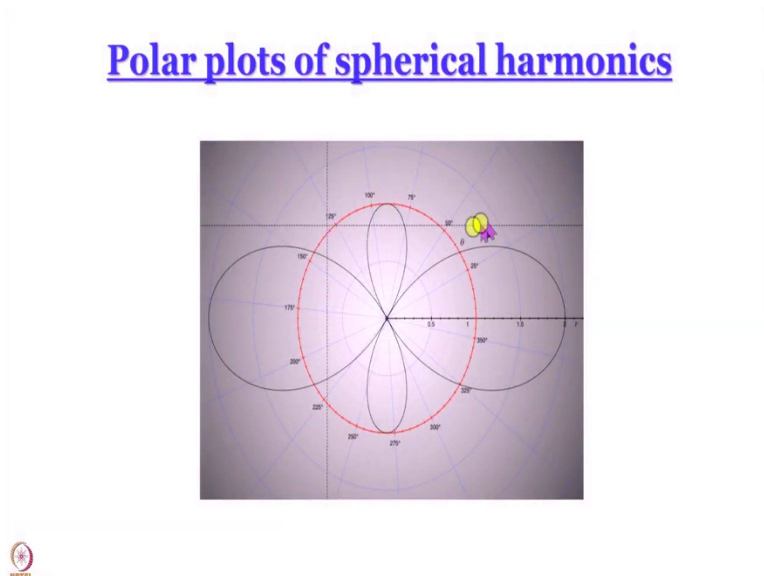
Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-21
Polar Plots of Spherical Harmonics

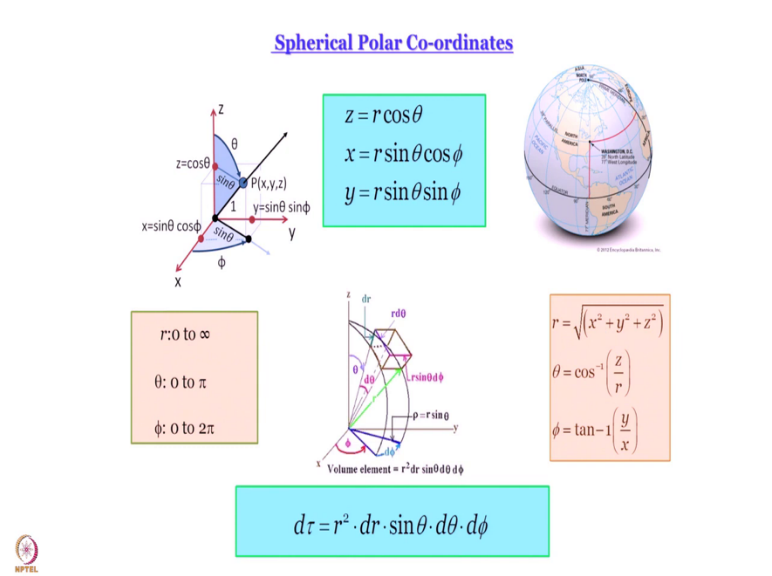
In the last module we had said that next we are going to discuss a little more about angular momentum but then as is often the case I had a second thought so what we will do is in the next module we are going to discuss angular momentum. But today let us finish up something that is a logical next step of the discussion we have had in the previous module. And that is something very interesting and often very useful. What we learn in this module is how do we draw pictures of spherical harmonics?

(Refer Slide Time: 00:58)



