Introductory Quantum Chemistry

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Lecture - 28
Atomic Orbitals - Part III

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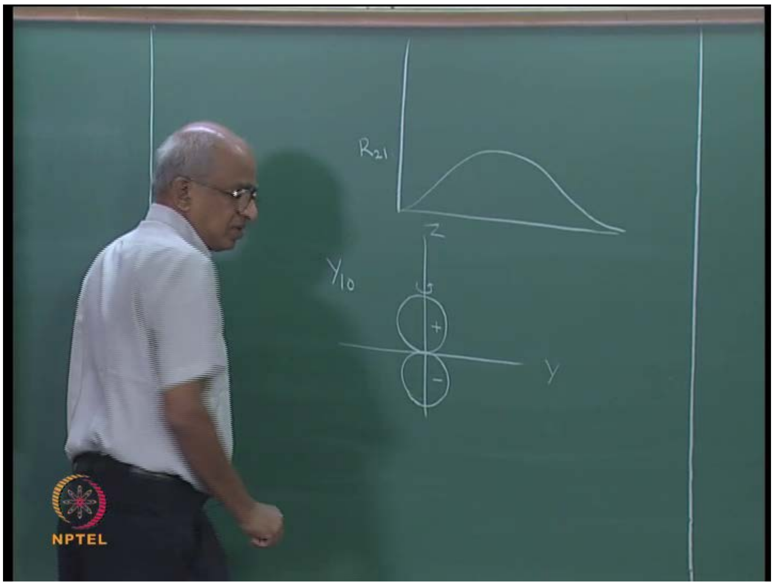

We were discussing the p z atomic orbital, if you remember we made a plot of radial part of the function and we found that it starts at the origin, and then increases reaches a maximum and then decreases this is the radial part. We also made a plot of the angular part and for that we used what is referred to as the polar plot and if you say that this is the y z plane.

Then what happens is that the polar plot consists of 2 circles of the same size just touching each other at the origin and I also argued that if you wanted to get the 3 dimensional appearance of this polar plot. What you should do is, you should take this figure rotate it about the z axis and then you will realize that the 2 circles will describe surfaces of 2 spheres, just like that touching each other at the origin.

So, this is the angular dependence that is the radial dependence I can, now combine both of them to get the actual 3 dimensional appearances which I shall represent by shading. But, before I forget, I also should tell you that in these directions the wave function was positive while in this in the downward directions the wave function was actually negative. So, this is the radial part which is actually R 2 1 and this is actually y 1 0 if you want to know what the functions are, so now how will you represent the function by shading.

The answer is quite simple if you say, here is the nucleus, and near the nucleus you will see that the radial part implies that the wave function has a small value. In fact, at the nucleus the value of the wave function is 0, but as you go away from the nucleus what does it say the wave function actually would increase correct. But, then you look at the angular part you see after all the wave function is a product of the radial and the angular part. So, the angular part has the maximum value in the either in the positive direction which has the largest value either in the positive z direction or in the negative z direction.

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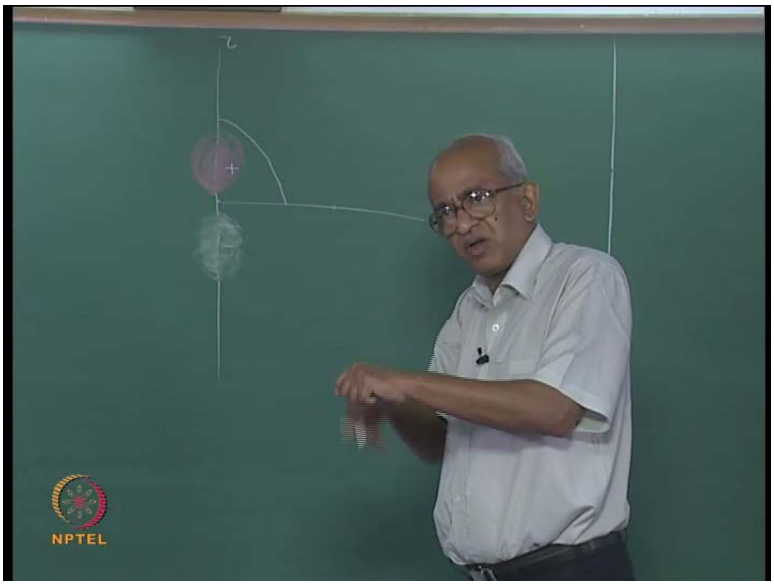

So, what will happen is that you will have let us say an appearance which I shall try to represent here see when I representing the shading, I would not have any density of shading near the origin. But, then when I go away from the origin it is going to the density of shading is going to increase, but the density will be actually the shading will be considered a long either the positive z direction or along the negative z direction.

