Concepts of Chemistry for Engineering

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Lecture 12

Radial Distribution Function

Now we are ready to plot some good-looking pictures of hydrogen atom wave functions that is, orbitals. We are used to drawing s orbitals like spheres. But what we will see today is that actually s orbitals look like this. How, let us see.

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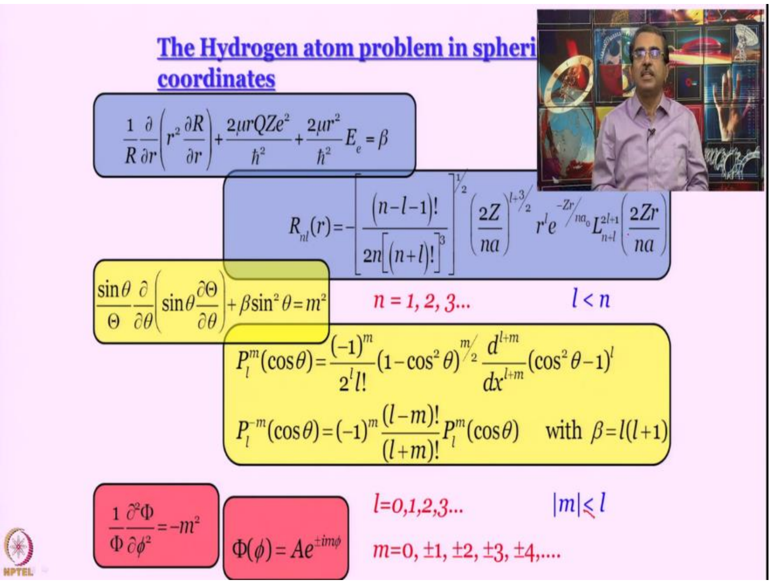

The Hydrogen atom problem in spheri
coordinates

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$R_{nl}(r)=-\left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2}r^l e^{-Zr/na_0}L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$n = 1, 2, 3\ldots$ $\quad l < n$

$$P_l^m(\cos\theta)=\frac{(-1)^m}{2^l l!}(1-\cos^2\theta)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(\cos^2\theta-1)^l$$

$$P_l^{-m}(\cos\theta)=(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta)\quad\text{with } \beta=l(l+1)$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

$$\Phi(\phi)=Ae^{\pm im\phi}$$

$l=0,1,2,3\ldots$ $\quad |m|\leq l$

$m=0, \pm1, \pm2, \pm3, \pm4,\ldots.$

This is what we have done so far, we have written down the hydrogen atom Schrodinger equation in spherical polar coordinates. And we have been able to separate the equation into 3 different parts; the radial equation $\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_c=\beta$; the theta equation $\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\Theta}{\partial\theta}\right)+\beta sin^2\theta=m^2$, and the phi equation $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$. The solution of phi equation gave us A, $\Phi(\phi)=Ae^{\pm im\phi}=\frac{1}{\sqrt{2\pi}}e^{\pm im\phi}$, from where we got the magnetic quantum number $m=0,\pm1,\pm2,\pm3$, so on and so forth.

And from the theta dependent part, we got the secondary quantum number $l=0,1,2,3$, so on and so forth. Also, we have seen why it is that magnitude of m, $|m|\leq l$, we have learned how that comes, that comes from the requirement of Z component of angular momentum never being greater than the total angular momentum.

Now, we have not solved the R and θ dependent parts, but we have told you what the wave functions look like, the θ dependent wave function is essentially a polynomial in $\cos\theta$, $P_l^m(cos\theta) = \frac{(-1)^m}{2^l l!}(1-cos^2\theta)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(cos^2\theta-1)^l$;

$P_l^{-m}(cos\theta) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(cos\theta)$ with $\beta = l(l+1)$, this is called a Legendre polynomial and the R dependent part essentially is a constant $-\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2}$ multiplied by $r^l e^{-Zr/na_o}$, multiplied by a Lagrangian function, $L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$, which is a polynomial.

And when we look at the solutions of radial part, you have not done it in detail, we have just told you the final results, we get the principal quantum number $n = 1, 2, 3$, and so on, so forth. We also get to learn that $l < n$. Now, what is the information about the molecule that we, about the atom that we get from these 3 different parts.

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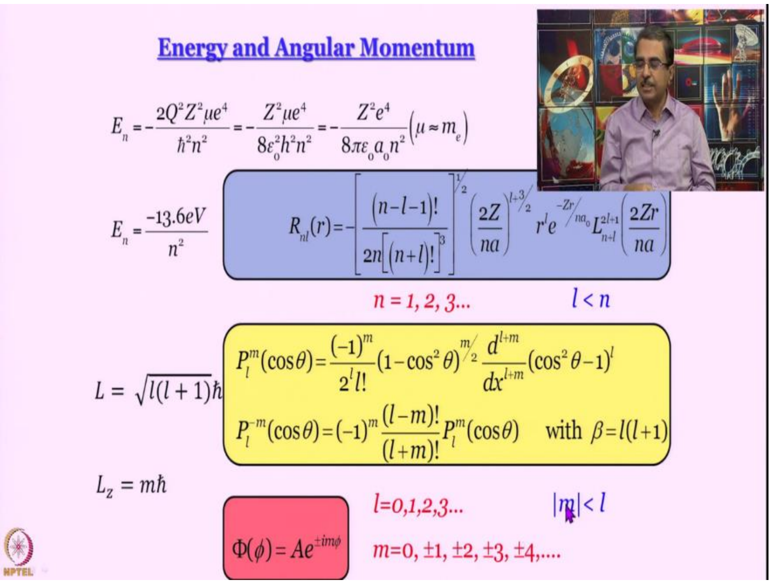

Energy and Angular Momentum

$$E_n = -\frac{2Q^2Z^2\mu e^4}{\hbar^2 n^2} = -\frac{Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{Z^2 e^4}{8\pi\varepsilon_0 a_0 n^2}(\mu \approx m_e)$$

$$E_n = \frac{-13.6eV}{n^2}$$

$$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2} r^l e^{-Zr/na_0} L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$$

$n = 1, 2, 3...$ $l < n$

$$L = \sqrt{l(l+1)}\hbar$$

$$P_l^m(\cos\theta) = \frac{(-1)^m}{2^l l!}(1-\cos^2\theta)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(\cos^2\theta-1)^l$$

$$P_l^{-m}(\cos\theta) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta) \quad \text{with } \beta = l(l+1)$$

$$L_z = m\hbar$$

$$\Phi(\phi) = Ae^{\pm im\phi}$$

$l=0,1,2,3...$ $|m| < l$

$m=0, \pm1, \pm2, \pm3, \pm4,....$

From the radial part we get to know the energy and the expression for energy is the same as what you get from Bohr theory, $E_n = \frac{-13.6\ eV}{n^2}$. From the angular part, the theta part we get to know the total angular momentum $L = \sqrt{l(l+1)}\hbar$, and from the phi dependent part we get the Z component of angular momentum $L_z = m\hbar$ and once again that is why $|m| \leq l$.

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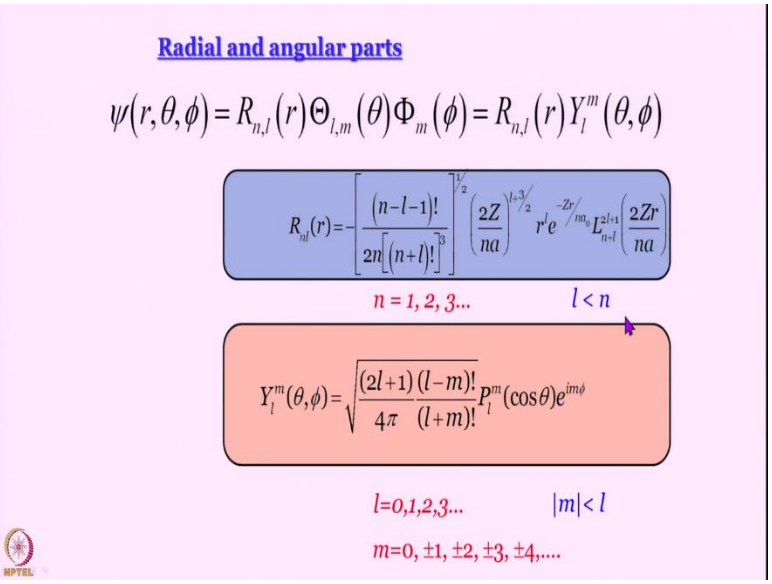

Radial and angular parts

$$\psi(r,\theta,\phi)=R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi)=R_{n,l}(r)Y_l^m(\theta,\phi)$$

$$R_{nl}(r)=-\left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2}r^l e^{-Zr/na_0}L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$$

$n = 1, 2, 3...$ $l < n$

$$Y_l^m(\theta,\phi)=\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}$$

$l=0,1,2,3...$ $|m|< l$

$m=0, \pm1, \pm2, \pm3, \pm4,....$

Now, what we often do is that we take the angular part together and we write this kind of an expression, $Y_l^m(\theta,\phi)=\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(cos\theta)e^{im\phi}$, this is called spherical harmonics. And that turns out to be your, the theta part $cos\theta$ multiplied by the phi part $e^{im\phi}$.

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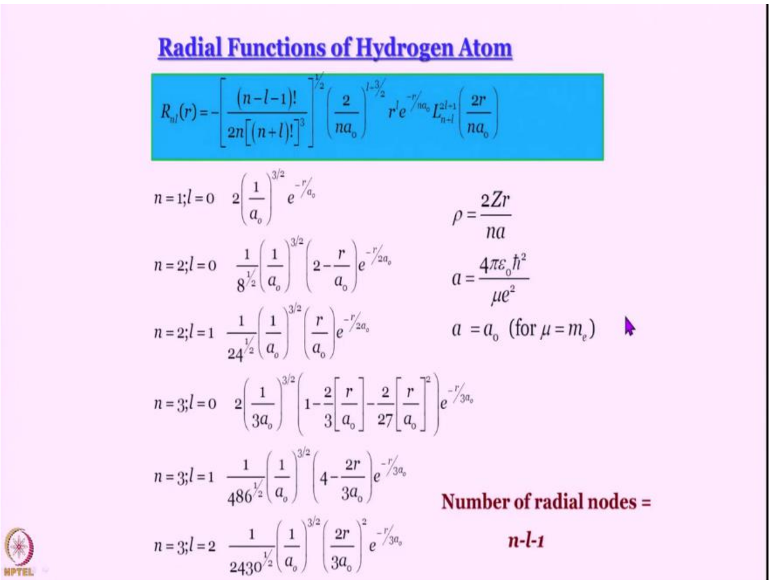

Radial Functions of Hydrogen Atom

$$R_{nl}(r)=-\left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{l-3/2}r^l e^{-r/na_0}L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$n=1;l=0$ $\quad 2\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}$

$n=2;l=0$ $\quad \frac{1}{8^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$

$n=2;l=1$ $\quad \frac{1}{24^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$

$n=3;l=0$ $\quad 2\left(\frac{1}{3a_0}\right)^{3/2}\left(1-\frac{2}{3}\left[\frac{r}{a_0}\right]-\frac{2}{27}\left[\frac{r}{a_0}\right]^2\right)e^{-r/3a_0}$

$n=3;l=1$ $\quad \frac{1}{486^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(4-\frac{2r}{3a_0}\right)e^{-r/3a_0}$

$n=3;l=2$ $\quad \frac{1}{2430^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{2r}{3a_0}\right)^2 e^{-r/3a_0}$

$$\rho=\frac{2Zr}{na}$$

$$a=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$$a=a_0\ (\text{for } \mu=m_e)$$

Number of radial nodes =

n-l-1

So, what we will do is we look at radial and angular parts separately. We have already shown you the radial functions of hydrogen atom and we have reminded you that number of radial nodes is $n-l-1$.

