**Quantum Chemistry of Atoms and Molecules**
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**Lecture – 30**
**2p orbitals**

We are discussing hydrogen atom wave functions we have shown you some beautiful pictures and we have learnt how to depict s orbitals 1s, 2s, 3s we have learnt how nodes come they have also learnt what happens when we can when we multiply them by this r square.

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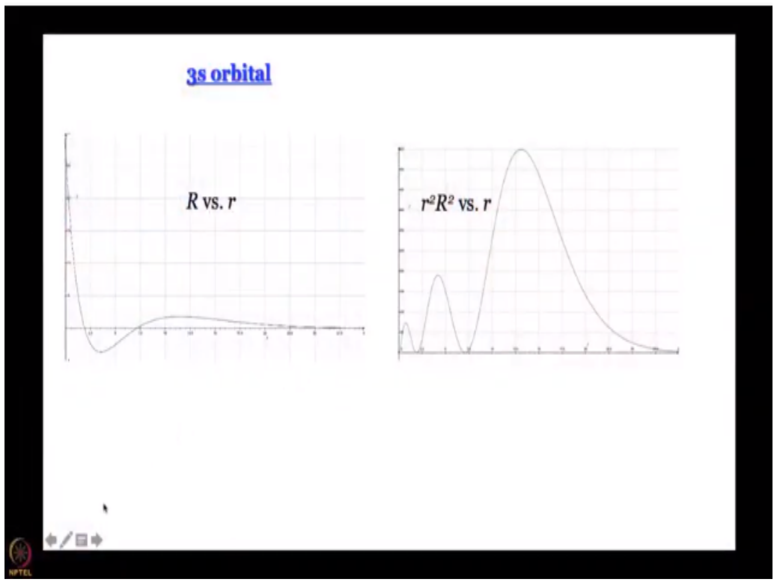


And generate the radial probability distribution function.

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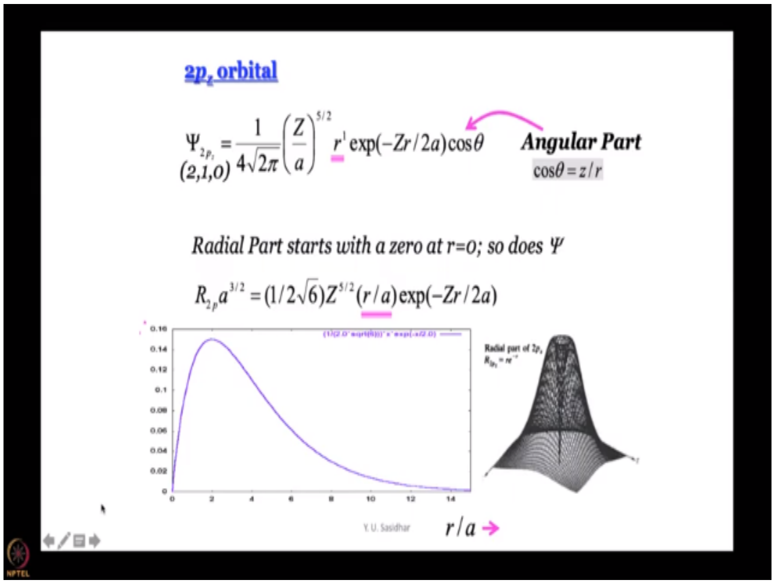


Now we try and show you some even more beautiful pictures.

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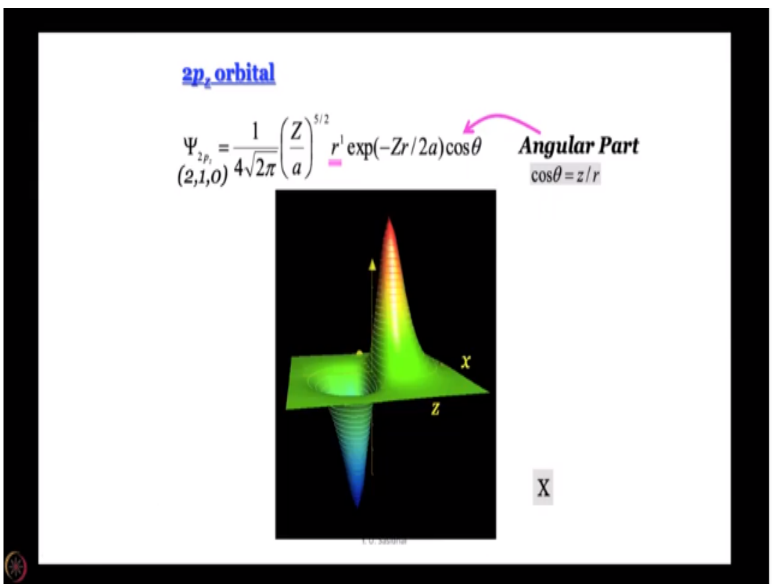