That is implied by the angular dependence and in the downward direction what will happen we will have again a similar kind of appearance. If you want I mean one can well of course these are identical though they do not appear to be same in what I have done except for their signs they are identical. So, this is plus and that is minus and not only that if you think of any point on the, on the y axis you would realize that for that point, the angle theta actually is 90 degrees and remember the angular part of the function was actually cos theta, this contained y 1 0 is proportional to cos theta.

So, what will happen is that if you if you think of any point along the y axis theta is 90 degrees and, therefore what will happen to cosine of 90 degrees which is actually equal to 0. So, anywhere on the y axis actually it is, but not only anywhere along the y axis you think of any point in the x y plane, the value of theta is 90 degrees. So, any point in the x y plane, if you remember polar coordinates you would realize that for any point in the x y plane the value of theta is 90 degrees. Therefore, any point on the x y plane, we will have a value 0 just above the x y plane you will have a positive value, while just below the x y plane you will have a value which is negative.

So, that is all the appearance is and in fact, I have a figure to show you this, so this is the appearance of the plot just confined to be x yes, here it is x z plane it does not matter whether it is x z or y z. So, that is how the appearance is and in fact, if you look at this part you see it will, it is going to be positive and if you look at this part it is going to be negative. As we can see, this actually is not just a density plot in addition to the density it also has plotted the condors the condors along which the function has constant value for example if you, if you look at this value.

We see along this condor everywhere along this condor the value of the function is 0.034 while along this condor what will happen is the function has magnitude wise it has exactly the same value. But, the sign is opposite and also it is possible to make polar plots of such functions using this nice software called mathematica and I would demonstrate that also. What we are interested is in a polar plot of p z and you say this is either polar plot 3 dimensional appearance of the polar plot would be. Now, the advantage of this kind of software is that you can actually view it from any angle if you like you can rotate it and view it.

So, the 3 dimensional appearance of the polar plot is clear you see what I have described it is just 2 spheres touching each other at the origin that is what happens with p z atomic orbital and, now we will look at the other p orbitals as I mentioned in the previous lecture.

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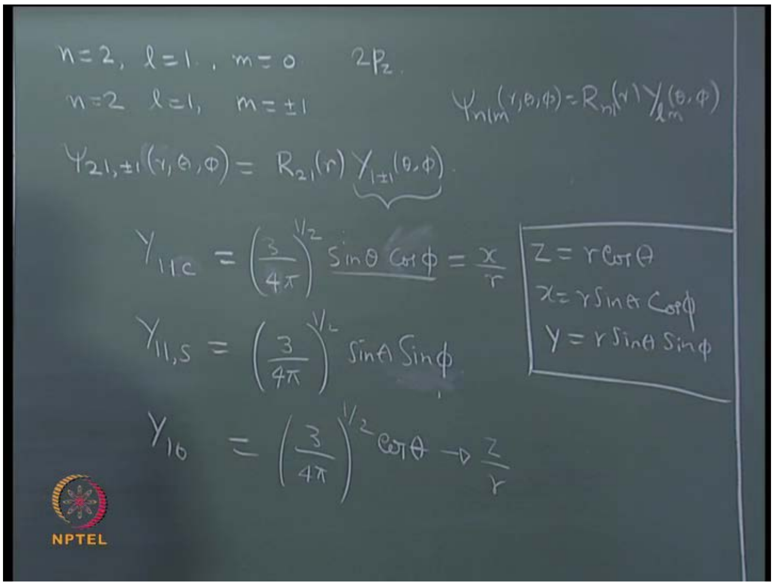

I am thinking of n is equal to 2, l is equal to 1 and then I said m is equal to 0, this gives me this particular atomic orbital which we now normally referred to as p z atomic orbital. To be very precise, we put a 2 p z because p 2 is the principle quantum number then if n is equal to 2 and l is equal to 1, and m is equal to may be plus 1 or minus 1 what is going to happen is I will have psi 2 1 plus or minus 1 I shall write them together. This R functions of R theta phi and it is going to be equal to R 2 1 of small R because remember the way, the wave function was even.

