Quantum Chemistry of Atoms and Molecules

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Lecture – 31
3pz and 3d orbitals

We are almost done with our discussion of orbitals we have seen these beautiful pretty pictures of orbitals that come up when you try to make 3d plots or contour plots of them we have discussed s orbitals, p orbitals this is how far we have got so far. Now let us conclude this part of the discussion by talking about d orbitals okay where does pz orbital get his name from why is it z? Well spdf come from some ancient spectroscopic nomenclature but why is it z? Because it is along z orbital sorry it is along z axis same symmetry as z or another way of thinking is that if we go back.

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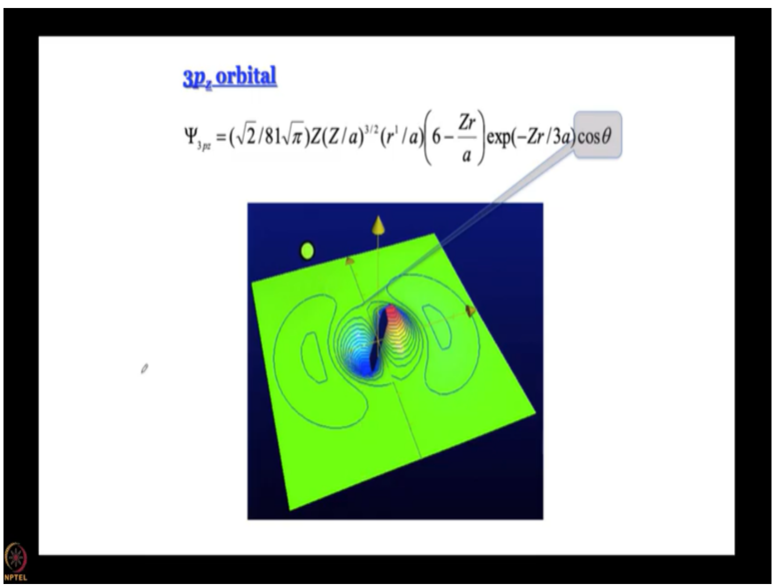

Where is the angular node? The angular node is at cos theta = 0 that is z =0.

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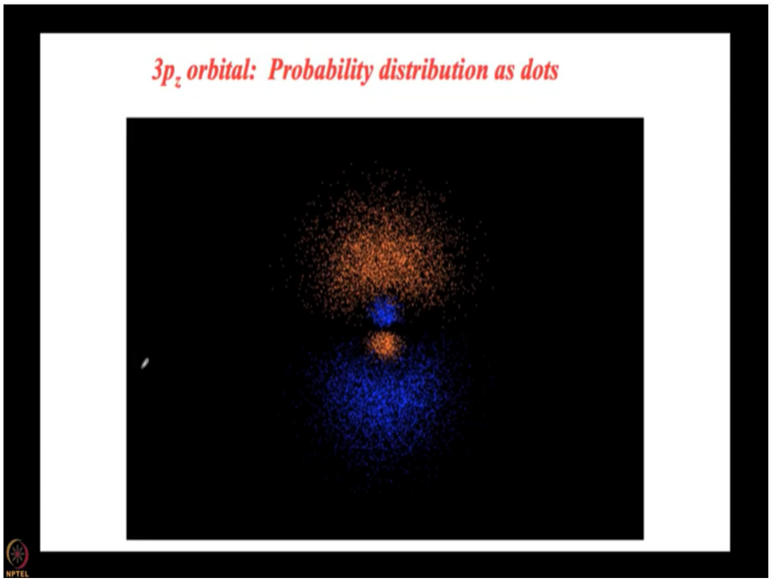

So, the left-hand side of the equation of the node is a subscript that it comes and that is how d orbitals also get their names?

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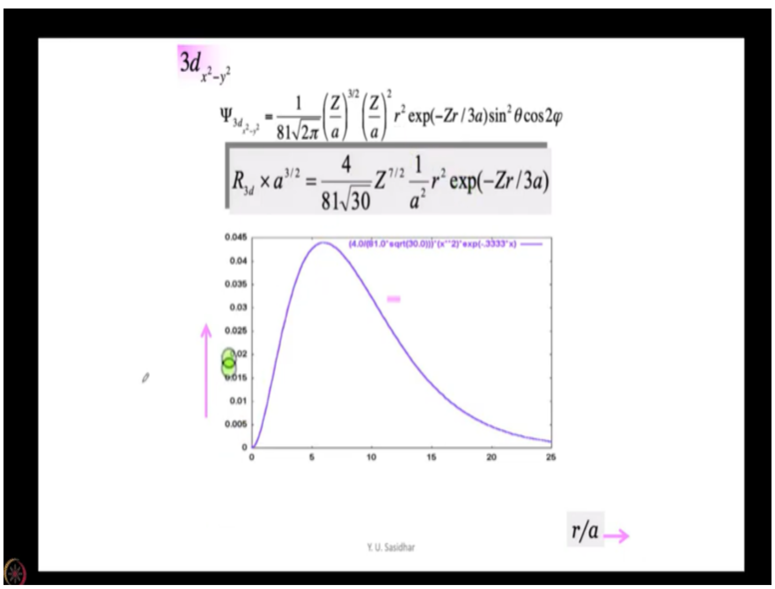