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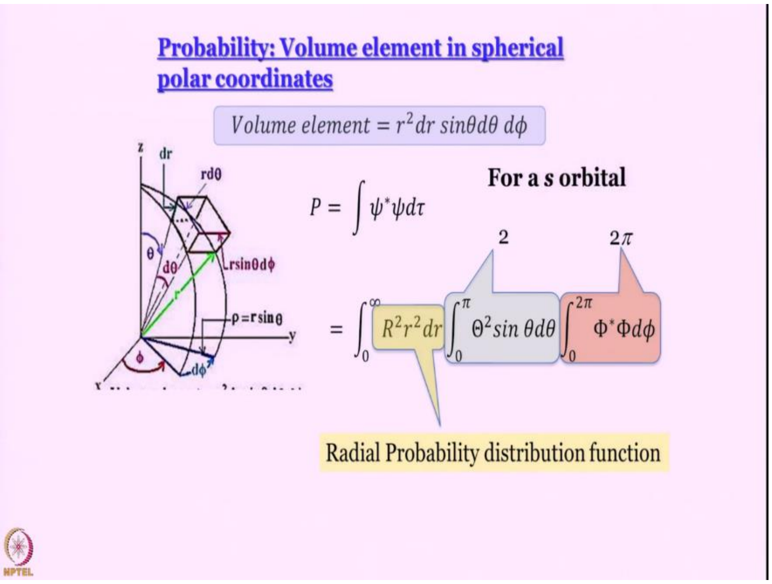

Probability: Volume element in spherical polar coordinates

$\text{Volume element} = r^2 dr \, \sin\theta d\theta \, d\phi$

$$P = \int \psi^* \psi d\tau$$

For a s orbital

2

2π

$$= \int_0^{\infty} R^2 r^2 dr \int_0^{\pi} \Theta^2 \sin\theta d\theta \int_0^{2\pi} \Phi^* \Phi d\phi$$

Radial Probability distribution function

We also remind ourselves that we have to talk about probability and not probability density. So, $R^2 r^2 dr$ essentially is radial probability distribution function, for s orbital this becomes $4\pi r^2 R^2 dr$, it is not very difficult to understand, I hope.

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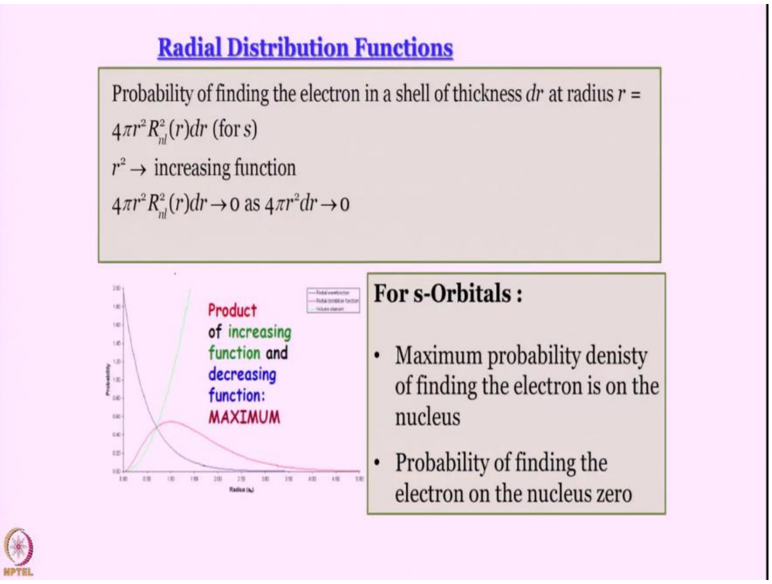

Radial Distribution Functions

Probability of finding the electron in a shell of thickness dr at radius r = $4\pi r^2 R_{nl}^2(r)dr$ (for s)

$r^2 \rightarrow$ increasing function

$4\pi r^2 R_{nl}^2(r)dr \rightarrow 0$ as $4\pi r^2 dr \rightarrow 0$

For s-Orbitals :

- Maximum probability denisty of finding the electron is on the nucleus
- Probability of finding the electron on the nucleus zero

So, taking into account volume element, there is some radius, non zero radius where radial distribution function undergoes a maximum.

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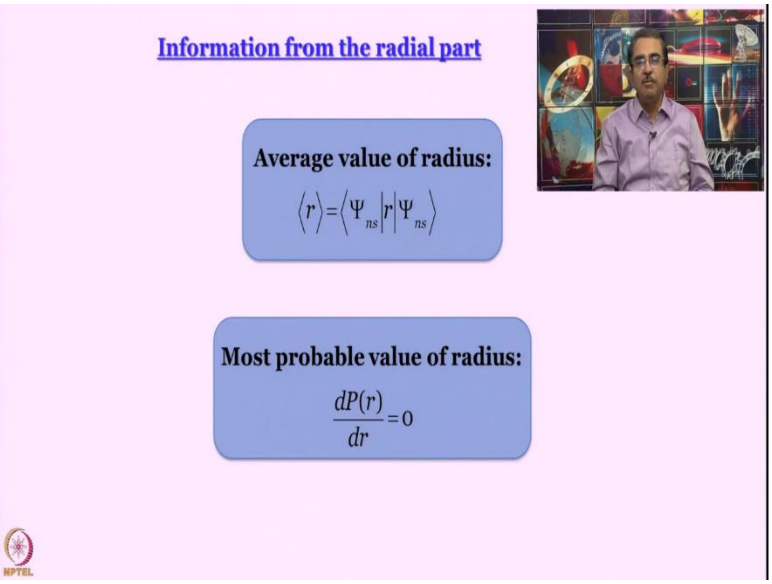

Information from the radial part

Average value of radius:

$$\langle r \rangle = \langle \Psi_{ns} | r | \Psi_{ns} \rangle$$

Most probable value of radius:

$$\frac{dP(r)}{dr} = 0$$

And we have briefly said that you can figure out the most probable value of radius and average value of radius and they are usually not the same.

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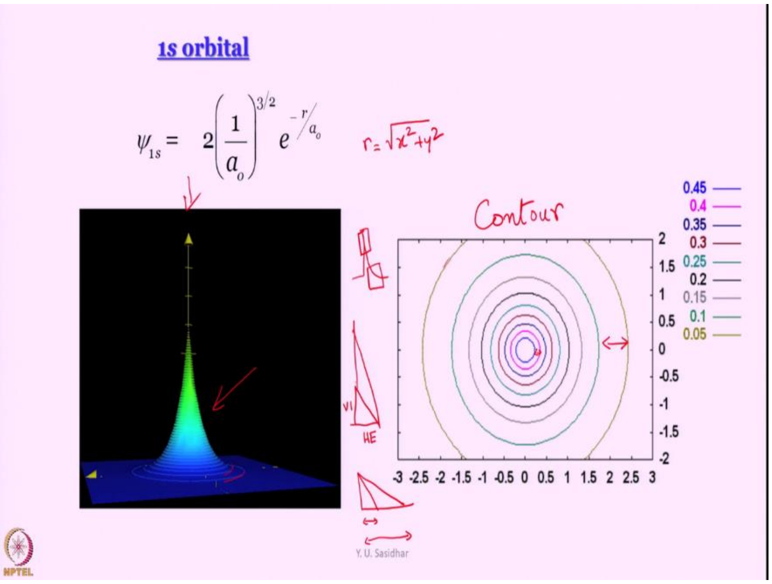

1s orbital

$$\psi_{1s} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$r = \sqrt{x^2+y^2}$

Now, let us try plotting the orbitals in this kind of 3d pictures. In these three dimensions, what is it, y axis is the orbital, the other 2 axes can be x and y, y and z, x and z, whatever we require. So, see, actually this is a four-dimensional picture, psi is the fourth dimension, the spatial dimensions are r, θ, ϕ. or x, y, z whatever you want, but psi is a fourth dimension.

How will I draw 4 dimensional picture, I cannot. So, I can only draw 3 dimensional sections and then we make contour plots of them. So, let us take the simplest case scenario, 1s orbital, where the radial part e^{-r/a_o} is the only part that is there in the wave function, exponential decay as we said.

Now, when I plot it against r, remember if this is x and this is y what is r, $r^2 = x^2 + y^2$. r is essentially equal to $\sqrt{x^2 + y^2}$, just like that. So, for any value of x and y, you have a value of r. So, this exponential decay that we draw, we can keep on changing x and y and what we will generate is this kind of a conical shape.

So, what you see here is sort of a 3-dimensional picture. And you can see these lines here, these lines join all points with the same value of psi, you might remember that we had encountered these when talking about 2D and 3D box. Now, if I look down from the top, what will I see, I will only see these lines. So, this is a projection of these 3-dimensional object in 2-dimensional plane.

So, these lines essentially join the, all the points having same psi. These are called contour diagrams. For 1s orbital of course, the contours are all circular. And one more thing to notice, see here, the spacing between contours is large in the outer part. Towards the center, the spacing between contours is small. Why, because the slope is more initially, it is not a straight line, slope is more initially and gradually it falls off.

What is the meaning of slope, if I draw like this? This I called horizontal equivalent, and here now I am using language that is used in your survey maps. And this is called vertical interval, VI means vertical interval, HE is horizontal equivalent. So, slope is VI divided by HE. What will happen if slope is more, then for same HE, VI will be more, something like this. Or I can draw like this, I will take the same vertical interval, like this.

So, you see when slope is more, then these 2 points are close, when slope is less these 2 points are far apart. So, wherever slope is less contour lines are far apart, wherever slope is more contour lines are close together. This is your 1s 3d picture, as well as contour diagram.