If you have 3 quantum numbers, n l and m R depends only up on 2 of them and the angle angular part of the wave function again depends only up on two of them. So, this is how the function is if you remember this is something that we had we had already discussed, so therefore if you had y psi 2 1 plus or minus 1 you are going to of R 2 1 multiplied by y 1 plus or minus 1 theta phi. As I told you, this function is known as the spherical harmonic function one of the spherical harmonics and this is the radial part of the wave function.

This R 2 1 actually we do not have to discuss because we have already discussed it in the case of 2 p z, so as far as the radial dependence is concerned this function and the two p z functions are the same there is no difference. So, therefore I have to look at the just y 1 plus or minus 1 you can evaluate it using the formulae that I had given earlier, but what I will do is I have come with a table.

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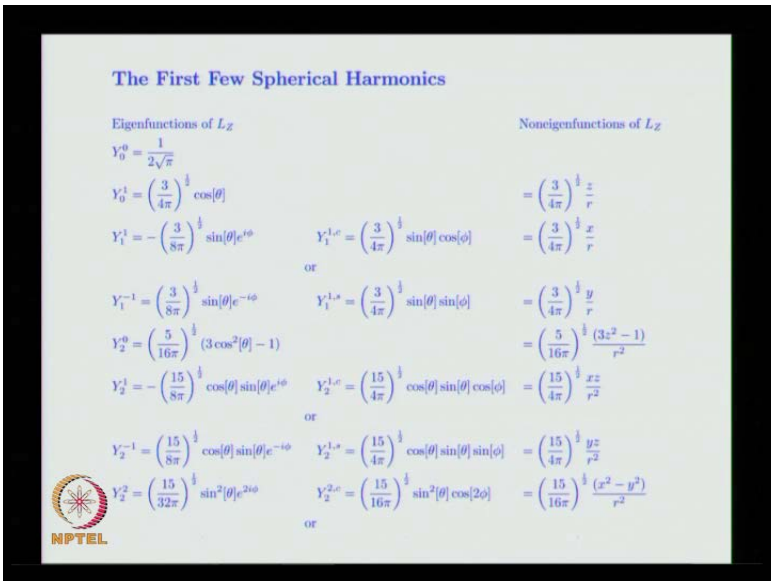

So, we can just use the table, so this here I have a table of all the spherical harmonics that we will ever need at least it recommends three lectures or most of them, so what we should do is we should look for y 1 plus or minus 1. So, if you if you look, here you get y 1 minus 1 the notation is slightly different because that minus 1, I am writing not on top, but at the bottom that is all. So, y 1 minus 1 is, here y 1 plus 1 where is it, there it is these are the two functions what is their form y 1 plus 1 for example means actually 3 by 8 pi we are terribly interested in this constant.

In fact, we can even omit it if you are thinking of just the angular dependence how it is changing as a function of angle this is just a constant when sine theta e to the power of I phi. Well if you look at the other function what will happen is that the you are going to have a minus sign instead of e to the power of plus I phi y we are going to have a minus I phi. So, I can write both of them together plus or minus, now visualizing this kind of function is difficult because what happens is that, this e to the power of plus or minus i phi will can be written as cosine of i phi plus or minus i sin phi.

Using a theorem for mathematics, we all have already discussed this and therefore it will contain a real part as well as an imaginary part. So, difficult to visualize, but there is nothing wrong with this function this is absolutely fine and if you want to use it you it can be used. So, what we do is, we do not make use of this plus or minus e to the power of plus or minus i phi, but instead we make use of functions which are obtained. As linear combinations of this e to the power of plus i phi and e to the power of minus i phi, I have told you this earlier.

So, the result is either cos phi or another possibility is you will get sine phi or something that I have already talked about, so those functions also are shown here. So, if you look, here is the spherical harmonics obtained by linearly combining these two, this is one possibility instead of e to the power of i phi all that happens is you get a cosine of i. But, then if you have the cosine, you can also have the sine and that is the next possibility, so therefore the way in which I will indicate them is I will say y 1, the magnitude of m for both the functions is actually 1.