Okay now before talking about d orbitals let me remind you something that we said in the previous module only 1 d orbital comes out to be real when we solve Schrodinger equation in the way that we have discussed and it is not 3d x square – y square orbital it is 3dz square orbital. For 3dz square orbital this m = 0 it is a real orbital these others that were talking about now are actually generated by appropriate linear combination of m = + - orbital and m = + - 2 orbitals.

I leave it to you to figure out which ones are generated by taking linear combination of m = +1 and -1 orbitals which ones are generated from m = + and – 2 orbitals. Okay with that background let us come back and see what a plot of 3dx square – y square would look like this is what we have we have a constant multiplied by r square multiplied by e to the power – Zr/3a multiplied by sin square theta cos 2 phi okay this is the angular part.

Let us worry about the radial part to start with the radial part again goes through a maximum right? When r = 0 it is 0, r = infinity it is m0 and in the middle r square keeps increasing and e to the power – Zr which has a maximum value at r = 0 keeps decreasing it is the product of course would go through a maximum very simple.

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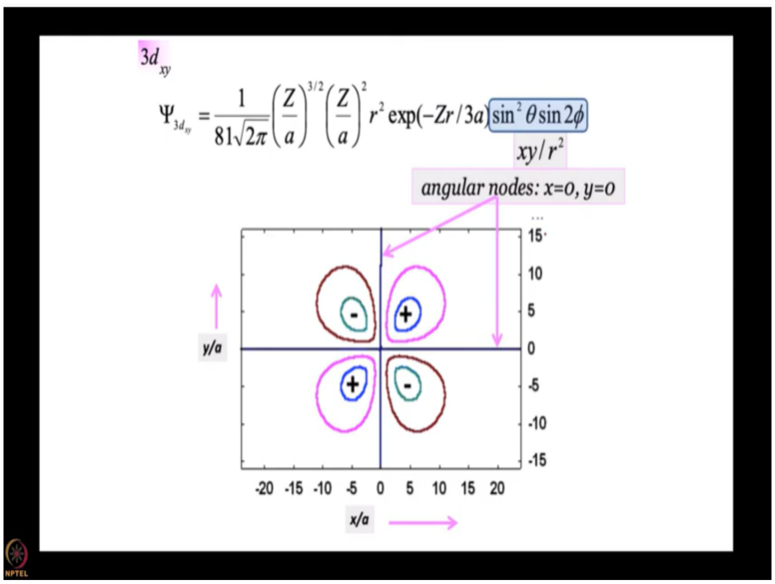

Let us have a look at the angular part of 3d x square- y square that will lead us to this label x square - y square in the first place. So, what we have there is sin square theta multiplied by cos 2 phi t to phi so what is cos 2 phi, cos 2 phi is let me write now cos 2 phi is essentially cos square phi – sin square phi right?

Now this is multiplied by sin square theta so I can write like this sin square theta here and here as well so what do we have here? Do you remember what sin square theta cos phi is r sin theta cos phi is essentially x right? So, sin square theta cos square phi is x square divided by r square is it not minus we have sin square theta sin square phi, sin theta sin phi is y, is it y? Actually, r sin theta sin phi = y.

So, sin theta sin phi = y/r and sin square theta sin square phi = y square/ r square. So, we get y square divided by r square. So, you can take r square common and you get this x square – y square divided by r square so that is what gives the name and then tell me now what is the node? How do I get the angular node? I get the angular node by equating x square minus y square by r square 2 0.

So, what I get essentially is angular node is x = + - y. So, as discussed earlier what we do is we draw the nodes first x = + - y and we draw a lobe across a node wave function changes sin cross the node again it changed the sin once again cross the node once again you see is a change in sin okay? So, this is 3d x square – y square for you. Now we come to 3d xy sin square theta sin 2 phi again using the relationship between sin 2 phi and sin phi cos phi what is sin 2 phi? Sin 2 phi is essentially 2 sin phi cos phi right?