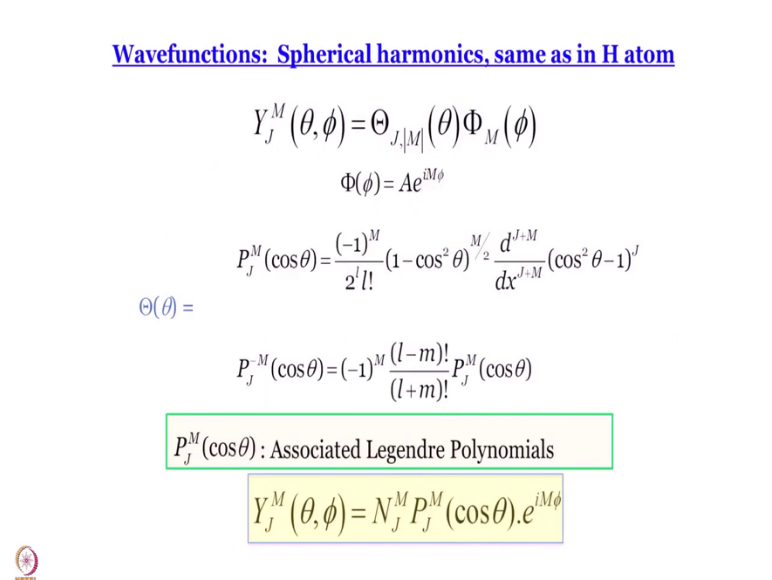
How do we draw picture especially of the theta part? To do that we learn something called polar plots. So, polar plots themselves are interesting and useful in many cases. So, this is a corollary of doing this course you get to learn something that is useful in other fields as well. This will capitulate we are discussing a rotating diatomic molecule we have deduced the two body problem to a one body problem by using reduced mass mu.

(Refer Slide Time: 01:34)



And we have understood that since we are talking about a rigid rotor we would better use spherical polar coordinates. In spherical polar coordinates r Theta Phi we have discussed the relationship among between the Cartesian coordinates and the spherical polar coordinates and we have said that we are going to take r as a constant r 0 because we are talking about a rigid rotor. But this theta Phi what is Theta what is Phi these are things as we have discussed in the previous module. And we continue to discuss them in this module as well.

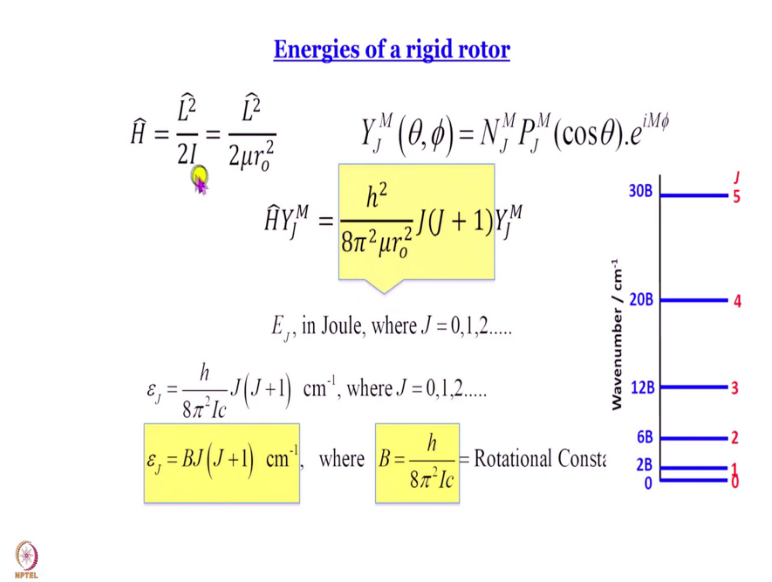
(Refer Slide Time: 02:11)



So, the point of discussion today starts from here, we know that the wave functions are essentially spherical harmonics product of a Phi part and a theta part. And we also said that well we worked out that the Phi part is an imaginary part of the wave function where it is a constant multiplied by e to the power I M Phi. What is M? M is 0 plus minus 1 plus minus 2 so on and so forth it is the magnetic quantum number if you want to call it that and as we seen our later it stands for the Z component of angular momentum.

The theta part is essentially associated legendary polynomials in cos theta, please remember in cos theta not in theta not in Phi not in xyz but in cos theta. So, you could say in z actually. So, this is the total wave function sum constant multiplied by a polynomial in cos theta multiplied by e to the power I M Phi.