So, I will write this as y 1 1 c, why c because I have put a cosine here and the other possibility is y 1 1 s it should be defined. To be well, the normalization factor is a little bit different, you will get a 4 pi, here 3 by 4 pi to the power of half is sine theta, sine phi. So, these are the functions, these are the angle dependant functions there we simply make use of them because the functions are real and therefore you see, you have to visualize. But, then what should what I should do is I should actually construct polar plots of these two functions, I can do that using mathematica it is not difficult at all.

But, I will, I will make use of a simple argument which should enable, you to construct the polar plot yourself to make that argument let me also look at y 1 0, y 1 0 is what y 1 0 is actually proportional to cos theta. There will be some multiplicative factor what is that multiplicative factor it should be there in the yes well it is, here well there is a small mistake. Here, this one should have been down here and 0 should have been up there it does not matter we never decreases, therefore the square root of 3 by 4 phi into cos theta. This is the function for which we already have made the polar plot and, so we know what exactly how the polar plot is, but then if you remember z is equal to R cos theta.

Remember our conversion from Cartesian coordinates to polar coordinates z actually was defined to be equal to R cos theta, x is equal to R sine theta cos phi y is equal to R sine theta sine phi, this is just to remind you. Now, if you look at cos theta, suppose I expressed it in terms of z, you can see that it can be expressed in terms of z. But, easily it is nothing but z divided by R and you see that if you made a plot of z by R the result actually consists of surfaces of 2 spheres which are located along the z axis, and with that information suppose you look at sine theta cos phi, sine theta cos phi actually is x by r.

So, suppose you make a polar plot of x by R what would be the result the result actually is very simple it has to consist of two spheres which are located along the x axis. Therefore, what happens is that this function represents what you normally referred to as the p x atomic orbital and this orbital and the previous orbital are different only in that their orientation in space is different. The previous one was over reined along the x z axis while this one is over reined along the x axis and the same kind of argument will enable.

You say that well this function is actually y by R and, therefore this will be this is going to be I mean the polar plot is going to of consists of two spheres the paired along the y axis. So, you can actually see them using mathematica if you want to have may be what I will do is I will plot all of them p x. It has gone with plot to all of them together in one figure I wanted them to be separate. So, let me try to separate them it is an interesting figure no it does not work how should I do we can write. Now, this is a p x this 1 is p x and these two are as you can see p y and p z we are having the previously the I made a mistake you could see all of them together in one figure now we will look at n equal to 3.

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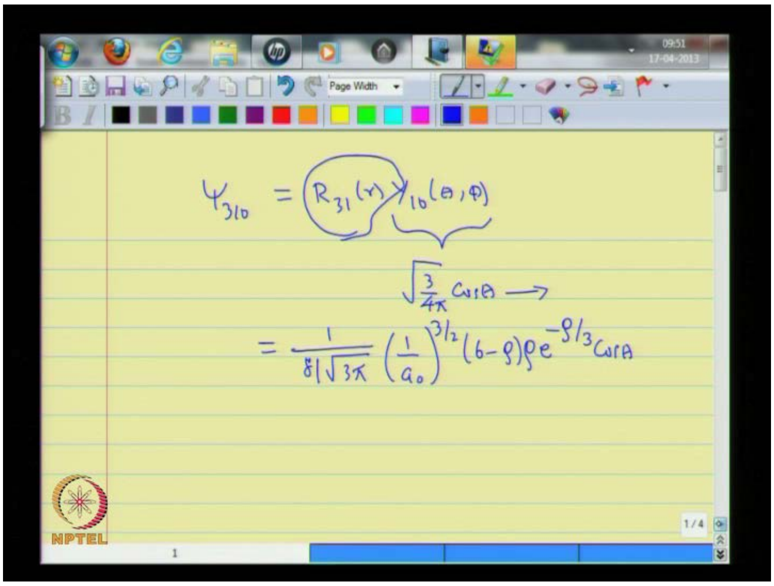

But, before I do that let me just remind you in this case we have found 4 atomic orbitals remember n is equal to 2, there are 4 atomic orbitals n is equal to 1, there are, there is only one atomic orbital. In general for any value of n what happens is that you have n square atomic orbitals for the hydrogen if you give me any value of n you have n square. That means, if I had n equal to three I would have nine atomic orbitals, so let us look at n equal to 3. So, if n is 3, I will have I can have l equal to 0 in which case m will be automatically be equal to 0, let us look at that case first.