Like this so where does this come from? Let us just see. So now we move on to p orbitals and the simplest p orbitals of course are 2pz orbitals here principle quantum number is 2, azimuthal quantum number is 1 magnetic quantum number for 2pz = 0. Now why is it called 2pz we will learn it very soon let us have a look at the functional form constant multiplied by now we have r, r to the power 1 multiplied by e to the power - Zr/2a so see increasing function of r and this one is an exponential decay multiply them together it is not a surprise that it goes to a maximum.

So what you see here is the radial part of the wave function starts with 0 at r = 0 and of course psi starts with 0 at r = 0 as well goes up and comes down and from the previous module previous couple of modules I think you are now familiar and you can make sense of this kind of three dimensional plots do not forget please that the vertical axis is really psi okay. In fact, in this case vertical axis is capital R. Now we have to start worrying about the angular part.

The angular part in case of 2p orbital is cos theta if you remember the relationship between the cartesian coordinates and circle polar coordinates you recall that cos theta = z/r. So, I can simply write z/r here so the effect will be that that r in the denominator and this r is going to cancel each other, right? So what we are left with is something in z so what will this orbital look like? now we bring in symmetry in a very qualitative manner would you agree with me?

If I say that this orbital will have exactly the same symmetry as the z axis if you have a problem with that let me put it in an even simpler form wherever z is positive this orbital is going to be positive remember it is being multiplied by an all positive or 0 function so except for r = 0 and r = infinity where the radial part is 0 the function has to be positive when z is positive and negative when z is negative right? So, where is the node.

The node arises from z = 0 equal to 0 and z = 0 being a node the function is going to change sign so the way we have drawn it here is I am not going through the exercise of trying to plot it in real time because you have seen enough of it now you can do it yourself so we have plotted that it is that the vertical axis is psi this horizontal axis is z and the one perpendicular to the plane of the projection is x I have neglected y for the time being.

So, cos theta is along z so on this side whereas it is positive cos theta is also positive and what you get is you get a positive part of the wave function and wherever z is negative you get a negative part of the wave function and why does it go through a maximum why is it sort of like a cone? Because if you go back to the previous projection see this is the r dependent part, right?

So r dependent part is multiplied by cos data wherever the cos theta is equal to one where is cos theta = 1 okay where is cos theta = 1 I think you know that at theta = 0 that is where it has 1 that is where it has a value of 1 and you have the you have purely the radial part in the total wave function then as cos theta decreases from 1 to 0 what happens is that this radial part keeps on getting smaller and smaller and smaller.

The radius dependent does not change what happens is that this maximum becomes a little smaller that is why you get this kind of a three dimensional picture and when z becomes negative of course the entire thing becomes negative and what you see here is the contour lines. So if I look from the top or from the bottom what kind of projection do, I get? what kind of a contour diagram do I get?

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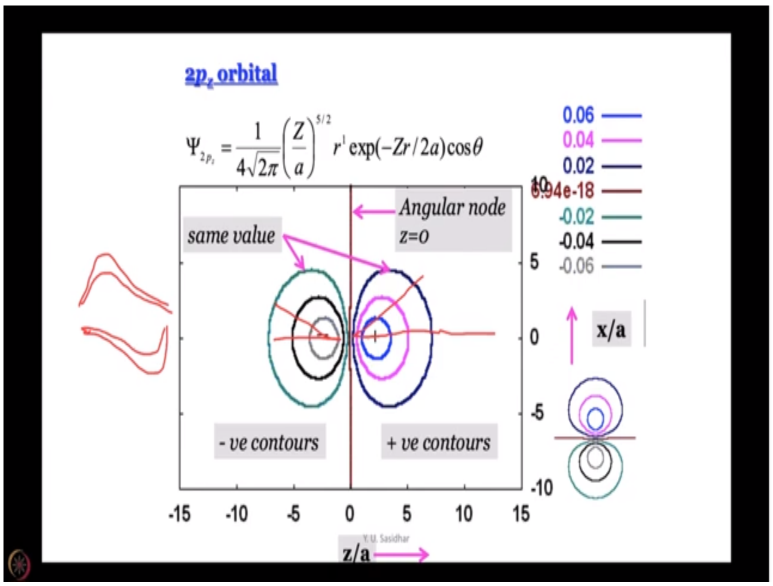