(Refer Slide Time: 03:22)



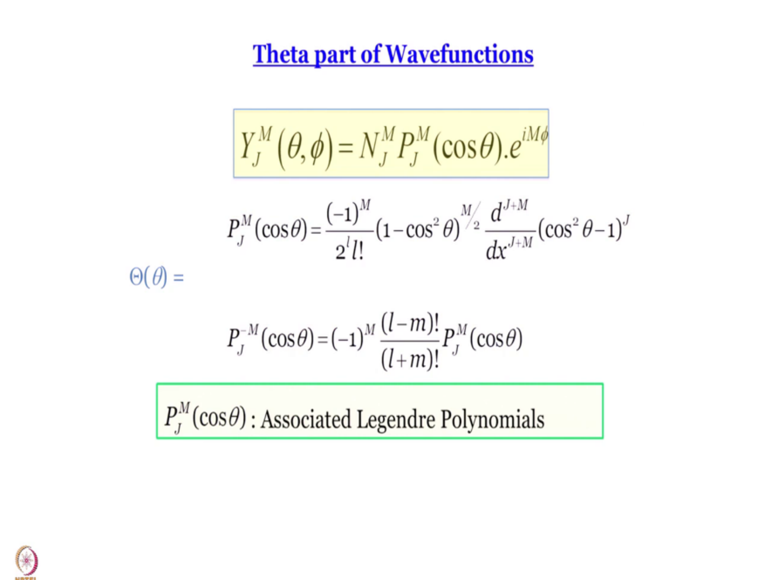
And then we learned that when we make this operator Hamiltonian and we worked out Hamiltonian from L square by 2 I knowing the classical relationship and knowing the operator L square or at least what implication it has on this wave functions. We formulated the Hamiltonian to be L square by 2 mu r 0 square again mu is rest mass sorry mu is reduced mass and r 0 is the length of the rigid rotor, bond length in case of diatomic molecule.

We make this operate on spherical harmonics and knowing that L square operates on spherical harmonics to give us J into J + 1 multiplied by a constant we get h squared divided by 8 pi square mu r 0 multiplied by J into J + 1 this eigen value of Hamiltonian is the energy in Joule the rotational energy and J is a rotational quantum number which ranges from 0 1 2 so on and so forth. And we also said that generally we like to represent epsilon J in terms of B where B is h by 8 pi square I C.

When we do that we write it in terms of centimeter inverse and the expression becomes very simply epsilon J is equal to B into J into J + 1 in centimeter inverse. And then we had said we had worked out these rotational energies for the different rotational quantum numbers and we found that the first of all of course energy is quantized. Secondly the energy gap keeps increasing as we go up the ladder.

But the difference in energy gaps is always 2B so we have 0, 2B, 6B, 12B this difference is 2B this difference is 6B. So, 6B, -2B is 4B right so on and so forth we can work this out. And we talked a little bit about your rotational spectrum. We said that for a rigid rotor we expect a an equiv spaced rotational spectrum and from there we can figure out B and hence we can get develop an understanding of the bond length of a diatomic molecule modeled by a rigid rotor. This is where we got until the last module ok.

(Refer Slide Time: 05:51)



Today let us focus on the theta part of the wave function the associated legendre polynomial multiplied by some constant.

(Refer Slide Time: 06:03)

Theta part of Wavefunctions

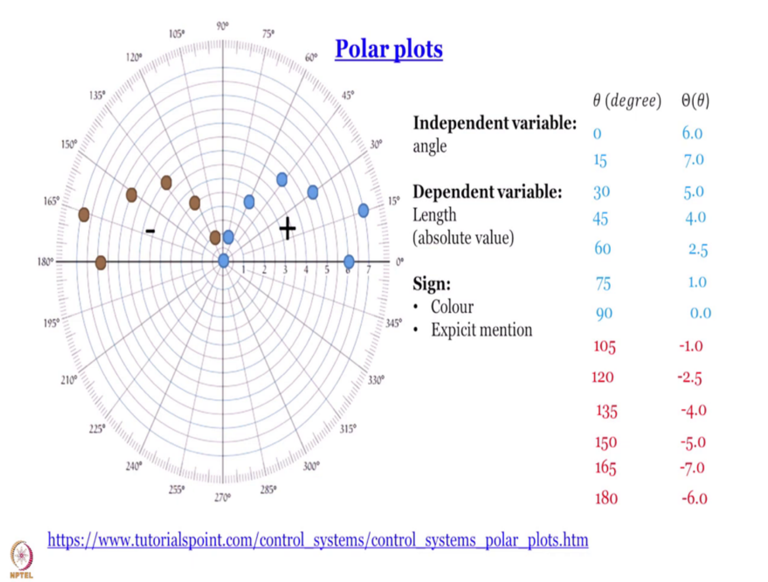
J	M	$\Theta_J^{\|M\|}(\cos\theta)$
0	0	$\frac{1}{\sqrt{2}}$
1	±1	$\sqrt{\frac{3}{4}}\sin\theta$
1	0	$\sqrt{\frac{3}{2}}\cos\theta$
2	±2	$\sqrt{\frac{15}{16}}sin^2\theta$
2	±1	$\sqrt{\frac{15}{14}}\sin\theta\cos\theta$
2	0	$\sqrt{\frac{5}{8}}(3cos^2\theta - 1)$