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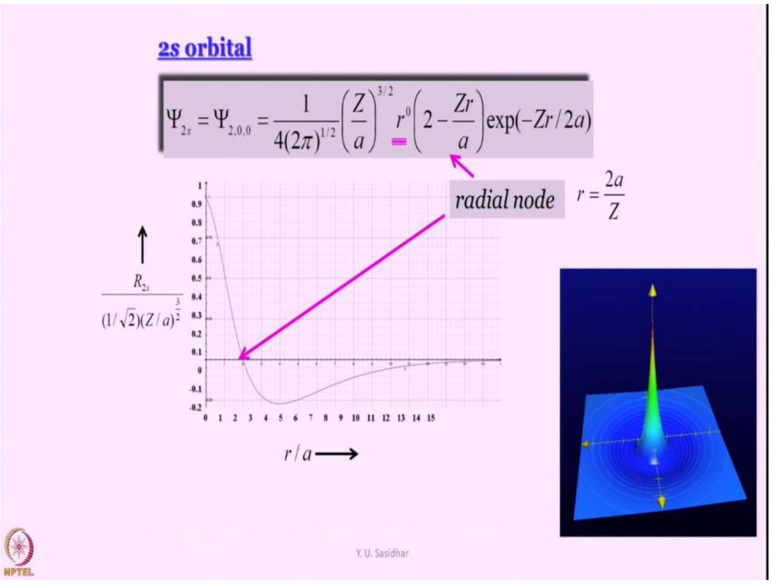
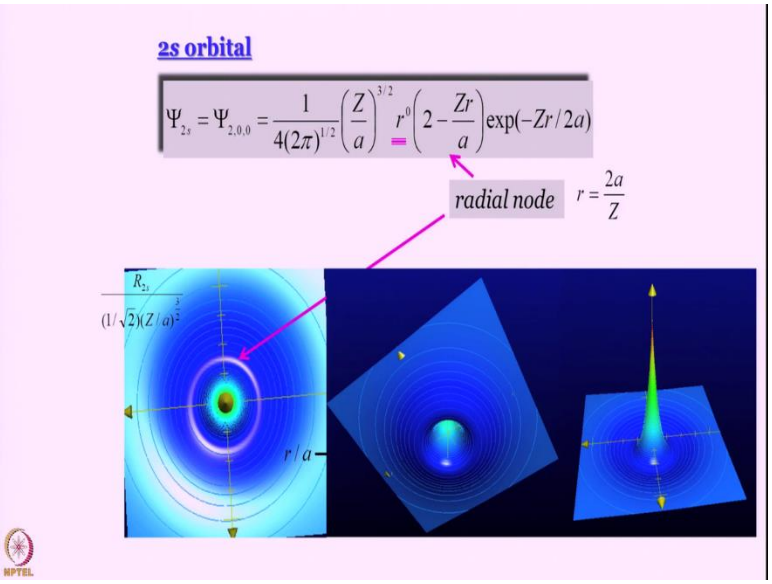


2s orbital

$$\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^0 \left(2-\frac{Zr}{a}\right)\exp(-Zr/2a)$$

radial node $r = \frac{2a}{Z}$

Y. U. Sasidhar



2s orbital

$$\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^0 \left(2-\frac{Zr}{a}\right)\exp(-Zr/2a)$$

radial node $r = \frac{2a}{Z}$

What about 2s? 2s has, $\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^0 \left(2-\frac{Zr}{a}\right) exp(-Zr/2a)$, remember, r^l multiplied by that Lagrange function $\left(2-\frac{Zr}{a}\right) exp(-Zr/2a)$. l here is 0, so r^0 is essentially 1, no problem with that. But the Laguerre polynomial not Lagrange function. Laguerre function is $\left(2-\frac{Zr}{a}\right)$, where a is Bohr radius. Where does the radial node occur then? $r = \frac{2a}{Z}$, that is why the function falls off becomes 0 at $r = \frac{2a}{Z}$ and changes signs. So, this is a nodal point.

Remember, node is a point where a wave function goes to 0 and changes sign, if it does not change sign, then it is not a node. Then again, it increases and becomes 0 asymptotically. This is something that I plotted myself, so do not take this number seriously, these numbers are just relative and I encourage you to plot yourself.

So, this is your 2s orbital. How does it look, if I try to make a similar 3 dimensional picture, all I have to do is I have to turn it around by 360 degrees with respect to the psi axis, this is what I get. Now see, this is the diagram that you get for 2s orbital, initially, very high value, it falls, crosses 0 and becomes negative. Do you see the basin here, this is the negative basin, and then it slowly recovers and becomes 0 at infinite value of small r.

This, these are the contour diagrams I had just taken this and turned it around. I have used Grapher to plot this in a MacBook, so it is very easy to do these things there. You can use whatever graph plotting software that you want. Turn around these are the contours, and once again see these lines are far apart, these lines keep on getting closer and closer and closer. Neglect this arrowhead, this is just an artifact from the program. I will show you another view, this is the top view.

Well, this is a side view, this is the top view, this is the bottom view, if you look from the bottom, you see this hole, where does this hole come from, well wavefunction has started from a certain value, so at r equal to 0 value is very positive. But the minimum value is actually negative, that is what is determined by this rim, this is the contour line where you have negative. And do you see the radial node in the contour diagram, this whitish circle that you see that is your radial node. So, this is how orbitals are usually depicted.

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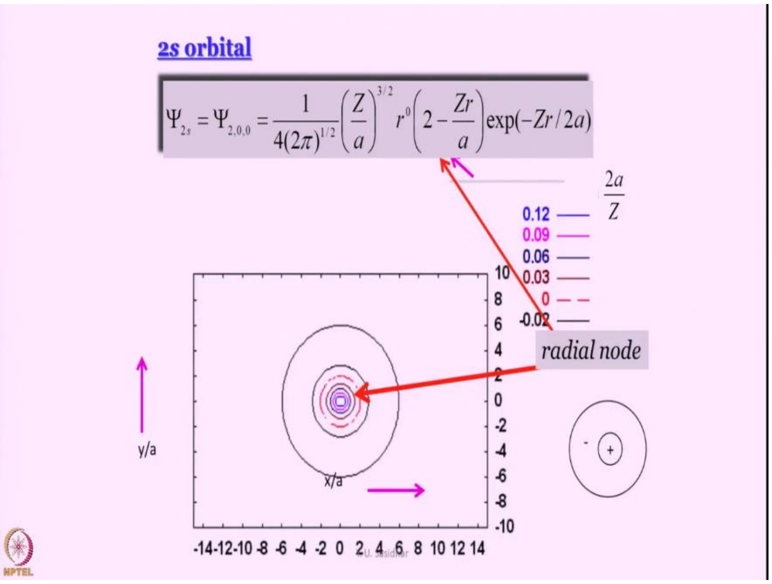

2s orbital

$$\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^{0}\left(2-\frac{Zr}{a}\right)\exp(-Zr/2a)$$

$\frac{2a}{Z}$

radial node

Orbital remember is a 1 electron wave function. And of course, if I asked you to just draw it on plain paper, this is how you can draw it. How do you show sign here, you either write explicitly or use different colors for different signs.

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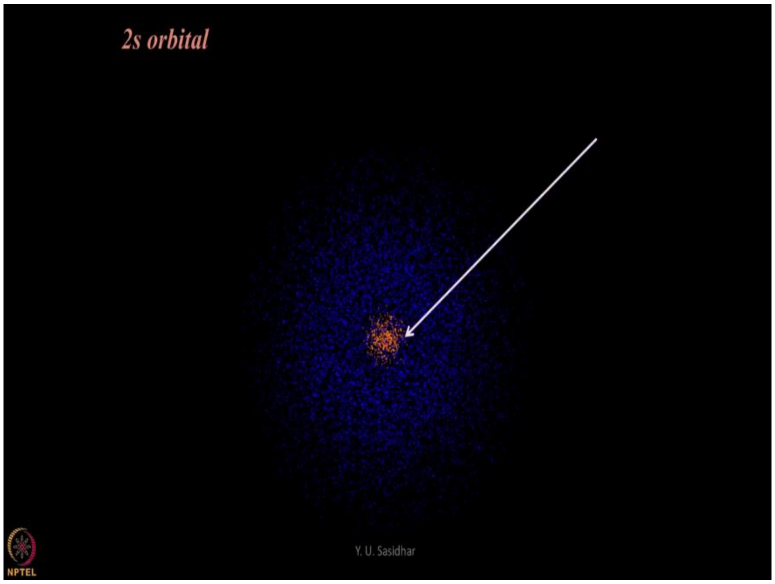

2s orbital

This is another way in which are orbitals are often depicted, lots of dots with different color, color denotes sign, and density of dots denotes probability. So, the way this is done is that, you plot more dots where the probability density is more and when you look at the entire picture, you get the probability distribution.

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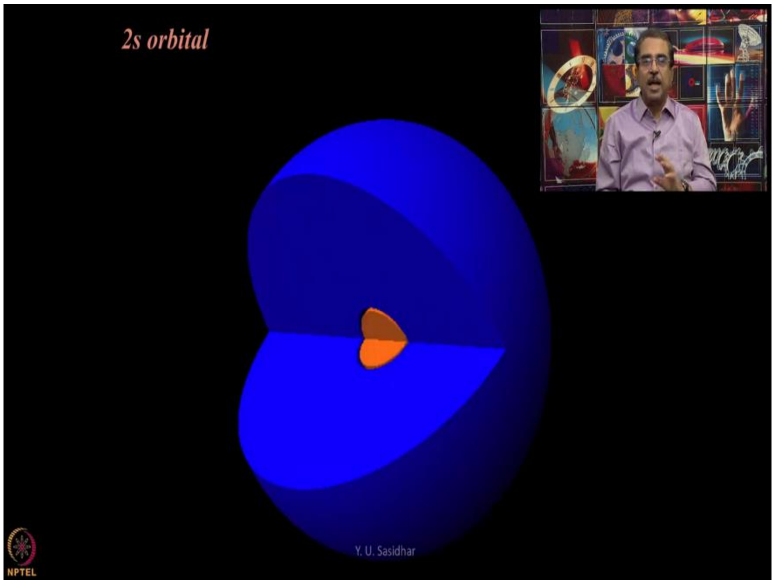

2s orbital

Another way of drawing it this Pac Man kind of figure, I do not know what these diagrams are called. These diagrams are all drawn by my senior colleague Professor. Y. U Sasidhar, you see his name here. So, this is another way of drawing it, you cut a section of the orbital, you can show there is 1 sign outside, 1 sign inside, very nice depictions.

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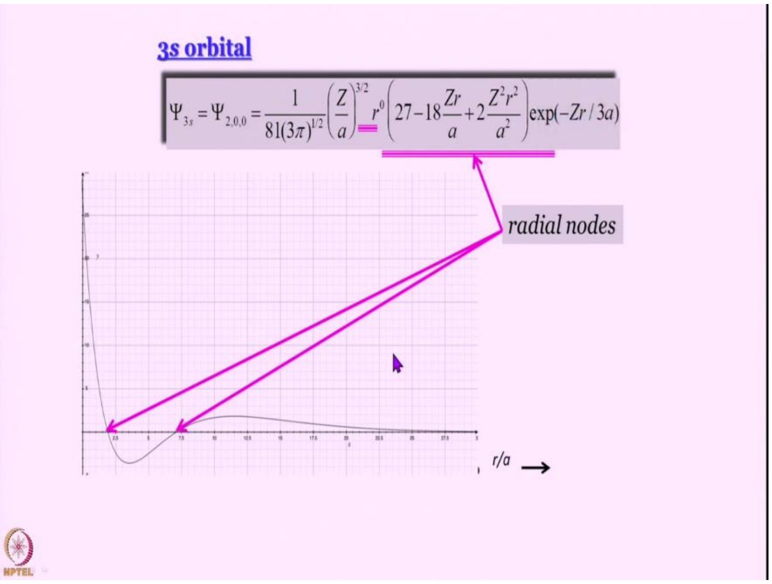

3s orbital

$$\Psi_{3s} = \Psi_{2,0,0} = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \underline{r^{0}} \underline{\left(27-18\frac{Zr}{a}+2\frac{Z^{2}r^{2}}{a^{2}}\right)} \exp(-Zr/3a)$$

For 3s orbital, $\Psi_{3s} = \Psi_{2,0,0} = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^{0}\left(27 - 18\frac{Zr}{a} + 2\frac{Z^2r^2}{a^2}\right) exp(-Zr/3a)$. 3s orbital as we said has a polynomial of second order $\left(27 - 18\frac{Zr}{a} + 2\frac{Z^2r^2}{a^2}\right)$. So naturally 2 roots. So, for 2 values of r, it becomes 0. And remember, these are Laguerre functions and property of Laguerre functions dictates that the roots are both real. Now, 2 nodes.