I get something like this you agree to down from the top this is where the positive peak is this is where the negative peak is check this is the z axis this is the x axis. So, wherever whenever z becomes negative the wave function becomes negative as well and go through any radius it goes through a maximum that its starting from here it goes through a maximum then comes down and if you remember what we had said when had shown you the example of contours of an island the lines are close together where the gradient is steep.

The lines are further apart from each other where the gradient is gentle. So just looking at it what you see is that near the node we have a steep gradient and then once it goes to the maximum which is somewhere here the fall off is much gentler. That is the case everywhere you go from this direction this direction this direction everywhere the same thing happens it is just that the maximum value of psi reaches is different depending on theta.

Let me maybe demonstrate that if I can. Let us say you take this section what will happen psi will go up, up to this value remember this is going up the values are given here is going up from out to in the inner point here is a maximum value. So you get a function that looks something like this. Now let us say I go along this radius what will happen still it goes up and then comes down but what I see is that I am not reaching this high value the value is lower.

So you get an similar looking function, but the maximum value reached is not going to be much it is not going to be that much what about here? When you go in this direction this is what you get what happens when you go let us say in this direction similar function given my poor artistic skills but maximum reached is lesser. So it is 0 of course wherever $z = 0$ and it is 0 at infinity as well $r =$ infinity as well.

So I just take you back and I ask you to take a look at this 3d plot vertical axis being psi and the contour and I will request you to make sure that you have completely understood the that this and this are one and the same there are two ways of drawing it. Now so here we get a node this node is a different from the node we had in 2s or 3s orbital why? Because those nodes arose by equating the radial part of the wave function to 0 here, I get the node by equating the angular part cos theta to be equal to 0 it is just said cos theta translates as $z = 0$ as well.

So this here is the node nodal plane you can say and is our familiar p orbital two lobes one with plus sign of wave function but with minus sign of wave function, right? What happens if I tried to construct psi square? Well we get two lobes once again just that will become positive then what should I multiply by? I should multiply by sin square theta should I multiply by sin square theta remember what is there in the volume element r square sin theta.

So I should multiply by r square sin theta and see what kind of shape we get we will not deliberate upon this question right now in the next module or the module after that we are going to come back and we are going to briefly discuss this issue for now let us just go through the your orbitals and have a look at p as well as d orbitals.

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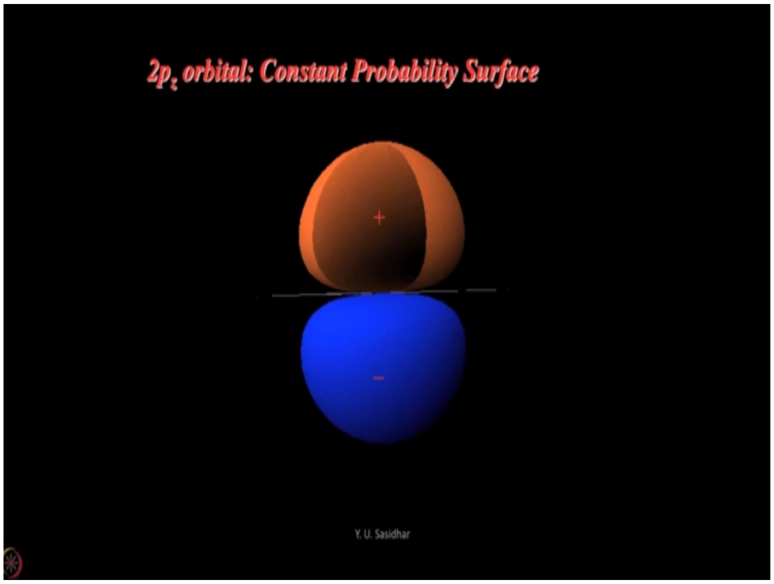


Okay now what the thing is you can construct the probability and the probability roughly follows qualitatively the shape of the contours that we had drawn but of course they will not be exactly the same. So this is the familiar p orbital that you get why is it that we like to plot constant probability surfaces? We like to do that because it is probability that tells you where the electron is so when you want to work out the things like bonding and all we do not know what probability is.