Wave function psi 3 1 0 and as you know it may be written as R 3 1 of R y 1 0 of theta phi and this y 1 0 is a function that we have already encountered. This function is nothing but square root of 3 divided by 4 pi into cos theta and this is just the same angle dependence that appeared in the case of 2 p z atomic orbital. Therefore, we should realize that this is a 3 p z atomic orbital that we are going to have and the angular dependence we have already discussed.

So, I am now going to discuss that, but you can look up R 3 1 from tables and to write the expression for the total wave function. The total wave function will then look like 1 by 81, 1 by 81 into square root of 3 pi into 1 by a 0 to the power of 3 by 2 into 6 minus rho, rho e to the power of minus rho by 3 into cos theta. We shall now make a plot of this R 3 1 against the distance from the, from the nucleus let us do that, so what we are going to do is you see we are essentially going to look at.

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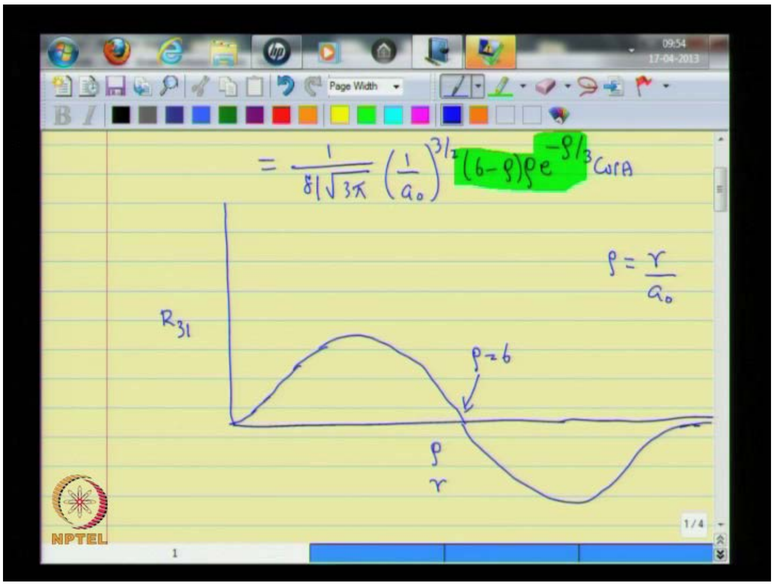

Look at this part and make a plot of it against rho or equivalently against r, so this is my vertical axis, along the vertical axis we are going to take R 3 1 and along the horizontal axis. As I said it can be either rho or equivalently R because rho is actually given by R divided by a 0, now because of the excisions of rho in my wave function what will, what is what will happen is that the wave function starts out to be 0 at the origin. That is at rho equal to 0 you see this something has happened I press somewhere, let me, let me draw this again.

So, therefore the plot actually would look like this it starts at 0 increases and eventually when rho is equal to 6, the function as you can see will become 0. So, therefore it turns around at rho equal to 6, this point is rho equal to 6 the wave function becomes 0 for R 3 1 becomes 0. Then beyond that the wave function actually turns out to be negative, so that if and eventually when rho is infinitely large the wave function will approach 0. So, that is a plot of R 3 1 against rho and, now all the information that we have we will combine together and make a plot which would give an idea of how the orbital is.

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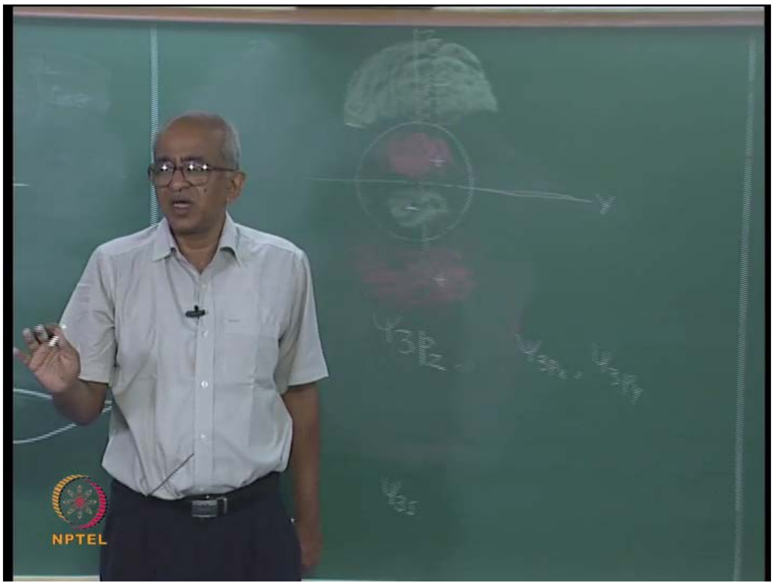