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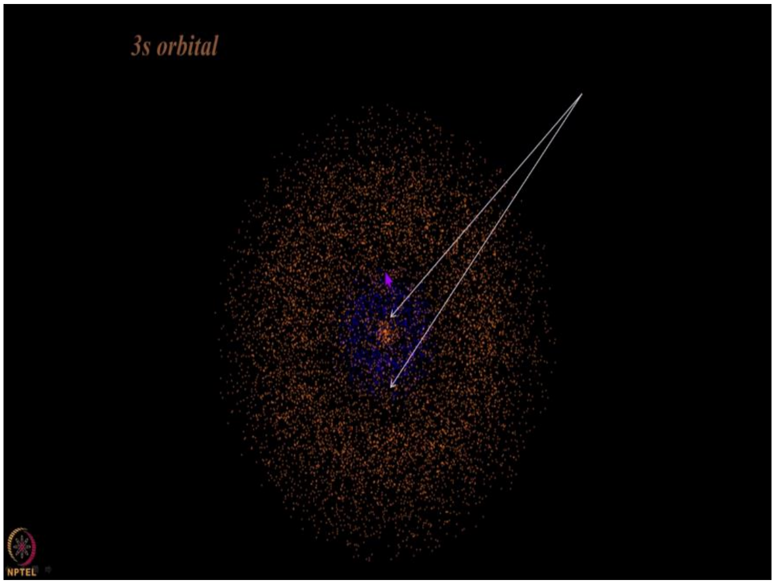
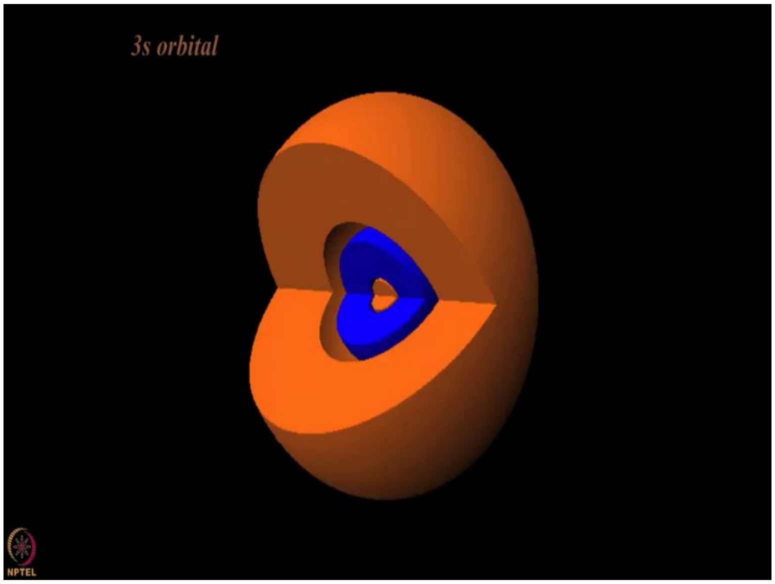


3s orbital



3s orbital

So, what will it look like, I do not have the 3d picture here, but the scatterplot looks like this. You can see there are 3 different regions, you can try to make the 3d plot yourself.

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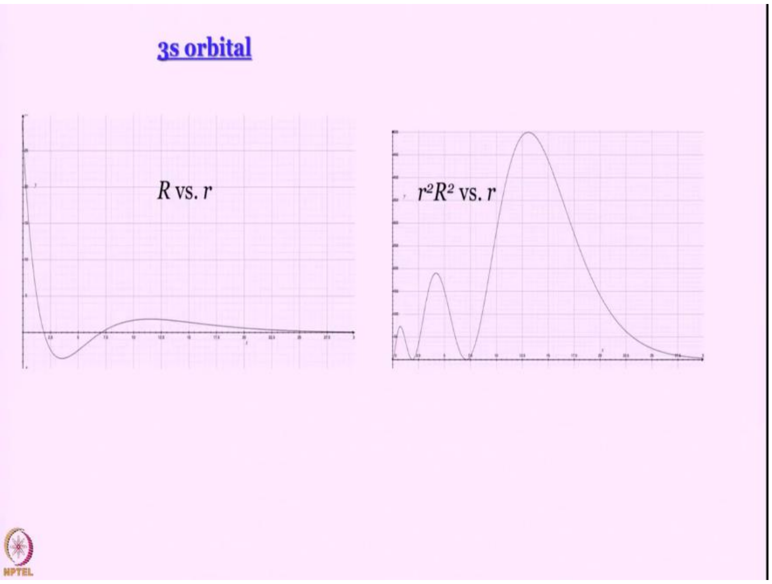

3s orbital

Now, another thing that I want to stress even though we have said earlier, see this here is the 3s orbital that we have plotted, the outermost slope is the smallest, when I multiply by smaller r, r^2 by, r^2R^2 is your probability density actually you have to multiply it by 4π.

Now, see what has happened, since you have multiplied by r square, the outermost slope, which was the smallest has actually become the largest. So, where is the probability of finding 3s orbital, 3s electron more outside in this major loop. So, these are probability distribution function plots.

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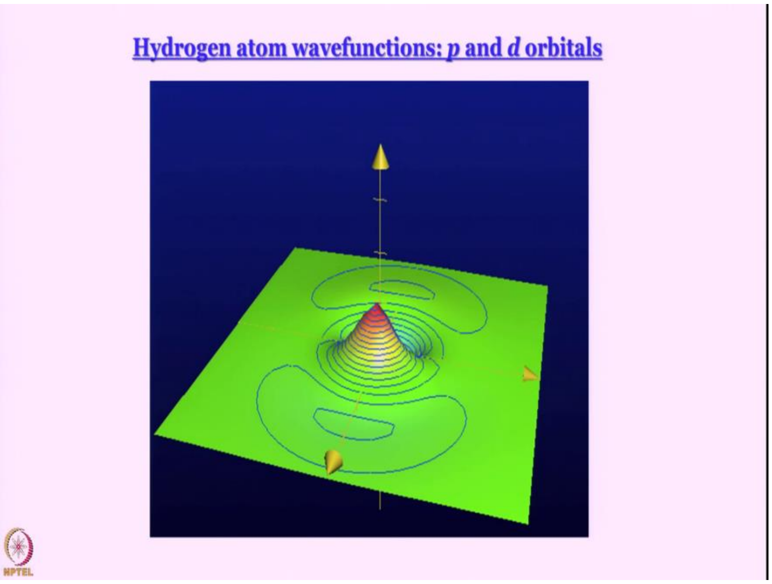

Hydrogen atom wavefunctions: *p* and *d* orbitals

Now, let us talk about p orbitals and d orbitals. So, this diagram that you see is actually of 3p orbital as we are going to arrive at slowly.

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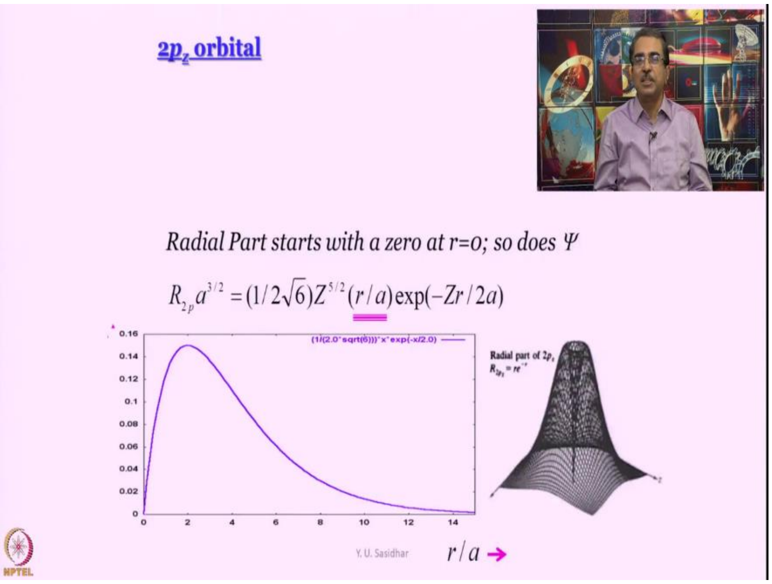

$2p_z$ orbital

Radial Part starts with a zero at r=0; so does Ψ

$R_{2p}a^{3/2} = (1/2\sqrt{6})Z^{5/2}\underline{(r/a)}\exp(-Zr/2a)$

But first let us talk about 2p orbitals. We will start with the simplest one $2p_z$ orbital. $R_{2p}a^{3/2} = (1/2\sqrt{6})Z^{5/2}(r/a)\,exp(-Zr/2a)$. Here, $(r/a)\,exp(-Zr/2a)$ is the radial part. See now, this time we have $(r/a)\,exp(-Zr/2a)$. r is an increasing function, $exp(-Zr/2a)$ is a decreasing function, multiply them together you get a maximum. And where does this maximum occur you can differentiate equal to 0, equate to 0, you can find out where the maximum, radial, maximum of the radial part of the wave function occurs.

Remember, the position of maximum of the radial part of the wave function will not be the same as the position of the maximum of r^2R^2. I encourage you to work out both and see for yourself whether it is same or whether they are different. This is the radial part, what about the angular part? $\Psi_{2p_z} = \Psi_{2,1,0} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r^1 exp(-Zr/2a)cos\theta$. The angular part has $cos\theta$. Now, $cos\theta = z/r$.

So, instead of cos theta I can just write z/r. So, r, this r^1 and that r will cancel, and we will be left with $exp(-Zr/2a)$ multiplied by Z. Interesting, that is why it is called a $2p_z$ orbital.

So now see, if I, I know how to get radial notes already, equate the radial part to 0. If I equate the angular part to 0, cos theta equal to 0, what is that, cos theta equal to 0 is Z equal to 0 that is the xy plane. So, xy plane turns out to be an angular node of the $2p_z$ orbital.

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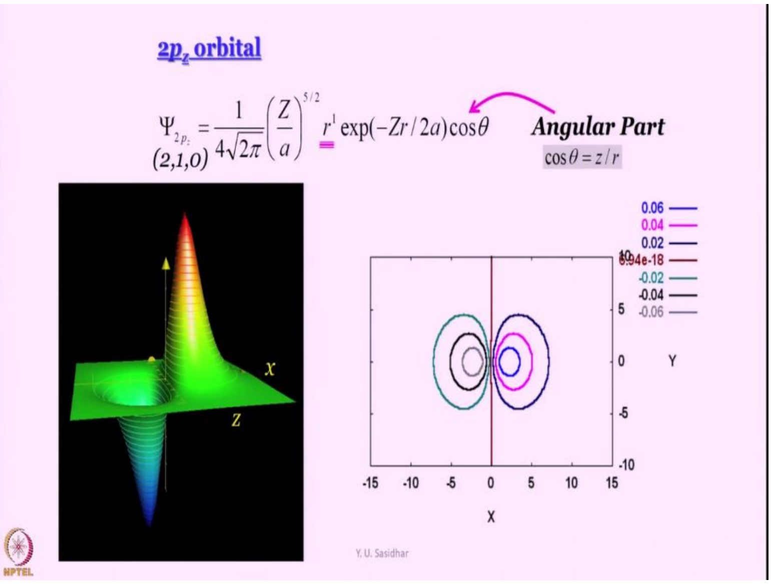

$2p_z$ orbital

$$\underset{(2,1,0)}{\Psi_{2p_z}} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} \underline{\underline{r^1}} \exp(-Zr/2a)\cos\theta$$

Angular Part

$\cos\theta = z/r$

Y. U. Sasidhar

So, that is why that 3d picture turns out to be like this. You start from 0, you get a positive going function, which then again decays to 0, negative going function that again decays to 0, but why is it positive, why is it negative, because see this y z plain must be, z x, what am I saying, x y plane must be a node. I am showing you the x z plane here. So, in this projection, remember here, the third axis is wave function.