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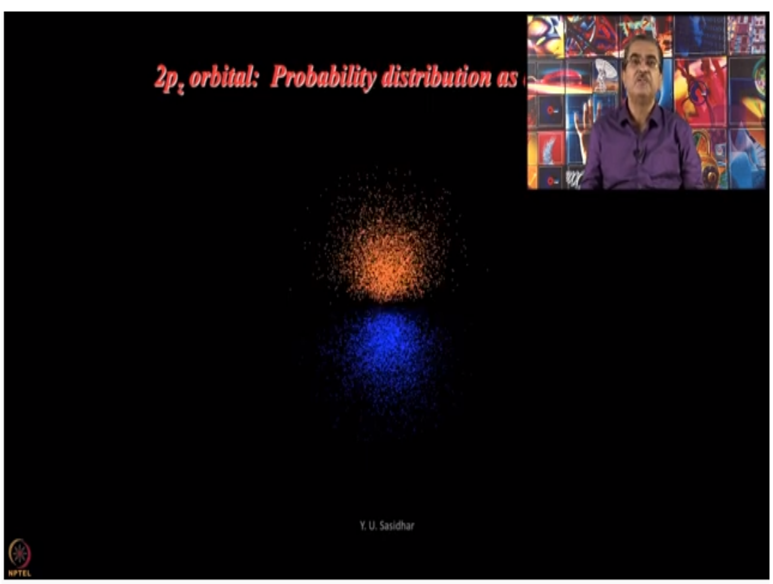

Okay now so this is another way of drawing the probability distribution as dots we are not familiar with this.

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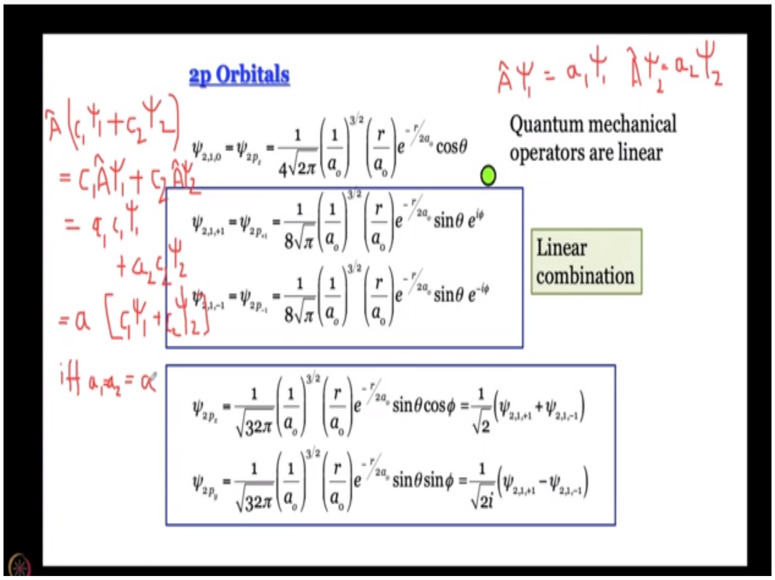


Now we come to a peculiar problem we have handled 2pz now the moment we try to go to the other two orbitals, orbitals for m = + 1 or m = - 1 we encounter the problem that we have e to the power I phi and e to the power – i phi there remember the phi part of the wave function is e to the power i and phi here I can take a value of + 1 and – 1 how am I supposed to draw it in a real surface? I cannot so what we do is we use a very convenient tool of quantum mechanics to try and make the situation such that we can draw something right?

More about this later let me just state here that the way to handle these imaginary orbitals is that we remember that quantum mechanical all orbitals are all linear we had said it towards the beginning of this course they are all linear what is the meaning of quantum mechanical orbitals being linear? It means that when a operates on some wave functions psi1 to give some eigen value and it operates on some other wave function to give some eigenvalue then a operates A1 psi1 to give a1 multiplied by eigenvalue of psi1 multiplied by psi1 this is the meaning of an operator being a linear also A hat operating on psi1 + psi 2 = A hat operating on psi1 + A hat operating on psi 2.