And here is a table of all the theta parts for J equal to 0, 1 and 2 of course you can go higher up but makes no sense. So, what you see is that this theta is really a function of J and mod M it does not matter whether M has a positive value and negative value you get the same theta part of the wave function. So, for J equal to 0 m equal to 0 the wave function is just a constant just a constant for J equal to 1 you can have three values of M, 0 and plus minus 1.

When M is plus minus 1 you get the theta part to be root over three by four sine theta and when M equal to 0 for J equal to 1 the theta part turns out to be root over 3 by 2 cos theta. When J equal to 2 you can have 5 values of M. Remember M takes up values of minus M to plus M through 0, increasing in steps of 1. So, when m equal to plus minus 2 for J equal to 2 we get the theta part of root over 15 by 16 sine square theta.

When it is plus minus 1 we get root over 15 by 14 sine theta cos theta and for M equal to 0 for J equal to 1 we get root over 5 by 8 and I really like this function 3 cos square theta – 1. I will maybe tell you later why I like this function very much but this is something that keeps occurring in many, many places in rigid rotor, hydrogen atom, NMR spectroscopy, fluorescence spectroscopy this 3 cos square theta - 1 keeps on recurring all the time more about it a little later.

(Refer Slide Time: 08:08)



Now let us learn how to draw these functions in a very nice manner of course you can draw it in Cartesian plane. But then this one gives you a more unique idea because here the way you draw what is called a polar plot is first of all as you can see this is a polar plot graph paper downloaded from this link as you see it is circular. And you have two kinds of coordinates one is an angle you can read here 0, 15 degree, 30 degree, 40 degree, 45 degrees, 60 degrees so on and so forth.

In this particular graph paper the angular increment shown is in 15 degrees then we go from 0 degrees to 360 degrees in the graph paper. And so the independent variable is this angle. How do you write the dependent variable? Suppose you want to plot something sine theta cos theta sine theta cos theta whatever there will be a function in theta is not it. That function in theta is a dependent variable and the absolute values please remember this, this is very important.

The absolute value of this function of the dependent variable is given by the length and we are going to just take an arbitrary example to start with and then we will show you some polar plots of actual theta parts of wave functions. So, just remember that the dependent variable well absolute value of the dependent variable is shown as the length. Suppose for let us go to the example and then we will see.

What happens when there is a minus sign it is not necessary that the all functions are going to be positive. What happens is the minus sign absolute value will still be the length. Remember if you go from this side to this side the length is still positive it is important to understand the axis here. One axis is like this an angle right well like this anti-clockwise in this case 0, 15, 30 like this. The other one is just the length I mean if you go here instead of going in this direction if you go in this direction it does not mean that the length has become negative length has remained positive.

Just that you have gone through 180. Suppose let us talk about this line here it does not mean well maybe this line does not mean that this length is negative. Suppose I read this, this is still 7 where the circle is right now this is still 7. It is just that the angle is 240 degrees please remember the length cannot be negative here. So, how do show us change in sign, suppose I want to plot sine theta cos theta which we will there will be a change in sign how do we show it we will see.