So, if third axis is function, where are you going to get this node, here it will be z equal to 0, this line. So, this is the meaning. So, these are the 2 lobes. Now, if you look down from the top what will you see, the contour diagram will look like this.

Remember the 2 lobes of p orbital, these are your 2 lobes of 2p orbital. When we go to 3p orbital we will see the situation becomes even more interesting. So, this is what it is. 1 plus lobe, 1 minus lobe, what is plus, what is minus, electrons do not become positively charged when they go to the plus lobe, sign of the wavefunction is positive, sign of the wavefunction is negative in the negative lobe.

So, plus and minus on the lobes denote the sign of the wavefunction and these lobes arise out of angular part. They have different signs because the angular plane, the angular node is essentially the y, x y plane. The angular node essentially is x y plane.

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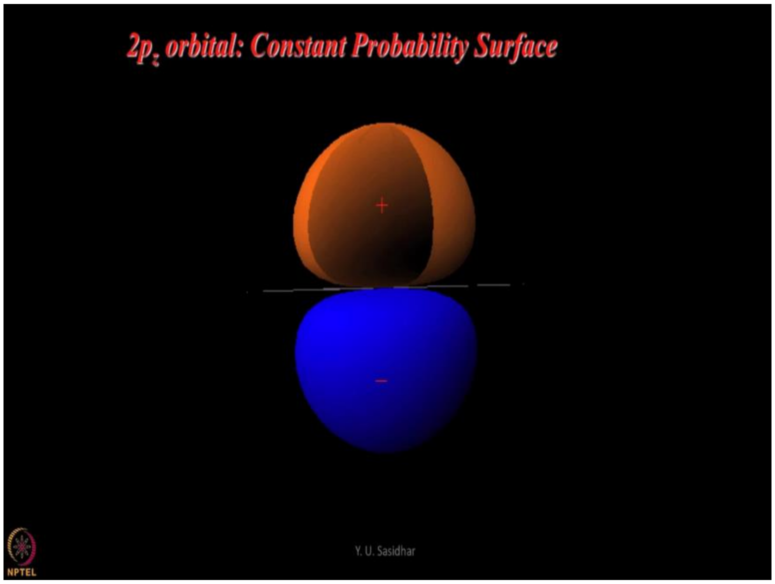

$2p_z$ orbital: Constant Probability Surface

Y. U. Sasidhar

And these are the constant probability surface. How do you plot them? You decide what psi psi star you want. Join all the points having that same psi psi star. Now, this is 3d space. You join all the, so for some x y z value, I know that psi psi star is 0.002 let us say, I joined all those points and then I get this kind of shape. Now, I know where psi is plus, where psi is minus, so I can use different color or write plus or minus. Then, what I do is I work out the volume inside this, the volume inside that will be probability of finding the electron within that constant probability surface.

Then, that is how you generate these pictures of probability distribution. And generally, people confuse that with orbitals, but hopefully after today, we will never confuse we will remember that orbitals are wave function and these shapes of probability distribution are generated using the functional forms of the orbitals, but not neglecting the spherical, (())(15:55) the volume element as well.

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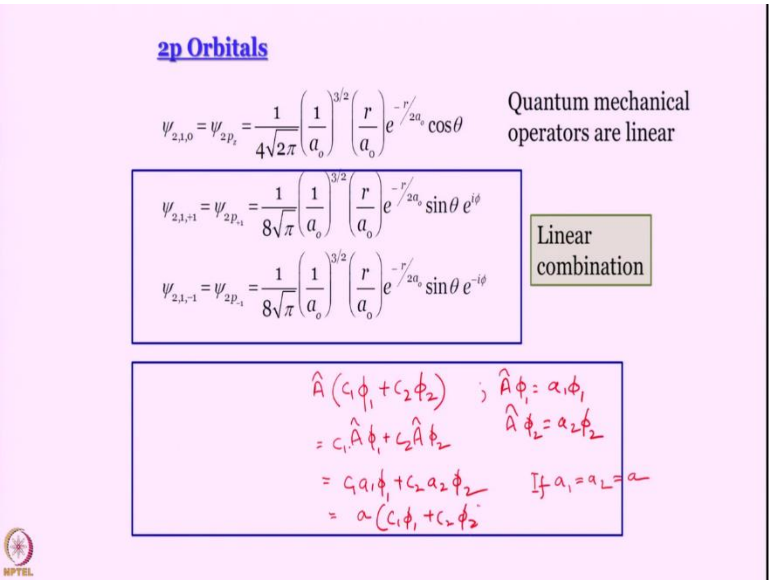


2p Orbitals

$$\psi_{2,1,0} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\cos\theta$$

Quantum mechanical operators are linear

$$\psi_{2,1,+1} = \psi_{2p_{+1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\, e^{i\phi}$$

$$\psi_{2,1,-1} = \psi_{2p_{-1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\, e^{-i\phi}$$

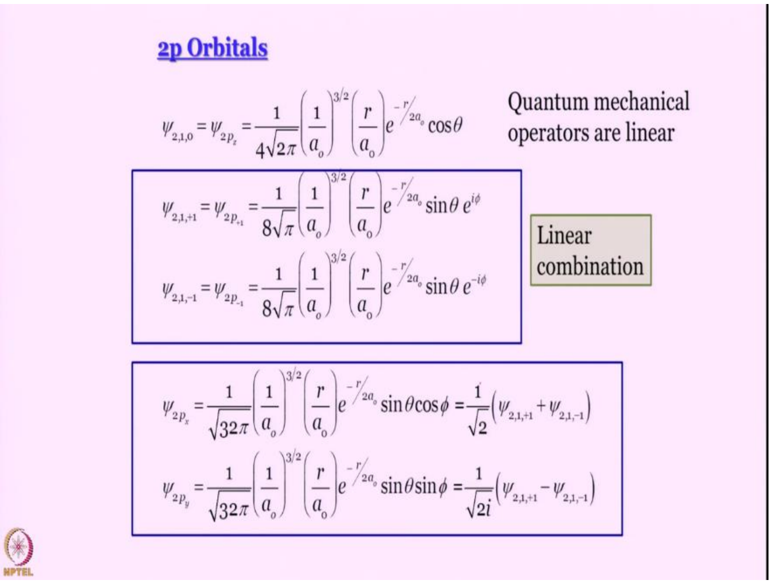
Linear combination

$$\hat{A}(c_1\phi_1 + c_2\phi_2) \quad ; \quad \hat{A}\phi_1 = a_1\phi_1$$

$$= c_1\hat{A}\phi_1 + c_2\hat{A}\phi_2 \qquad \hat{A}\phi_2 = a_2\phi_2$$

$$= c_1 a_1\phi_1 + c_2 a_2\phi_2 \qquad \text{If } a_1 = a_2 = a$$

$$= a(c_1\phi_1 + c_2\phi_2$$



2p Orbitals

$$\psi_{2,1,0} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\cos\theta$$

Quantum mechanical operators are linear

$$\psi_{2,1,+1} = \psi_{2p_{+1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\, e^{i\phi}$$

$$\psi_{2,1,-1} = \psi_{2p_{-1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\, e^{-i\phi}$$

Linear combination

$$\psi_{2p_x} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\cos\phi = \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right)$$

$$\psi_{2p_y} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\sin\phi = \frac{1}{\sqrt{2i}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right)$$

Now, now we come to an interesting situation. $2p_z$ is something we could plot very easily. What about this $m = +1$ and $m = -1$? See here, $\psi_{2,1,0} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\, cos\theta$,

phi part was 1, because m equal to 0, phi part is 1. So, it is a real orbital. However, for $m = +1$, $\psi_{2,1,+1} = \psi_{2p_{+1}} = \frac{1}{8\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\, sin\theta\, e^{i\phi}$ and $m = -1$, $\psi_{2,1,-1} = \psi_{2p_{-1}} = \frac{1}{8\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\, sin\theta\, e^{-i\phi}$ we have orbitals that are imaginary, and we cannot draw them in real space, you can actually do whatever you want to do with them, but you cannot plot them. And in chemistry, we like to plot things; it is easier to understand.

So, what we do is we remember a theorem. What is a theorem, that, we remember a theorem that the quantum mechanical operators are linear. So, if quantum mechanical operators are linear, then if I take a linear combination of wave functions, then what happens? I have poor memories I do not remember whether I work this out earlier. In any case, we will do it once. But I will write and I will delete also. So, see take some any operator $\hat{A}$, let us say it operates on $c_1\phi_1 + c_2\phi_2$, where ϕ_1 and ϕ_2 are wave functions, c_1, c_2 are coefficients.

And let us say, also I think we did it, $\hat{A}\phi_1 = a_1\phi_1$ and $\hat{A}\phi_2 = a_2\phi_2$. So now, what is this, since the linear operator $\hat{A}(c_1\phi_1 + c_2\phi_2)$, I can write it as $c_1\hat{A}\phi_1 + c_2\hat{A}\phi_2$. What is $\hat{A}\phi_1$ we know, what is $\hat{A}\phi_2$ we know as well. So, I will write $c_1a_1\phi_1 + c_2a_2\phi_2$. Is this an eigenvalue equation, in the general case no. In a special case, where a_1 is equal to a_2 that is same eigenvalues, let us say both are equal to a, then I can take it out. I can write $a(c_1\phi_1 + c_2\phi_2)$.

Now, see, look at this I will call them p plus p minus orbital. They are eigen functions of Hamiltonian operator and they are eigen functions with the same eigenvalue. Remember, energy depends only on n, only on the radial part. So, there is no problem I can take linear combination and whatever linear combination I take will have the same energy as these orbitals. So, I take two linear combinations. First, I add them, $\frac{1}{\sqrt{2}}(\psi_{2,1,+1} + \psi_{2,1,-1})$. What happens when I add $e^{i\phi}$ and $e^{-i\phi}$, remember $e^{i\phi}$ is $cos\phi + isin\phi$ and $e^{-i\phi}$ is $cos\phi - isin\phi$. So, when we add that this is what happens, $\frac{1}{\sqrt{2}}(\psi_{2,1,+1} + \psi_{2,1,-1}) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\,sin\theta cos\phi$. You are left with $cos\phi$, the $isin\phi$ terms cancel each other. So, I got $sin\theta cos\phi$. What happens, what is that, that is actually $\psi_{2p_x,}$ why, because remember $rsin\theta cos\phi$ is x. So, this $2p_x$ orbital now behaves like your z orbital. The only difference is, for $2p_x$ orbital, the angular node is the yz plane. Nice.

What, what happens if you take a minus combination, $\frac{1}{i\sqrt{2}}(\psi_{2,1,+1} - \psi_{2,1,-1})$, the only difference here is that now the cos phi terms will vanish, and sin phi terms will be there. They have i in their coefficient, so you have to divide by i also, this is root 2 multiplied by i, this is not root over i, please do not this is not very clear. $i\sqrt{2}$, that is what it is. So, then I get $sin\theta sin\phi,\ rsin\theta sin\phi$is y remember, so this is your familiar ψ_{2p_y} orbitals.