Since we have said it quite some time ago why do not I just write it once? what I am saying is the meaning of quantum mechanical operators being linear is let us say I have some operator A hat operating on psi1 to give some eigenvalue a1 and a2 sorry A hat operating on psi 2 sorry for my childish hand writing is what I mean is that suppose A hat operates on say c1 psi1 + c2 psi2 then I get c1 A hat psi1 + c2 A hat psi2 this is a meaning of an operator being linear.

Okay we are going to use this and try to use some linear combination. So, what we are saying essentially is that we are if you have a linear combination of acceptable solutions then they should also be acceptable functions is it always the case or is it not the case always let us see. So let us write this down what I get is I get a1 c1 psi 1 + a2 c2 psi 2 should have actually included this in the slide itself.

So now see if this is to be an eigenvalue equation what is the condition? Eigen value equation means this c1 psi + c2 psi 2 should somehow be able to go into a bracket that is only possible if you can take out a1 and a2 when will that happen? It will happen when you can write like this a multiplied by A hat sorry about that I do not need to write A hat here c1 psi 1 + c2 psi 2 when will this happen? this will happen only if and only if a1 = a2 = a or in other words the linear combination of two acceptable wave functions is two acceptable eigen functions of an operator is also an eigen function provided the two wave functions have the same eigen value.

So here think of Hamiltonian operators what are we using orbitals for so far to find out energy. So Hamiltonian operator is a total energy operator what is the eigenvalue for 2pz and 2p +1 and 2p -1 they are the same whatever is the eigenvalue for n = 2 is the eigenvalue energy eigen value for all these orbitals remember l and m do not make any contribution to energy for a one electron system is n all the way so these two psi + 1 and psi – 1 these p orbitals actually satisfy the condition that they have the same eigen values.

So if you take any linear combination you will generate another wave function which will be an eigenvalue of Hamiltonian with the same energy associated with it that is very important okay? And so we do not care see we have solved you are solving that equation in a particular way that is where we have got the solutions. If you solve it in some other way, we could have got perfectly valid solutions that are different from this one that might sound a little confusing but that is how it is.

So were always allowed to generate new functions new solutions knowing already existing acceptable solutions and what I have shown you is that if the if you have two functions whose eigenvalues of an operator are the same then the linear combinations no matter which linear combination I took c1 and c2 they are perfectly general you take any linear combination of these wave functions. Now may I use the word degenerate since were using energy here if we have to degenerate wave functions same energy eigenvalue.

Then any linear combination of these two, two wave functions is also going to be degenerate with the functions that we started with we will have the same eigen value. So we are allowed to take such linear combinations okay? Now we know what happens when we add say e to the power i phi with e to the power - i phi it becomes real or we subtract right? So, we will use those relationships between trigonometric and exponential forms of imaginary numbers, and this is what we will do.

The first linear combination we take is 1/root 2 multiplied by psi 2 3 + 1 + psi sorry 2, 1 – 1 and psi 2, 1 + 1 you just add them what do we get? 1/8 root pi 1/ao to the power 3/2 r/a0 e to the power -r/2a0 the radial part and the constant part is the same that is why energy is same so that goes outside the bracket well even sin theta goes outside the bracket and you are left with e to the power i phi e to the power - i phi in inside the bracket what is e to the power i phi + e to the power – i phi it turns out to be cos phi right it turns out to be cos phi not exactly cos phi there is a factor of 2.

So, you are left with sin theta cos phi 1/root over 32 pi 1/a0 to the power 3/2 multiplied by r/a0 e to the power -r/2a0 sin theta cos phi it is a real function, right? It is a real function moreover do you remember where sin theta cos phi arises cz = r cos theta what is x? x = sin theta cos phi r sin theta cos phi. So, sin that cos phi is a function which lies along x has the same symmetry as x, so this is familiar psi 2px orbital.

Similarly, if you take a if you subtract one of these are orbitals from the other in that case, we need and i in the denominator is not root over i root over 2 into i. So, this if you have and i in the denominator then we get something like this sin theta sin phi. If you remember sin theta sin phi multiplied by r is nothing but y so this is your 2py orbital. So, what we have learnt here is something that once again we miss when we study a high secondary or B.Sc. or even M.Sc. very common question that you ask often in Ph.D. admission interviews or in other places is what is the m value for 2px orbital?

Once again, many students do not know what to say many students arbitrarily say + 1 many students arbitrarily say +2 sorry - 1 many students say it can be + or – 1. None of these answers are completely correct some are outright from the last one is not completely correct see what we get here is that we obtain 2px orbital or 2py orbital for that matter by taking a linear combination of the orbitals for which n values are defined.