So, sin square theta multiplied by sin phi cos phi becomes sin theta sin phi multiplied by sin theta cos phi okay so you get xy and of course it has to be divided by r multiplied by r so you get xy/ r square. So xy = 0 xy = 0 means x = 0 is a node and y = 0 is a node so once again the moment you cross wherever you cross the node wave function has to change sign okay? So, this is 3d xy.

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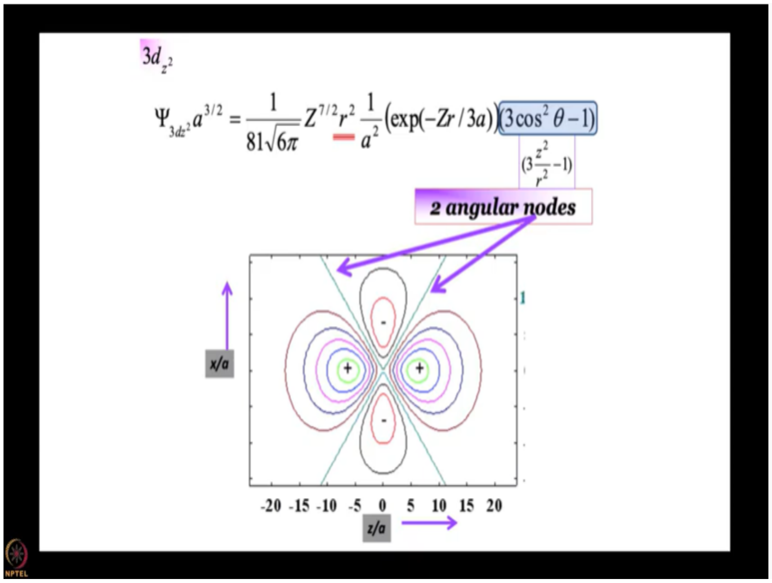

Now we come to 3d z square the most interesting d orbital as far as I am concerned here the angular part is 3 cos square theta - 1 and I believe we have worked out the polar plot of 3 cos square theta – 1 some time ago that I told you that when this is equated to 0 you get magic angle which has applications in many different fields. So, 3 cos square theta -1 what will it be is going to be 3 z square/r square - 1 okay.

So, you get two angular nodes where will the angle nodes be here it is easier for me to think in terms of theta angular nodes will be at theta = 54.7 degrees and 180 – 54.7 degrees we had worked this out earlier. So, these are the two angular nodes remember these are the two angular nodes theta = 54.7 degrees and theta = 54 180 – 54.7 degrees please do not think that this is one angular node straight line.

This is another angular node straight line they are not they are actually two funnel shaped angular nodes and now since theta is 54.7 degrees this angular space available is smaller that is why this slope is larger this slope is smaller and every time you cross a node sign has to change okay so this is 3dz square.

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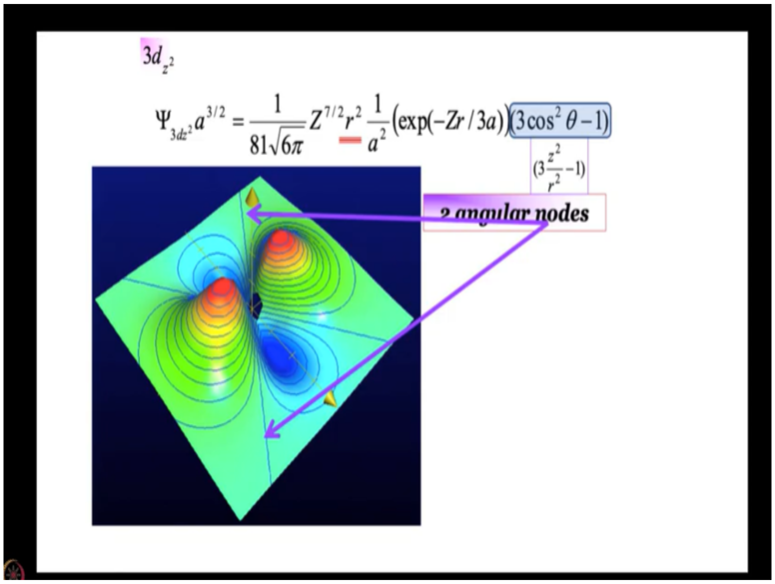

Let me show you the 3d plot along with contours I hope you can relate this with the one that we showed earlier. These are the two nodes once, again right? This is one angular node remember this is z axis so this is theta this way as well as that way this is another value of theta so this is one node this is another node here the way I have drawn it the bigger lobes have plus sign of psi the smaller lobes have minus sign of psi right?