So, remember that for $2p_x$ and $2p_y$, for p_x and p_y orbitals, m values are not defined, we generate them by taking linear combinations of $m = +1$ and $m = -1$ orbitals. So, if m value is not defined, what is not defined is the z component of angular momentum. So, remember the particle in a box wave function, it was a linear sum of a wave function that denoted the linear motion in plus x direction and another one that denoted linear motion in minus x direction, it is sort of like that.

$+m\hbar$ and $-n\hbar$ they are combined. So, z component of angular momentum is indeterminate. If you perform a measurement then you will see either $z = +1$ or $z = -1$. But p_x and p_y orbitals, they are not eigen functions of the L_z operator, they are eigen functions of your energy, Hamiltonian operator and also angular momentum operator, L^2.

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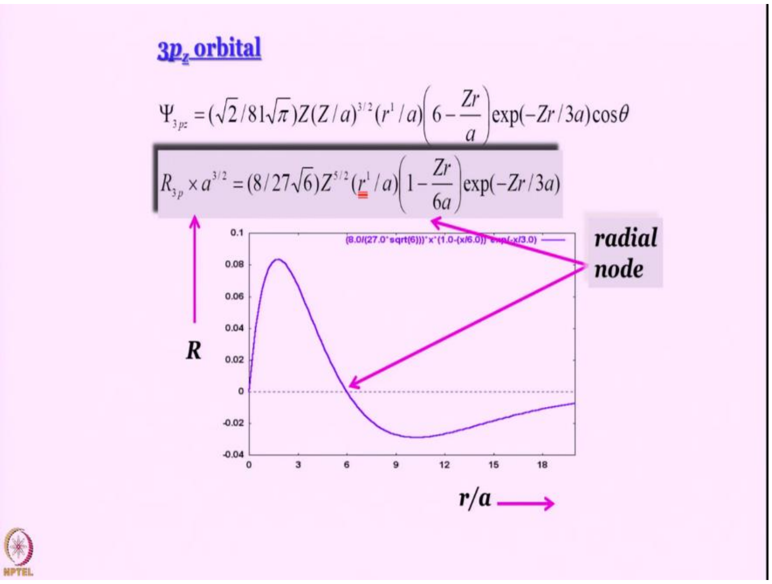

3p_z orbital

$$\Psi_{3pz} = (\sqrt{2}/81\sqrt{\pi})Z(Z/a)^{3/2}(r^1/a)\left(6-\frac{Zr}{a}\right)\exp(-Zr/3a)\cos\theta$$

$$R_{3p} \times a^{3/2} = (8/27\sqrt{6})Z^{5/2}(r^1/a)\left(1-\frac{Zr}{6a}\right)\exp(-Zr/3a)$$

Let us quickly talk about 3p$_z$. $\Psi_{3p_z} = (\sqrt{2}/81\sqrt{\pi})\mathrm{Z}(Z/a)^{3/2}(r^1/a)\left(6-\frac{Zr}{a}\right)\ exp(-Zr/3a)cos\theta$

In 3p$_z$, the complicating factor is a radial node, you have $\left(6-\frac{Zr}{a}\right)$ in the radial part. So, what happens if I equate that to 0, that gives me

R_{3p} x $a^{3/2} = \ (8/27\sqrt{6})Z^{5/2}(r^1/a)\left(1-\frac{Zr}{6a}\right)\ exp(-Zr/3a)$, a radial node that was not there for 2p orbitals.

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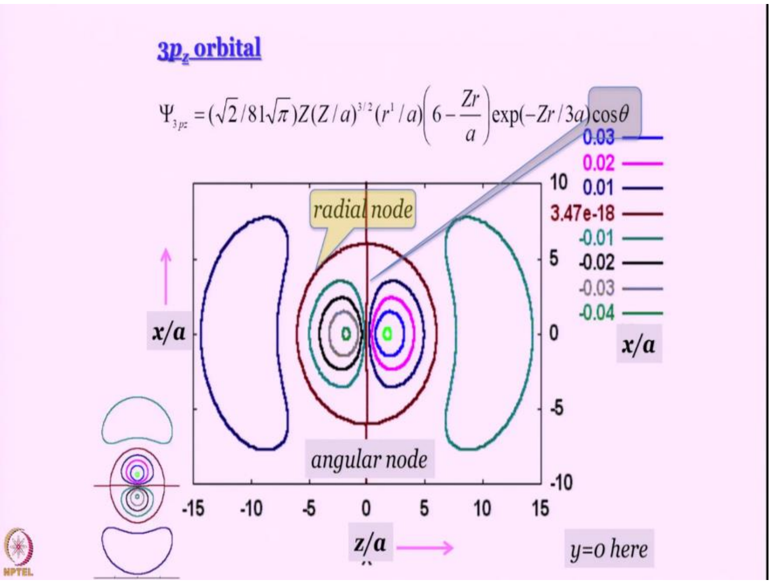

3p$_z$ orbital

$$\Psi_{3pz} = (\sqrt{2}/81\sqrt{\pi})Z(Z/a)^{3/2}(r^1/a)\left(6-\frac{Zr}{a}\right)\exp(-Zr/3a)\cos\theta$$

radial node

angular node

y=0 here

So now, I will just show you how to draw an orbital. If I give you the function, the first thing to do is to draw the nodes, this radial node is going to be a circle in this section and angular node is going to be a line. Now, what I do is I draw any one of the lobes and you call it either plus or minus does not matter. What it means is that if you cross the node, you cross this node, sign will change. So, if this is plus, you will get minus, if you cross this node then also sign will change. So, if this is plus it will become minus.

And once again the same thing will happen when you cross this node. So, if this was plus now this is minus, this is going to be plus and this is going to be minus. So, this is the contour diagram of 3p$_z$ orbital. Remember contour diagram of 2p$_z$ and 3p$_z$ orbitals have this difference because of the radial node.

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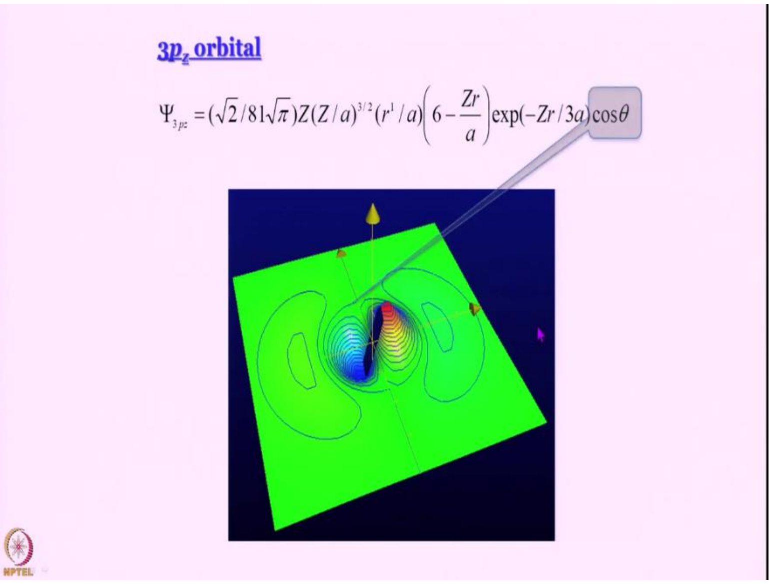

$3p_z$ orbital

$$\Psi_{3pz} = (\sqrt{2}/81\sqrt{\pi})Z(Z/a)^{3/2}(r^1/a)\left(6-\frac{Zr}{a}\right)\exp(-Zr/3a)\boxed{\cos\theta}$$

Let me show you the 3d picture, nice. And here you can see the contours as well. So, you see you have a big hill, a big turf followed by a small turf and a small hill. In fact, to get this diagram is very difficult these are so small, but multiply them by r square will take square of this and multiply them by r square this is going to blow up.

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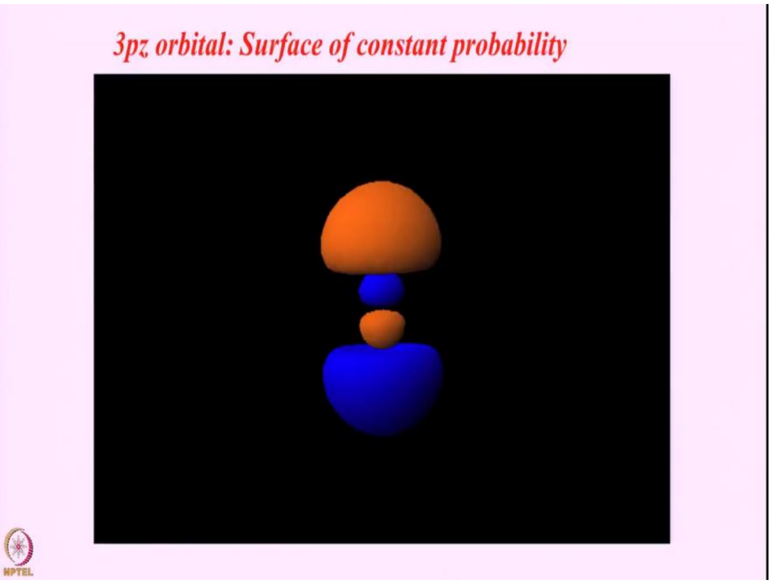
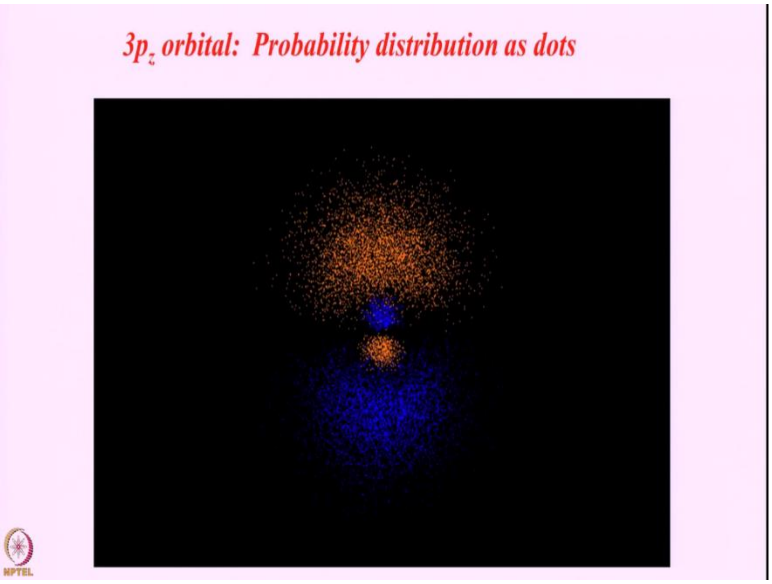


3pz orbital: Surface of constant probability



$3p_z$ orbital: Probability distribution as dots

Then similarly, you can plot this 3pz orbitals.