So m value is not defined for 2px or 2py right? It is not associated with any particular m value if you now go back to our initial discussions what is the meaning of m value? Meaning of m value is the z component of angular momentum, right? And the possible m values here are +1 and – 1. So, the z component of angular momentum is going to be +1 or – 1. So, if you take this e to the power i phi wave function and somehow measure the z component of angular momentum every time you measure you get + 1.

If you take this second one m = -1 e to the power – i phi wave function every time you measure you get -. If you take 2px and if you perform say a 10 lakh measurements for 50% of the time 50000 times well no for 10 lakh right so 5 lakh times you will get + 1 for the remaining 5 lakh times you will get - 1 okay. It is not please remember 2px and 2py orbitals are not eigen functions of the lz operators okay.

So average value you see what the average value will be if it is + 1 half the time and - 1 half the time you cannot measure lz like that? Okay so do not forget that they are actually generated from m = + 1 m = - 1 orbital m is not defined z component of angular momentum is not defined is the total angular momentum defined actually it is because total angular momentum is root over l into l + 1 and l here is = 1 1.

So the length of the arrow is defined theta is not defined that is what I am saying if you measure many times half the time you will get one value the remaining of the time you will get another value okay? So but that solves our problem we have generated this and now we can draw similar figures such that instead of being along z they will be along x and y respectively.

So interestingly the pz orbital arises automatically because there the m value is 0 e to the power I phi = 1 that is why you do not even have a phi-part showing up here just 1 so when m = 0 the orbital is already a real orbital real wave function we do not have to do anything if m is non 0 however then we in chemistry we always generate real wave functions by taking appropriate linear combinations.

Why is it so because we do not want to do too much of math, and you might roll your eyes and say that what you are doing in this course believe me it is not much. You take a quantum physics course it will be much more rigorous mathematically. So students of physics are absolutely fine with e to the power i phi e to the power – i phi they can understand it we understand better if you can draw some picture that is why without loss of generality, we prefer to take this appropriate linear combinations and generate orbitals that are real.

So that is how we generate px and py orbitals similarly for d orbitals what is the m value going to be? It will be 0 + - 1 + - 2 you can understand for m = 0 we will get a real d orbital anyway however for other m values you are not going to get an imaginary value so what you do is you take linear combinations of m = + 1 orbitals you generate something you take linear combinations of m = + 2 orbitals what I am saying m = + - 2 orbitals generate something else I will say that again for d orbitals m = 0 once again is a real orbital.

And we will see what it is in the next module I thought we will discuss p and orbitals in the same module but time is running out so we will take a break and if you take m = + - 1 they are again then you will get exponential terms like this e to the power i phi e to the power – i phi what we do is we take appropriate linear combination then the other one will be e to the power 2i phi e to the power -2i phi for m = + - 2 we take linear combinations of those two as well.

We do not take linear combination of e to the power i phi and e to the power -2i phi we always take linear combinations of wave functions where m values are same as far as modulus is concerned okay that is how we generate the d orbitals. So, like p orbitals even in those familiar phi d orbitals that we have only one comes directly the other are generated from imaginary orbitals that we get from solution of Schrodinger equation, right? So that is what I wanted to say about 2p orbitals let us move on to 3p orbitals this is a 3pz orbital and understandably we will only talk about z.

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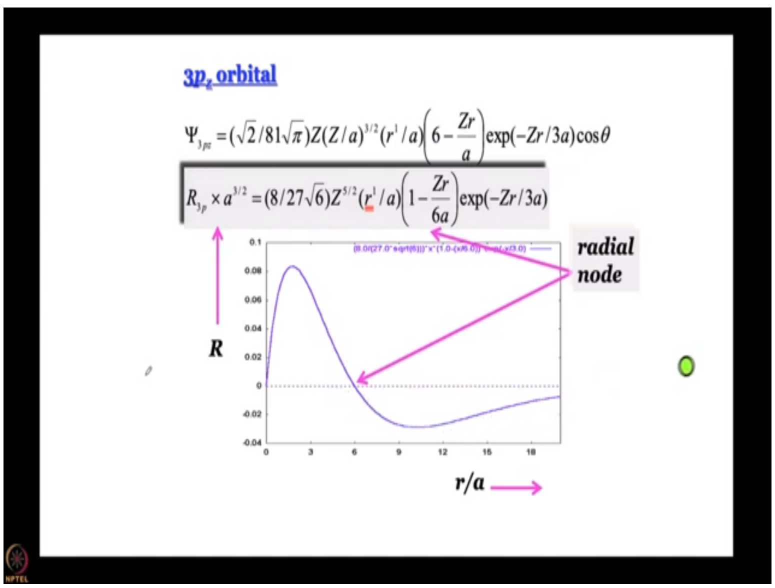