We will cross that bridge when we come to it right now let us take one step at a time. So, what we will do is we will just give you some arbitrary values of some function of theta, capital theta for each value of theta and we will go in increments of 15 degrees and we are going to plot it on this graph by the time we are done I hope everybody will understand how to draw polar plots. So, let us get going, let us say that the value of capital theta the function remember capital letter denotes function small letter denotes variable or coordinate.

Let us say capital theta for theta equal to 0 degree is 6. What does that mean 0 degrees is the angle and if you read of the length that is 6. So, this is where we should put a point like this ok theta equal to 0 degrees capital theta is 6 degrees this is where the point comes capital theta is just read off 6. Next let us say for 15 degrees it is 7, the function capital theta has a value of 7 when theta as a value of 15 degree that means what from here you have to go here 15 degrees and it is marked here.

How far should we go here along this line so all these lines are radial lines is not they do you see all these lines actually go through the center is not it. So, these are basically radii, so along the radius a certain length along the radius is what stands for the absolute value of the function in theta. So, if it is 7 then have to read of 7 this is the 7 is so this is where it will be dependent variable theta equal to 15 degrees and well sorry independent variable theta is 15 degrees and dependent variable capital theta has a value of 7 so this is where the point should come.

So we put the point there. Now let us say for theta equal to 30 degrees capital theta is 5. Similarly what do we do go from 0 up to 30 degrees capital theta is 5 so read of 5 so it is that will be this circle so this is where the point should come. Now let us say for 45 degrees capital theta is 4 can you try to put the point yourself. Just put it on your computer or mobile screen with your finger and then when the point comes; you can verify whether you have got it right or not.

Have you done it yeah please put the finger where you think the point should come for a theta equal to 45 degrees all right this is where it should come theta is 45 degrees capital theta is 4 degrees. I hope you have put the finger in the right spot if not here is one more chance. For 60 degrees I am saying the value of capital theta is 2.5 can you put your finger where theta equal to 60 degrees and capital theta equal to 2.5 would be put a finger on your screen and check whether you have put the finger in the right place which is this ok.

Let us say for 75 degrees it is at 1 and I show you where it is it is here let us say for 90 degrees it is 0. I want you to become 0 because I want you to change sign and we also want to discuss what happens when how you show a change in sign ok. So, this is what it is. Next let us say for 105 degrees very 105 degrees just go like this 105 degrees is what it is. So, it will come somewhere along this line is not it. For 105 degrees I am saying that the value of capital theta is minus 1.

How do I show it? They said the distance is only an absolute value. How do I show minus sign? Well there are two ways first is you can use color or you can just write plus or minus by the time you are done with this plot we are going to do both right now let us change the color from what it was in when capital theta was positive. Since capital theta is negative when theta equal to 105 degrees we use a different color and put the spot here.

For 120 degrees it is – 2.5 so where will it be please remember 120 to 5 degrees is this it will not come here because it is negative because that is actually 300 degrees. It has to be somewhere on this line itself and the color has to be that of negative functions. So, this is it I think I goofed a little bit with this 105 degrees one is moved a little but it is fine anything you understand. 135 degrees I am saying it is -4 where will it be put your finger and do not forget the color right.

And for 150 degrees it is here for 165 degrees is -7 and for 180 degrees is -6. So, I have generated a set of fairly symmetric functions ok. So, what we have learnt is how to make polar plots and how to include sign in polar plots as well because in polar plots as they are there is no provision for sine. You have to either use color or write plus and minus in the regions where the function is plus or minus and that is how you get the polar plot.