So, this is your 3d z square please have a look at this diagram and look at the good thing here is that the 3d plots have contours shown in them I hope it is not very difficult for you to correlate this with this one and now I think you understand the shape of d orbitals and also why d orbitals are called why d orbitals have got the subscripts that they have got.

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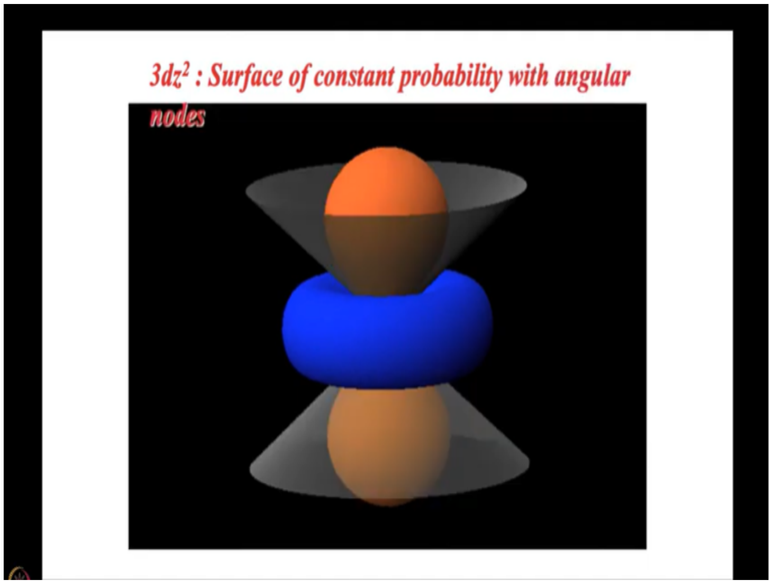

So once again you can work out the surface a constant probability these are the angular nodes shown with the surface.

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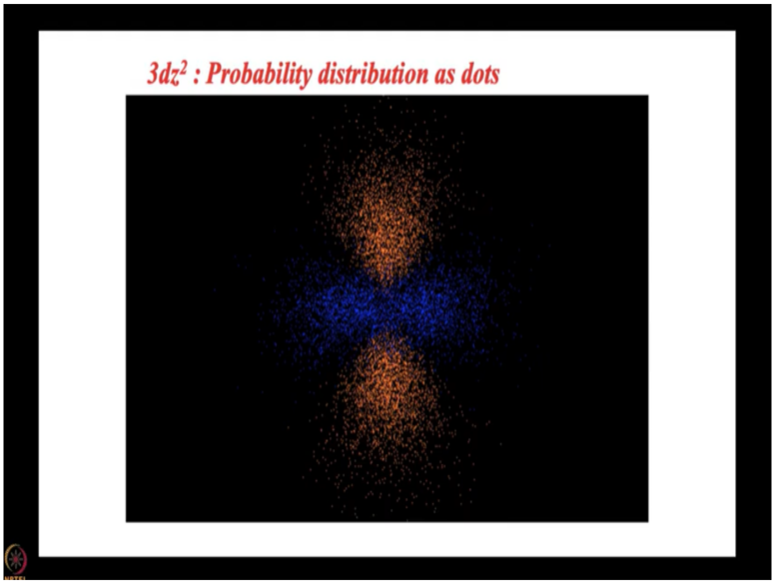

And this is how you can show probability distribution as dots.

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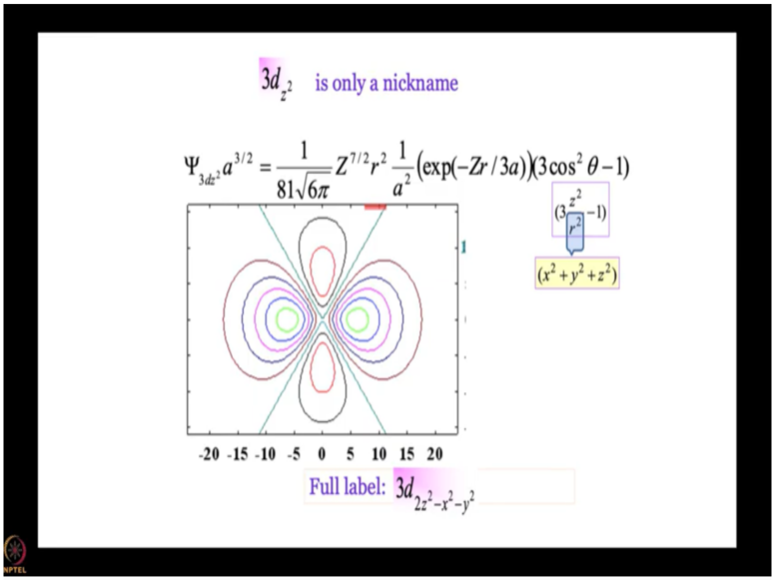