What you have here is constant multiplied by r multiplied by 6- Zr/a so where is the node going to be r = 6a divided by z if you write in terms of a and z =1 it is just going to be 6, e to the power r- Zr/3a no problem with that multiplied by cos theta of course now what happens? see when you create this you get this radial node as we said already. So the function will start from 0 why? Because r is there go through a maximum come down go through the node change sign and then become 0 asymptotically okay. So this is your radial node what is the locus of the radial node sphere of course alright.

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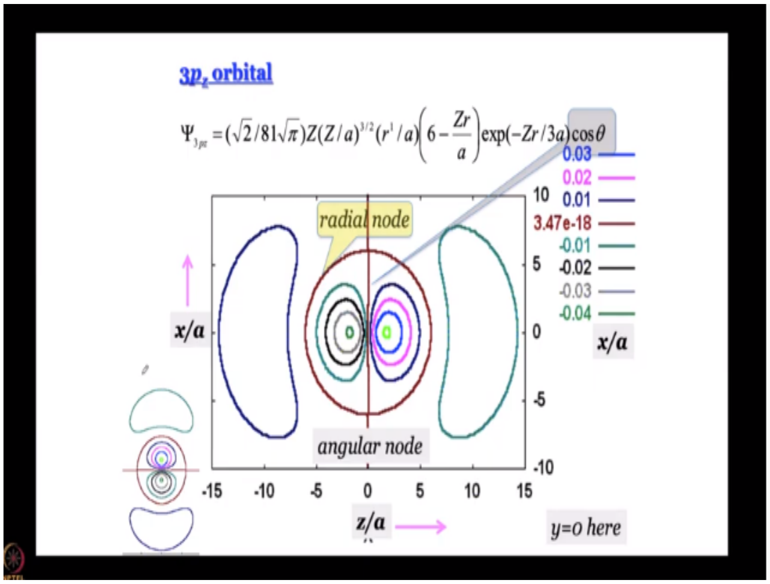


Now without showing you that good-looking picture to start with let us see how we can draw the wave function without actually plotting it completely we actually working on the numbers how we can draw the contour plot. So what we do is first of all draw the radial node then draw the angular node cos theta = 0 that is z = 0 draw the angular node. Now what happens is whenever the wave function process any of these nodes it has to change function it has to change sign is it not.

So let us draw some contours somewhere and we know very well that the contour lines come closer to each other towards one of the nodes and then they are further, apart right? when the contour is in angular node. Let us do something it can be plus can be minus does not matter just draw this so what happens is when you start drawing from here draw the line here it has to turn right because it cannot cross the node without changing sign and here, we want to retain the same value.

So no change in sign so this is what it is now across any of the nodes sign would have changed. Let us say crossing angular node sign changes you get a similar looking lobe but with opposite sign right. Now let us cross the radial node once again sign change will be there, and you get a lobe like this and all on the other side also you get a lobe like this. So every time we cross a node sign change is going to be this what I am saying is that if you are asked to plot an orbital or any function ever figure out the nodes draw the lobe that occurs to you first and then remember that as you cross a node sign has to change that is the same thing.

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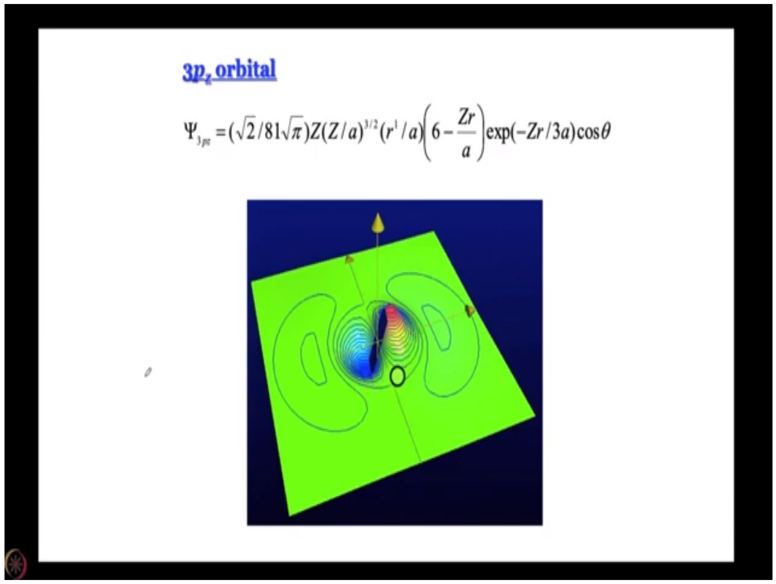