So, how will I represent this function, well I am going to represent it by shading here is the circle or maybe I can say the sphere with rho equal to 4. This is the sphere that has a then inside the sphere what will happen the function is actually was it the while outside the sphere the function is negative on the sphere the function is 0. So, therefore let me represent this function by shading you see suppose I am somewhere here, suppose I am somewhere here.

Then I know that the radial part of the wave function is actually positive that is clear from this plots you are somewhere here the radial part is positive the angular part also is positive because I am taking a positive z direction. So, therefore the total wave function which is the product of these two is going to be positive in this region right at the origin it has a 0 value, this is a mistake R 3 1.

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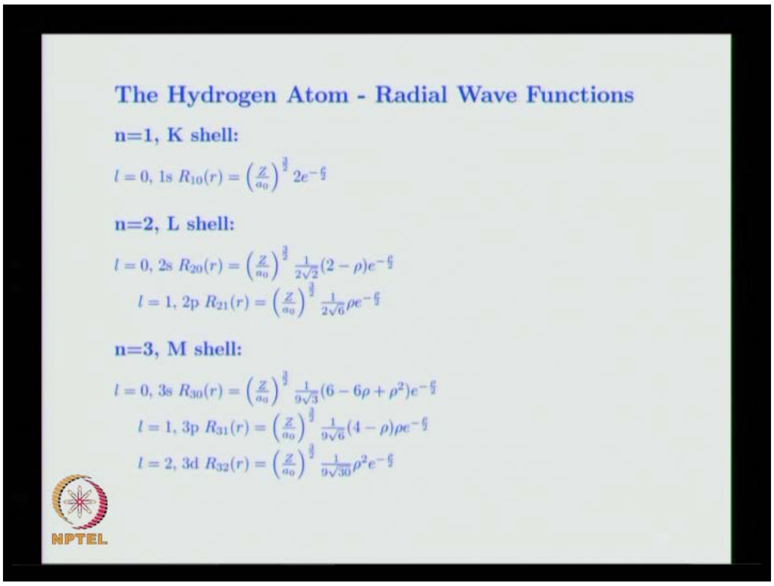

I did not copy it correctly, if you, if you look at the expression I am sorry the expression that is written there is correct where is it R 3 1 is having 4 minus rho into rho, this rho I forgot to copy. So, whatever I have told you by looking at the function is not correct, I what I do is I just look at the function and tell you how it behaves, I do not remember all these things. So, if you that rho actually implies that implies that this plot has to be only slightly modified fortunately.

It starts with the value 0 there then increases and then decreases that is all, so therefore what will happen because of that at the nucleus the function actually has the value 0 and as you go away from the nucleus, what will happen the function increases. So, the function increases, but on the surface of the sphere the function actually becomes 0 and as you cross the sphere what will happen to the function it will change sign. So, you will have a region, here where the function becomes negative, but then suppose you are in the downward direction in the downward direction what will happen.

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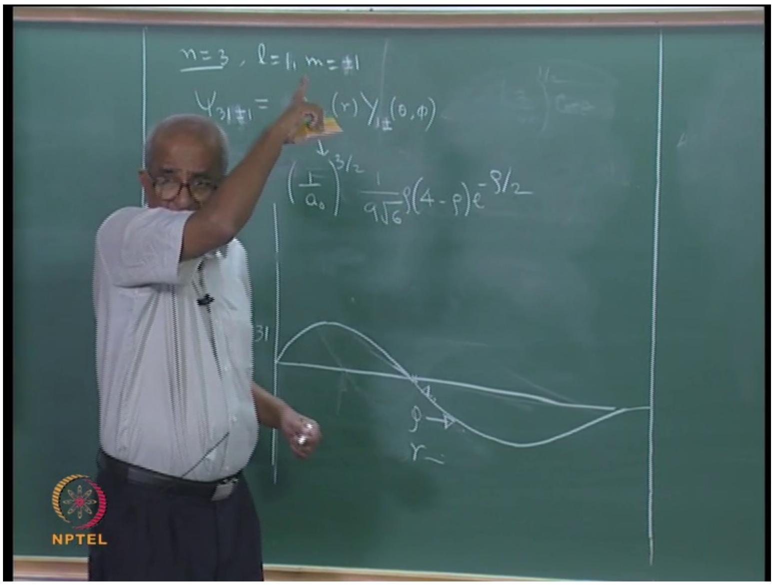