To conclude this discussion let me say that 3d square 3d z square is actually a nickname why? Because the way we had written it here we are not surely converted completely to cartesian coordinates right? So, z square/ r square is there so if we want to complete a convert completely to cartesian coordinates we should remember that r square is x square + y square + z square. So, when you substitute that and equate to 0, we get 2z square - x square - y square = 0.

So, the full label of 3dz square is really 3d 2z square - x square - y square this comes handy when you try to discuss things like d orbitals splitting in an octahedron field or whatever field it is in using symmetry using what are called character tables. So, it is important to understand what these names mean.

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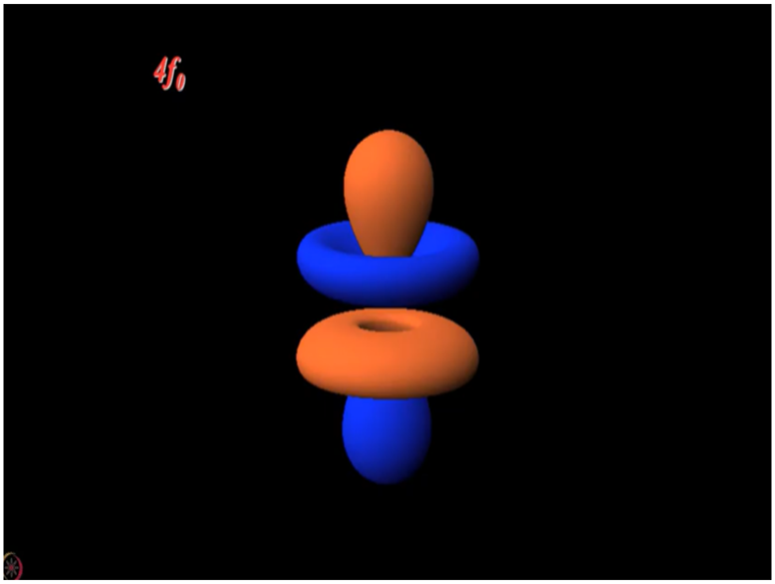

We are not going to discuss f orbitals we will stop at d but let me for the sake of completeness show you some constant probability surface for f orbitals.

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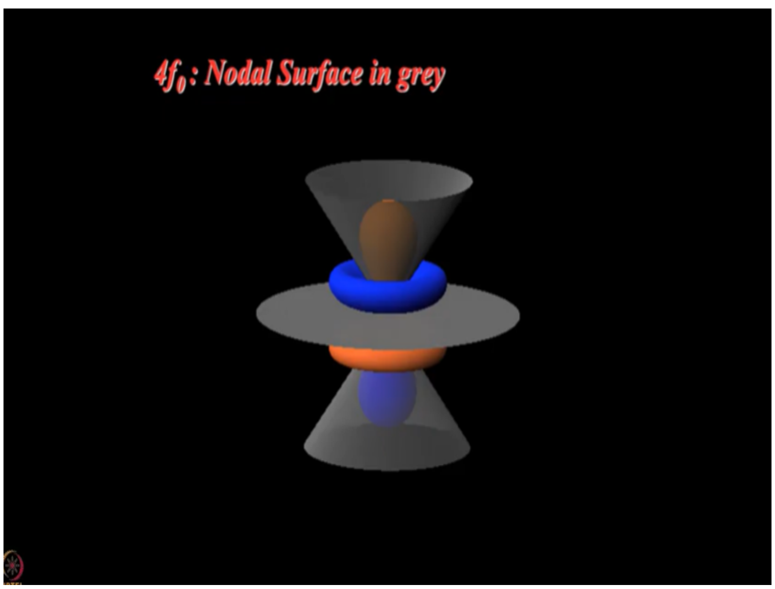

Along with nodal planes as well that brings us to an end of this part of the discussion we have something more to say about orbitals and then we will see how they are used at least as a first approximation in multi electron systems and that is where we can answer that question how is it that we can use 1s, 2s, 2p in say lithium or beryllium or other multi electron atoms even though we have emphasized so much that orbitals are one electron functions.