Okay now this is your contour diagram and a different orientation, and this is what we have been waiting to see the 3d plot with contours the point I want to emphasize here is that once again you see the inner lobes of the orbital are so much larger. In fact, it is not very easy to get these contours when you make the plot because they are very shallow okay? This is plus this is minus this is minus this is plus.

Their maximum value is so small that you have to work a little bit to even draw the contours even to get those fellows not so easy but when you incorporate the volume element then these become the major lobes because we start talking about probability right? so this here cos theta is a node.

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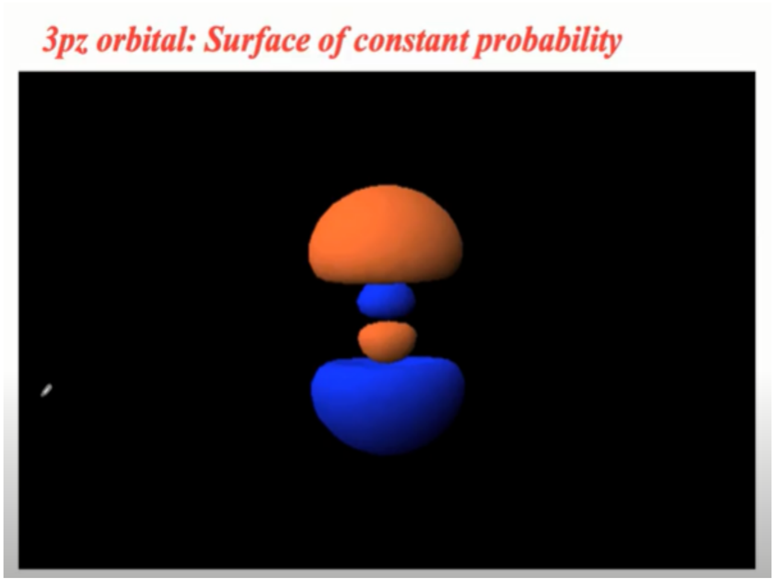


So this is the surface of constant probability for 3pz orbitals and we are showing it please do not forget the science when you do that.

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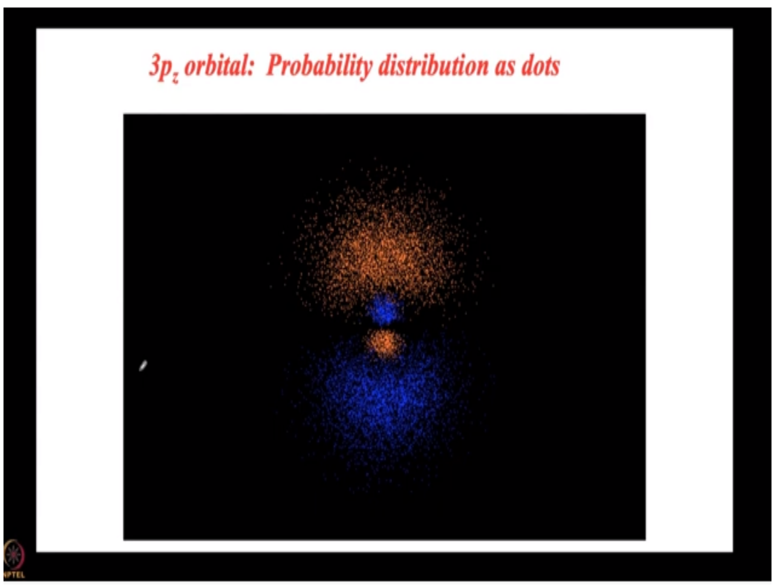


And as usual this is another way of showing it using distribution as dots, right? That is what we wanted to say about p orbitals in the next module well talk about d orbitals.