So, the radial part of the wave function is still positive, but the angular part actually is negative in the downward direction. So, therefore in this region the function will be negative and then when you cross the sphere what will happen the function changes sign and you will have a region where the function is positive. You should also realize if you say that this is the which axis would you like to say the y axis there is the z axis and you can say the x axis is perpendicular to this any point on the x y plane the function is actually the angular part is cos theta.

So, for any point on the x y plane cos theta has the value 0, so this is actually a nodal plane, so how many nodes does this function have it has two nodes one is this plane x y plane. The other is the surface of this sphere there is again thank you this is another mistake, so this is negative, so there is the orbital that we refer to as 3 p z or may be premorphasizely. You can put a psi also which usually people do not write psi 3 p z and then we have we have to think of m equal to plus or minus 1, I just modify things here m equal to plus or minus 1. That means, I have to think of y plus or minus 1 and instead of 0, I will just put plus or minus 1 here and then plus or minus 1 there and then what will happen.

You will have e to the power of i phi or e to the power of minus i phi, but we are not happy with that, so what do we do we make use of functions which are real and eventually. What is going to happen is that you are going to get two other atomic orbitals which will be 3 p x and psi 3 p y, their appearance everything will be this same as this one except for the fact that they are now oriented along the x or the y axis that is all. Then we think of the next situation where n is equal to 3 and l is equal to 2, so if n is equal to 3 and l is equal to 2, m can actually have what are the values that are possible let me, let me use them.

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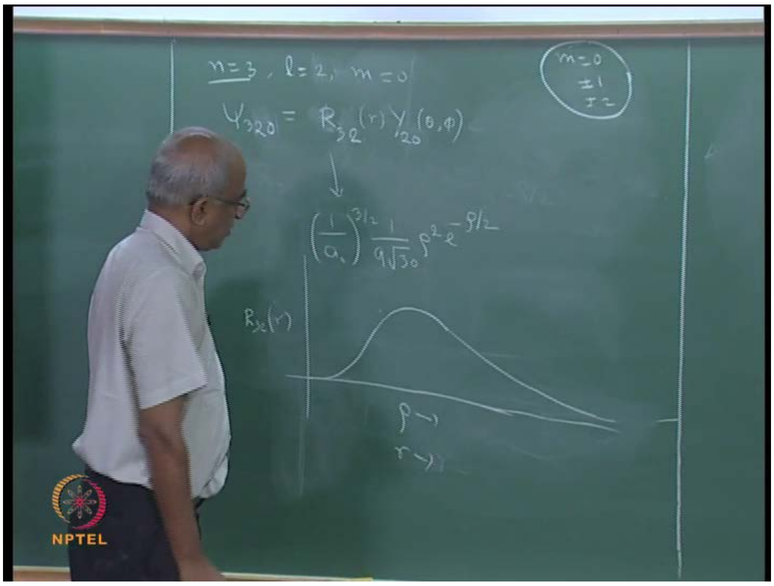

Here, m can be 0 over plus or minus 1 over plus or minus 2, these are their 4 different values that are possible each one of them will give you a solution of the Schrodinger equation. So, therefore I have 5 orbitals when l is equal to 2, so the first one will have m equal to 0 and what will that be you are going to have psi let me just modify things. Here, psi 3 2 0 it is going to be R 3 2 into y 2 0, and y 2 0 we can take from the from the tables, but before I do that maybe I can take R 3 2 because it is right there on the screen, here it is R 3 2 1 by a 0 to the power of 3 by 2, it is difficult for me to see standing there.