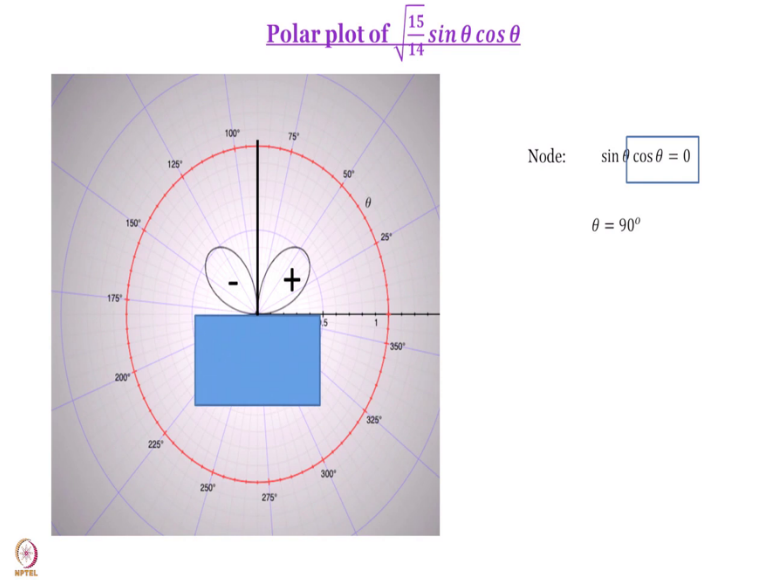
One thing I forgot to include in this plot but we have in the subsequent slides is where is the node? You can see here obviously node is at 90 degrees yeah the 90 degrees not only is capital theta 0 but it also changes sign from one at 75 degrees to -1 at 105 degrees so where is the node theta equal to 90 degrees where is that? Right here if you draw a line like this that is your theta equal to 90 degree node.

Nodes are very important in our discussions that I have to follow. Before we go to more realistic capital theta functions let me remind you that the range of theta is 0 to 180 degrees only. So, even though the polar plot graph paper goes all the way from 0 to 360 degrees when talking about some function of theta we should never use the part of the graph paper from 180 degrees to 360 degrees because theta is not and values of theta greater than 180 degrees is not even there right.

The graph paper has to be more general because suppose you want to plot phi down then what will happen you need to go from 0 to 360 degrees. But for theta please do not draw dots on this site also please stop at theta equal to 180 degrees. You are going to generate functions and I am going to show you. You cannot generate values for theta greater than 180 degrees also but it does not make sense because the upper limit of theta is 180 degrees by definition.

So please remember you should not draw anything beyond theta equal to 180 degrees. If you if you are drawing a function in Phi then it is fine you can go up to 360 degrees you should go up to 360 degrees. So, this is how one draws polar plots. Now let us go ahead and let us see examples of polar plots of actual spherical harmonics in theta.

(Refer Slide Time: 20:02)



If you might remember that this was one of the wave functions root over 15 by 14 sine theta cos theta and what I show you here is a polar plot of this function. I have made this diagram ugly by putting this rectangle explicitly just to highlight the fact that there is no theta beyond 180 degrees. So, you should not draw anything here. In fact I used the program grapher for generating this plot and grapher does not know that I am working with theta so it had actually generated all the way from 0 to 360 degrees.

We should not when we construct functions of the azimuthal angle theta because as we said several times theta has an upper limit of 180 degrees. Now let us look at this a little closely so at theta equal to 0 degrees what is the value of sine theta? What is the value of cos theta? Value of cos theta is 1 and value of sine theta is 0. So, the product sine theta cos theta will of course be equal to 0.

So for theta equal to 0 sine theta cos theta equal to 0 where does it become 0 once again? Well where does sine theta become zero once again at theta equal to PI theta equal to 180 degrees then again the product is 0. Where does cos theta become equal to 0? When theta equal to 90 degrees right and as we see that is really the node, we will come back to that. So, where is a node? The node is if I write sine theta cos theta equal to 0, sine theta equal to zero is not a node remember because sine theta equal to 0 at theta equal to 0 and theta equal to PI.

Still theta equal to 0 and theta equal to PI they are like the limit is of the universe as far as theta is concerned theta does not exist beyond a value of 0 degrees and beyond a value of 180 degrees also. So, those are sort of the boundaries so those are not nodes. So, sine theta equal to 0 would not give you the nodes what gives you nodes is cos theta equal to 0 and cos theta equal to 0 means theta is equal to 90 degrees.