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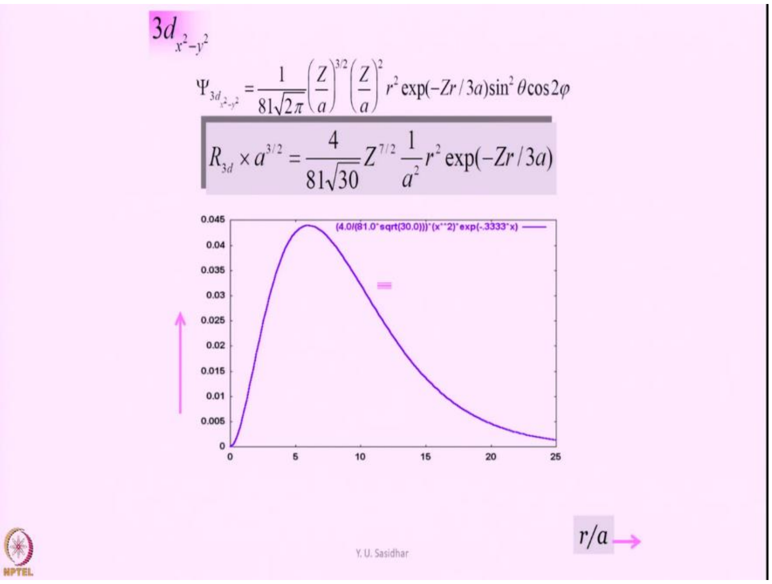

$3d_{x^2-y^2}$

$$\Psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z}{a}\right)^{2} r^2 \exp(-Zr/3a)\sin^2\theta\cos 2\varphi$$

$$R_{3d} \times a^{3/2} = \frac{4}{81\sqrt{30}} Z^{7/2} \frac{1}{a^2} r^2 \exp(-Zr/3a)$$

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Let us talk about d orbitals, $3_{d_{x^2+y^2}}$ orbital. This here is the wave function, $\Psi_{3_{d_{x^2+y^2}}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z}{a}\right)^{2} r^2\, exp(-Zr/3a) sin^2\theta cos2\phi.$ It has $sin^2\theta cos2\phi$. How do I write cos 2 phi in terms of sin phi and cos phi?

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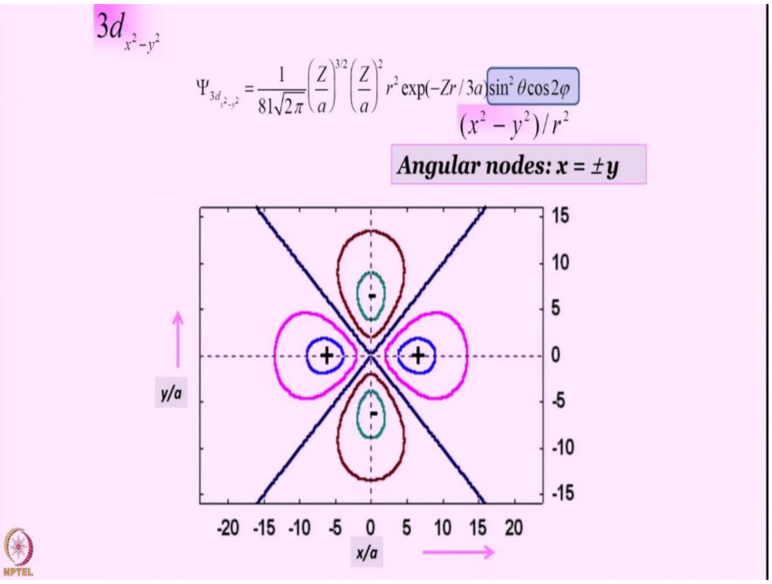

$3d_{x^2-y^2}$

$$\Psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z}{a}\right)^{2} r^2 \exp(-Zr/3a)\boxed{\sin^2\theta\cos 2\varphi}$$

$$(x^2-y^2)/r^2$$

Angular nodes: $x = \pm y$

I hope that is not very difficult for us. When we do that, we will see that this $sin^2\theta cos2\phi$ becomes $(x^2-y^2)/r^2$ and when you equate that to 0, you get the angular node $x = \pm y$. These are the angular nodes. Now, we can draw the lobes this is minus and this will be plus, this will be minus, this will be plus.

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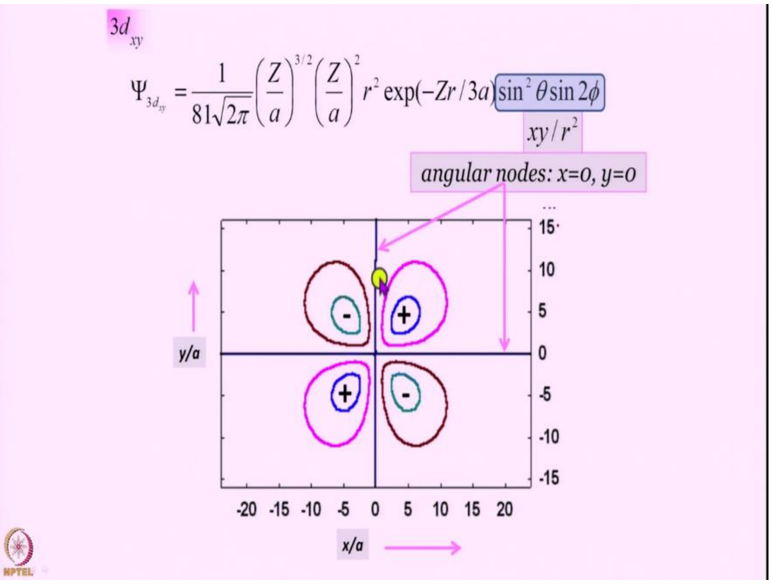

$3d_{xy}$

$$\Psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z}{a}\right)^{2} r^2 \exp(-Zr/3a)\boxed{\sin^2\theta\sin 2\phi}$$

$$xy/r^2$$

angular nodes: x=0, y=0

What about d_{xy}? For d_{xy}, the angular part of the wave function $\Psi_{3_{d_{xy}}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z}{a}\right)^{2} r^2\, exp(-Zr/3a) sin^2\theta sin2\phi$ is $sin^2\theta sin2\phi$, that turns out to be xy/r^2. What is $sin2\phi$? $sin2\phi = 2sin\phi cos\phi$. So, 1 $sin\phi$ gets multiplied by $sin\theta$ and the other $sin\phi$ gets multiplied by $cos\phi$, that is how you get xy. Angular nodes become $xy = 0$, that is, $x = 0, y = 0$. That is how you get these lobes.

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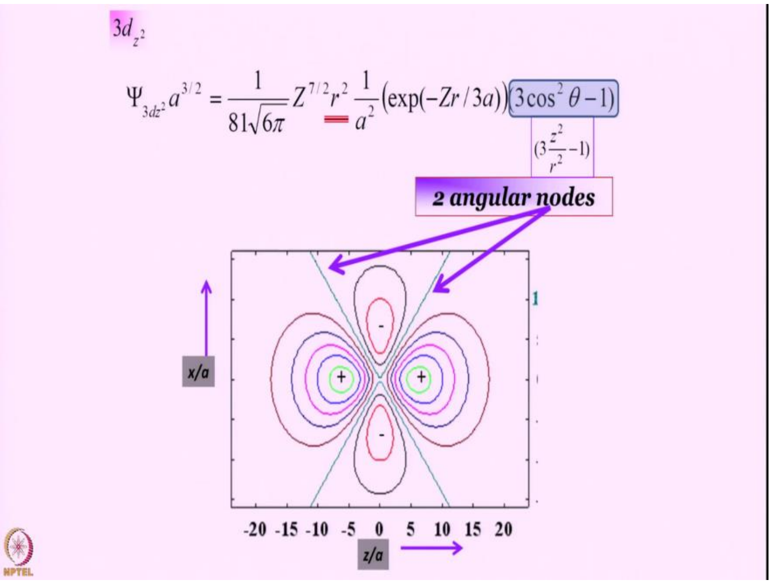

$3d_{z^2}$

$$\Psi_{3dz^2} a^{3/2} = \frac{1}{81\sqrt{6\pi}} Z^{7/2} r^2 \frac{1}{a^2}(\exp(-Zr/3a))\boxed{(3\cos^2\theta-1)}$$

$$(3\frac{z^2}{r^2}-1)$$

2 angular nodes

Similarly, for $3dz^2$, no, one more thing.

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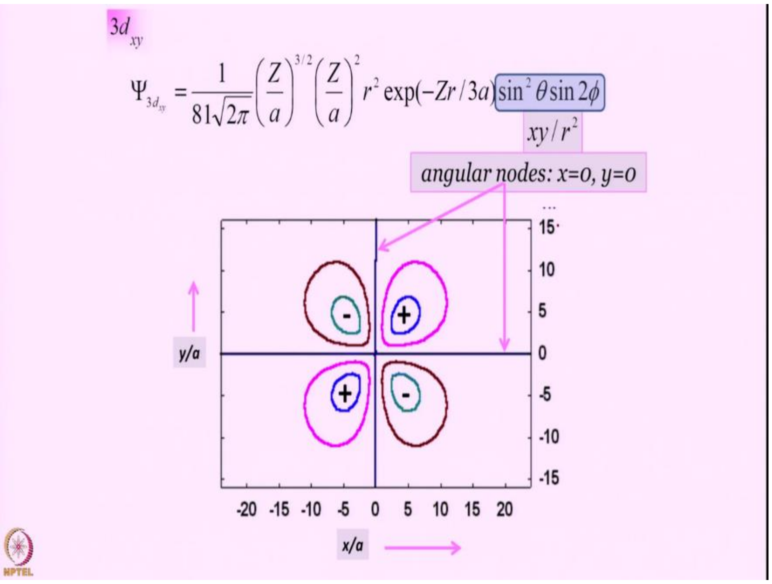

$3d_{xy}$

$$\Psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z}{a}\right)^{2} r^{2}\exp(-Zr/3a)\boxed{\sin^{2}\theta\sin 2\phi}$$

xy/r^2

angular nodes: x=0, y=0

See remember, this $3d_{xy,yz,xz,x^2-y^2}$ these are actually obtained by taking linear combinations. One set is obtained by taking linear combinations of m equal to plus 1, m equal to minus 1 orbitals and the other one is generated by taking linear combinations of m equal to plus 2 and m equal to minus 2 orbitals, which gives you which I leave that for you to figure out.