So, this is the function and what happens is that you have rho square into e to the power of minus rho by 2 and this actually ensures that if I made a plot of R 3 2 of R against rho or equivalently r. So, what happens is that we have this term R square which actually makes the function vanish at the nucleus, so the appearance of the phi the plot will look something like this it reaches the maximum and then it decreases to 0. Now, the angular part of the function again I will make use of my tables, so somewhere in the tables I should find y 2 0, there it is y 2 0.

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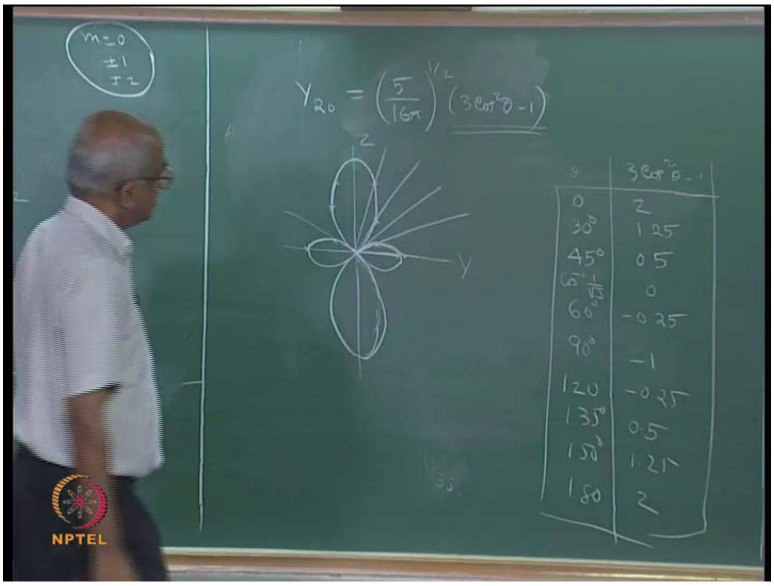

So, this is the function and well the function has this constant I am not worry going to worry about that constant, I will just construct I will imagine that I am going to consider only this part and I shall make a polar plot of this function. Let me do it very quickly because we know the procedure, now the first thing that I will do is, I will put make a table of theta and values of 3 cos square theta minus 1. If I put theta equal to 0, I can easily evaluate it I shall get the answer 2 if I put the answer, I mean if I put 30 degrees. You will get the answer 1.25, 45 degrees the answer will turn out to be 0.5, 60 degrees it is minus 0.25, 90 degrees minus 1 then 120, 135.

So, this is my small table which is not difficult to calculate and this you can make use of to construct the polar plots as I said I will do it rather quickly, let me confine myself to the y z plane I realize that when theta is equal to 0 the value is actually 2 units. So, I will have to put a point somewhere there such that the distance of the point from the origin is 2 units, then 30 degrees the point is 1.25, 45 degrees the point is at a distance of 0.5.

Well, as you go from 45 to 60 you find that the function actually changes sign, so therefore there is some point in between where the function will take the value 0 what is that value. You can easily calculate that it is going to be cos inverse of 1 by root 3, so at that value which you come around 53 point some angle which will be something like this, at that angle the point that you have to put actually coincides with the origin.

You can do the same kind of thing on the other side and then if you are thinking of the, of the y axis along the y axis I know, you know the theta is 90 degrees the function actually is negative. But, remember my prescription while if the function turns out to be negative then you will forget the negative sign which means that you are taking the magnitude. So, along the y axis the function actually turns out to be negative and, so we will put a point such that its distance from the origin is equal to 1 unit, I have not accounted for this.

This is actually at an angle of 60 degrees, this is 60 let me say and that the along that direction you see the value is 0.25, so point is somewhere here same kind of thing you can do in the other direction. So, may be somewhere here you will have a point somewhere there you will have a point you can continue to do that as I said this is not a difficult thing. Therefore, let me just join together the points that I have obtained, so these are directions in which the function is positive, then we can have these points going together and you can continue the plot down downwards using the table.

So, this is the appearance that you will get, but to remind you it is in the upper directions the function is positive, let me remove all these lines that I had put, maybe I will draw it once again. So, the function is positive in these directions the function is negative and further you should notice that the function has no theta dependence. Therefore, if I, sorry the function has no phi dependence and therefore if I wanted to get the 3 dimensional appearance all that I need to do is take this and rotate it about the z axis right, this orbital I will continue discussing this in the next lecture this is referred to as 3 d z square atomic orbital.

So, thank you.