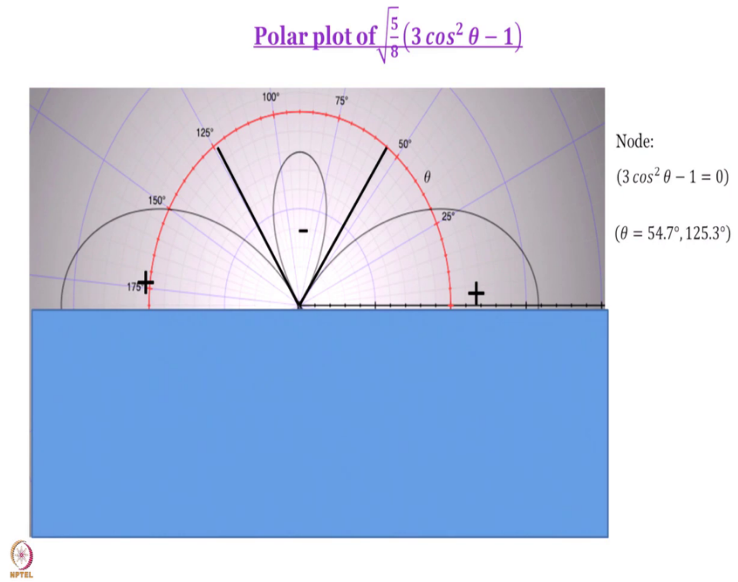
This is what we had sort of mentioned in the previous slide also. This here is your node. So, let us convince ourselves in a different way this is from 0 to 90 degrees first quadrant sine theta is positive cos theta is also positive so the product will be positive. What about the second quadrant? Where theta lies between 90 degrees and 180 degrees there sine theta is still positive remember all sine, tan, cos.

So, sine theta is still positive but cos theta is negative so sine theta cos theta has to become negative, right so we verify that when you go from theta little less than 90 degree to little more than 90 degree then theta actually goes to 0 and changes sign all right. So we have drawn the we have drawn the node let us now write the science explicitly in the first quadrant we said the sine is going to be positive and the second quadrant sine is going to be negative.

Does this remind you of anything? This positive negative business I will help you a little bit by telling you that this thing that we see here is called a lobe. So, we have a lobe with a plus sign and we have a lobe with a minus sign. So, the lobe where we have written a plus sign is the lobe in which the wave function capital theta has a positive sign and the lobe where there is a minus sign is a wave function where is a lobe where the wave function has a minus sign.

So the plus and minus is really the sign or phase if you want to put it that way well sign is better I think sign of the wave function in that region great.

(Refer Slide Time: 24:29)



Now let me draw let us show you my favorite function 3 cos square theta - 1 multiplied by some constant all right. So, we have given you a spoiler by showing you the diagram already but let us explain nevertheless. Why do we have this color triangle here because remember theta goes from 0 to 180 degrees there is no theta beyond 180 degrees. So, it makes no sense to try and draw the function in this phase as well.

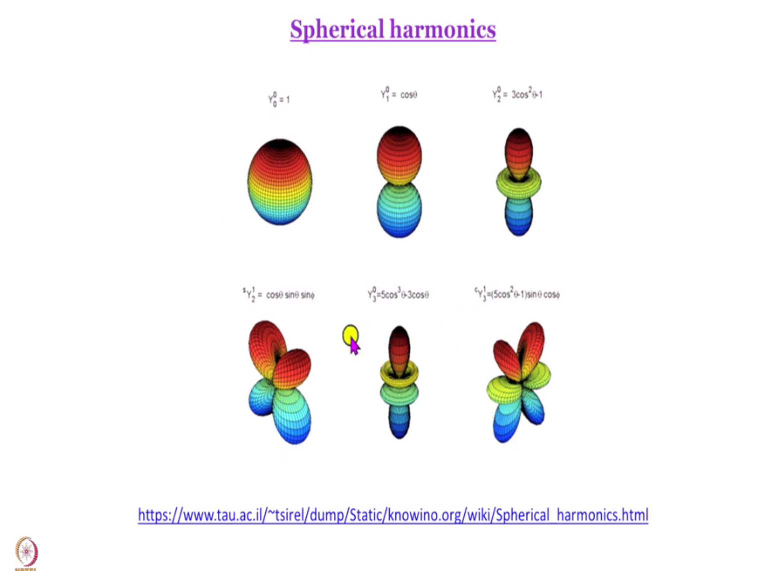
So I sort of dotted it out now 3 cos square theta - 1 it is always easy to work with 0 where is that equal to 0, where cos square theta - 1 equal to 0 or cos theta equal to 1 by root over 3 is that right, cos theta equal to 1 by root over 3 is that right? Partially right because when we say cos square theta equal to 1 by 3 there is no reason why we should neglect cos theta equal to -1 by root 3. So, you should consider that also ok. So, cos theta equal to -1 by root 3 will obviously come in the second quadrant.