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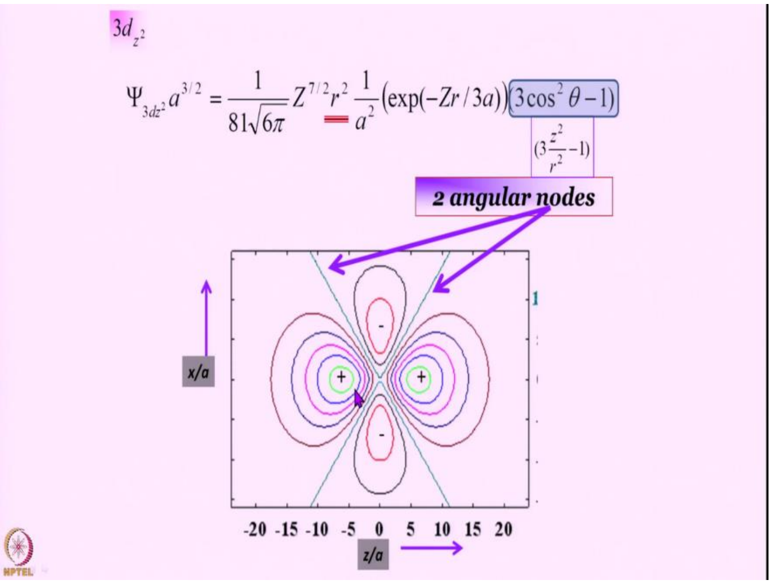
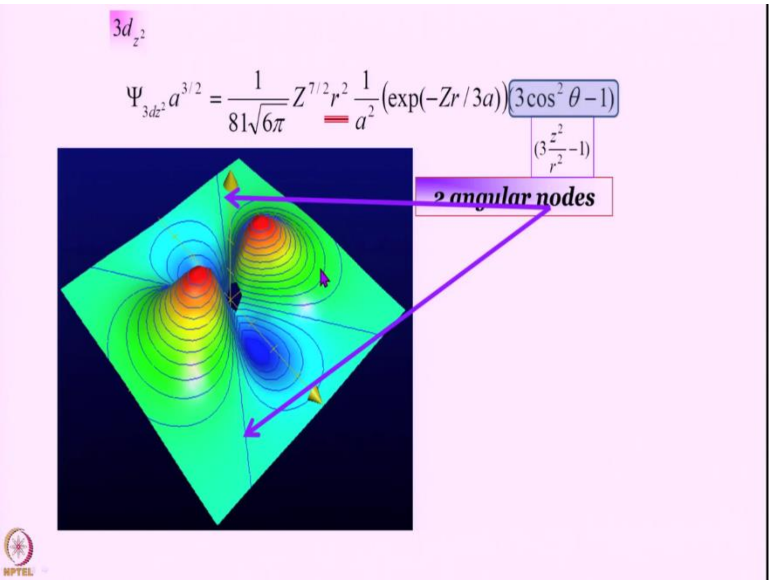


$3d_{z^2}$

$$\Psi_{3dz^2} a^{3/2} = \frac{1}{81\sqrt{6\pi}} Z^{7/2} r^{2}\frac{1}{a^{2}}(\exp(-Zr/3a))\boxed{(3\cos^{2}\theta-1)}$$

$(3\frac{z^2}{r^2}-1)$

2 angular nodes



$3d_{z^2}$

$$\Psi_{3d_{z^2}} a^{3/2} = \frac{1}{81\sqrt{6\pi}} Z^{7/2} r^2 \frac{1}{a^2} (\exp(-Zr/3a)) \boxed{(3\cos^2\theta - 1)}$$

$$(3\frac{z^2}{r^2} - 1)$$

2 angular nodes

Last orbital that I want to talk about is your 3dz^2, my favorite orbital. $\Psi_{3dz^2} a^{3/2} = \frac{1}{81\sqrt{6\pi}} Z^{7/2}\, r^2\, \frac{1}{a^2} \big(exp(-Zr/3a)\big)(3cos^2\theta - 1)$

Because the angular part is $(3cos^2\theta - 1)$. In fact, if we equate this to 0, you will get $\theta = cos^{-1}\left({}^{1}/_{\sqrt{3}}\right)$, which comes out to be 54.7 degrees. This is called Magic angle, and this quantity keeps on coming back to haunt us in many, many different areas. But we will not talk about that anymore. What I want to say is that 54.7 degrees is not the only solution. There is another solution. And that solution is, I will be lazy and I will say 180 degrees minus 54.7 degrees.

So, remember, this is 1 node, conical nodes here, this is another node. And since the angle is 54.7 degrees, more than 45 degrees, that is why 1 lobe is bigger, the other lobe is smaller. And since it is conical, this one turns out to be when you just turn it around, the smaller lobe turns out to be a belt. But this here is really the 3d picture. So plus, plus; minus, minus, this is what 3dz^2 orbital is.

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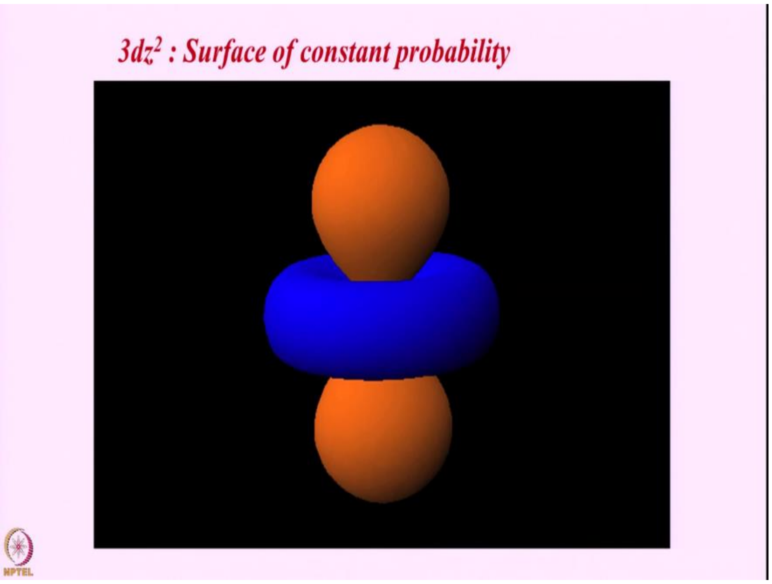
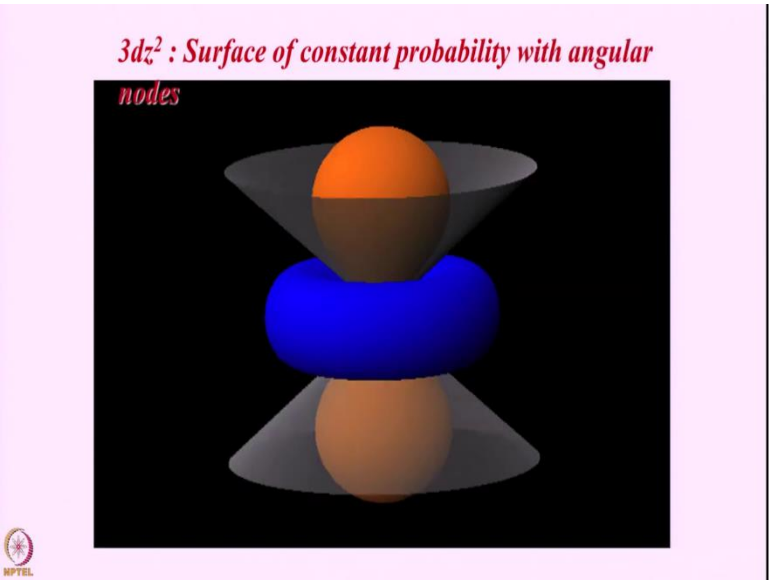


$3dz^2$: Surface of constant probability



$3dz^2$: Surface of constant probability with angular nodes

You can generate surface of constant probability and then you get this familiar picture. Now, you can go on and draw the nodes here, you are going to get two conical nodes.

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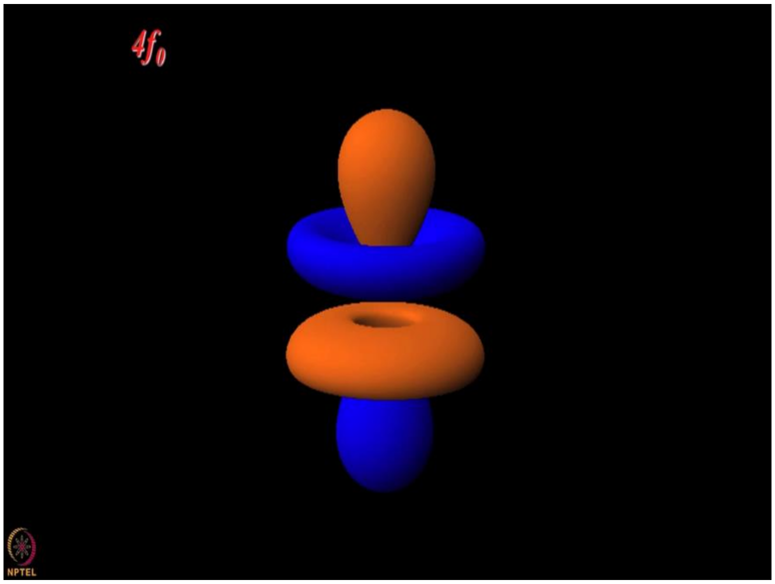
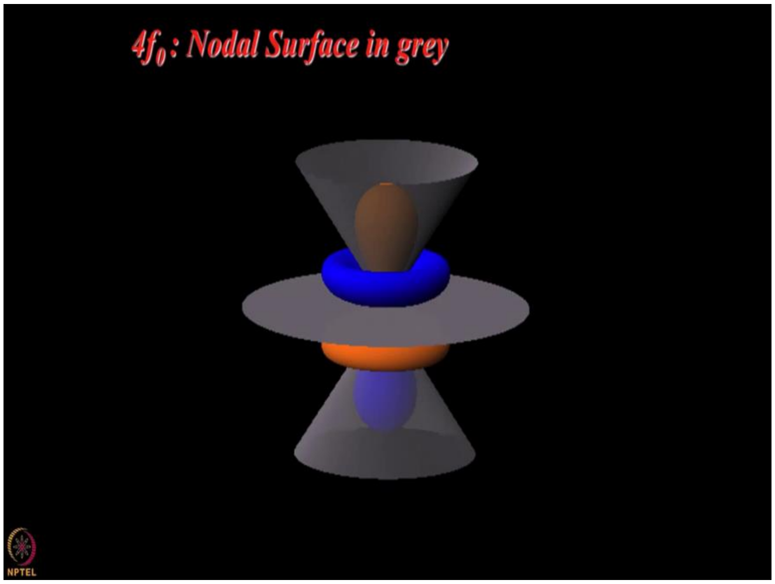


$4f_0$



$4f_0$: Nodal Surface in grey

Similarly, we are not going to talk about f orbitals, but I will just show you the constant probability surfaces of the f_0 orbital. And these are the nodal surfaces.

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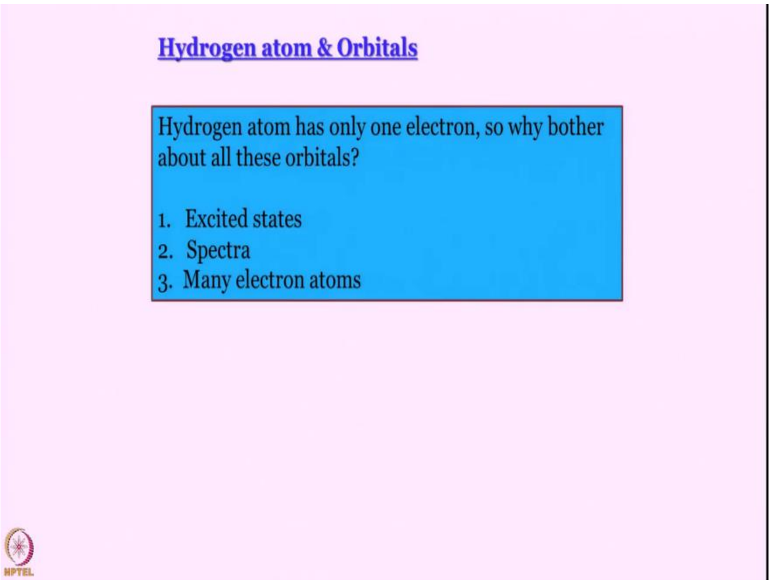

Hydrogen atom & Orbitals

Hydrogen atom has only one electron, so why bother about all these orbitals?

1. Excited states
2. Spectra
3. Many electron atoms

This, so this is what we wanted to say about hydrogen atom wave functions that are orbitals. Now the question is this, hydrogen has only 1 electron, so why do we need s, p, d, f so many orbitals, n equal to 1, 2, 3. Because, first of all, we want to access excited states. We want to talk about spectra. We want to talk about many electron atoms. We are going to see how these orbitals are used to work out wave functions for a simple molecule, molecular ion if you call it, that is H_2^+, they are called molecular orbitals.