simplest of spherical harmonics through a graphical representation by first breaking that two variable problem into a one variable problem and then extrapolate in that into the second dimension and seeing the full three dimensional structure.