The second quadrant; because that is where cos theta is negative and we do not have to worry about beyond that because as we said there is no theta beyond 180 degrees, so, where is the node or rather where are the nodes at theta equal to cos inverse well at theta equal to cos inverse 1 by root 3 yeah that gives us node at 54.7 degree and 180 degrees -54.7 degrees which is 125.3 degree. 54.7 degree is called magic angle and remember at magic angle cos theta equal to 1 by root maybe later on if possible we will come back to why what is so magical about this magic angle.

So this is these are the nodes and we have already shown the nodes by the black lines here. So, then what happens for theta less than 54.7 degrees yeah 3 cos square theta -1 is obviously positive right it has a plus sign we put a plus here. What happens between theta equal to 54.7 degree at theta equal to 125.3 degree. So, these are node so sign change has taken place and here again sign change will take place.

So here in this lobe the sign is obviously minus and then when you cross the second node again the sign becomes plus. So, this is the kind of picture that we generate for 3 cos square theta -1 when we try and draw a polar plot of it and put in the nodes as well. This is 3 cos square theta -1 and you can go back and see for which wave function we get 3 cos square theta -1 for which value of J which value of M and please do not forget that we are going to encounter exactly the same wave functions when we talk about a hydrogen atom shortly.

(Refer Slide Time: 28:18)



Now to conclude this discussion let me show you from this link here the way spherical harmonics are usually designated in textbooks to get this nice looking pictures where this is Psi 0, 0 that means J equal to 0 M equal to 0 that Psi that Y rather is just equal to 1 you normalize it that way. Y 1 0 is cos theta, Y 2 0 is 3 cos square theta -1 that is what we have worked out. Y2 1 is cos theta sine theta sine Phi.

So, here this Phi term also comes into play what are we doing here how have you generated this picture? We have taken what we have obtained earlier and then do not forget CT equal to 0 means this is sort of the z axis is not it. So, about the z axis you perform a rotation when you do that you essentially scan all values of Phi and that is when you generate these 3d pictures but remember in this 3d picture what are the coordinates that are there?

One coordinate is theta fine another coordinate is Phi fine. The third coordinate is not r the third coordinate is the wave function actually magnitude of wave function and sign here also is shown by this very nice certain colors you can see that this plus and this is minus and you can see this nodal plane that is there. So, I hope you can relate this picture with the one that we are drawn for 3 cos square theta -1 and I hope that you can relate this picture with what we had drawn for your for the earlier one sine theta cos theta.

But do these pictures remind you of something yeah even if you have never heard of spherical harmonics earlier you have seen pictures that look like this have not you? Actually you have and I think most of you by now would have remembered where you saw these pictures? You saw these pictures when you talked about orbitals. And these were touted to be the shape of orbital's where orbitals were supposed to have been regions of space where probability of finding the electron is maximum.

So we are going to debunk that definition in the next two or three well not two or three next three or four modules but again let us wait for that. What I want to say is that the spherical harmonics we get for rigid rotor look remarkably like the pictures that you're familiar to seeing familiar with seeing for so called orbital's. And that is because you have a similar part for a hydrogen atom Schrodinger equation there are similar solutions.

That concludes for now our discussion on rigid rotor. In the next module we will discuss angular momentum and it is components in a little more detail then we go on to hydrogen atom.