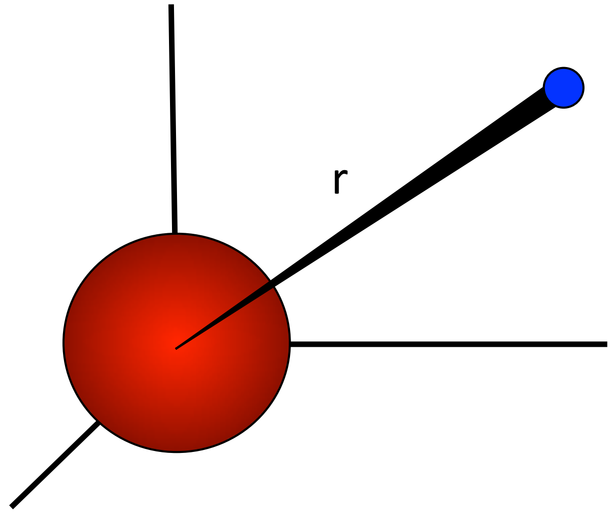
The Hydrogen Atom
(Take home messages from last class)

Hydrogenic Atoms: 2-Particle System

1 electron moving around a

(massive) central nucleus (+ve)



Schrodinger Eq. for Hydrogen Atom

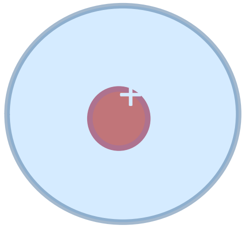
$$\hat{H} = -\frac{\hbar^2}{2m_{Nucleus}}\nabla^2_{Nucleus} - \frac{\hbar^2}{2m_{Electron}}\nabla^2_{Electron} + \hat{V}_{Electron-Nucleus}$$

$$\hat{H} = -\frac{\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_N^2} + \frac{\partial^2}{\partial z_N^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}\right) - \frac{Ze^2}{r}$$

$$\text{where } r = \sqrt{\left(x_e - x_N\right)^2 + \left(y_e - y_N\right)^2 + \left(z_e - z_N\right)^2}$$

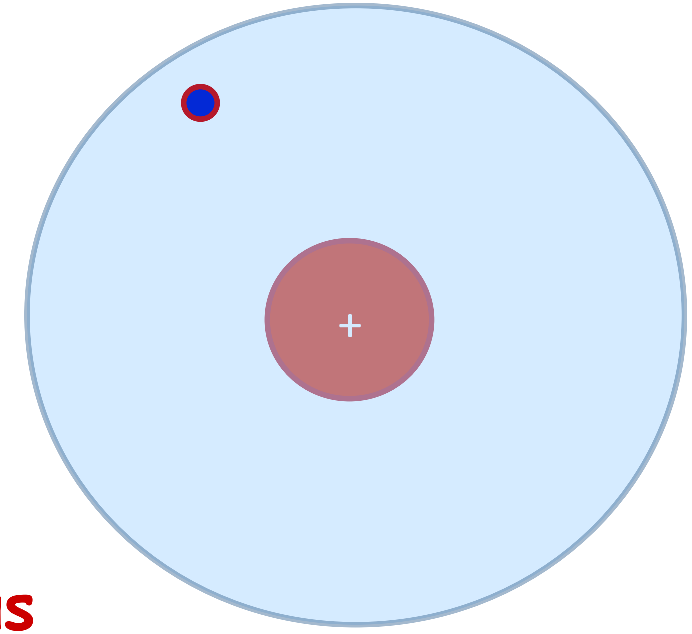
Schrodinger Eq. for Hydrogen Atom

$$-\frac{\hbar^2}{2m_N}\nabla_N^2\Psi\left(\vec{r_e},\vec{r_N}\right)-\frac{\hbar^2}{2m_e}\nabla_e^2\Psi\left(\vec{r_e},\vec{r_N}\right)-\frac{Ze^2}{r}\Psi\left(\vec{r_e},\vec{r_N}\right)=E_{Total}\Psi\left(\vec{r_e},\vec{r_N}\right)$$



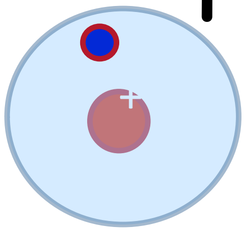
Movement of
the whole atom in
absence of field

Separation of these two motions
Can be done → Center of Mass
And relative electronic coordinates



Relative motion
of Electron with
respect to Nucleus

Separation to Relative Frame



Free Particle movement of the whole atom
We solved it!

$$-\frac{\hbar^2}{2M}\nabla^2_{CM}\Psi_{CM} = E_{CM}\Psi_{CM}$$

Relative motion of electron wrt nucleus

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2_r - \frac{Ze^2}{|r|}\right)\Psi_r = E_r\Psi_r$$

We are only interested in this part

H-Atom: Are we ready to solve TISE?

$$\left(-\frac{\hbar^2}{2\mu}\nabla_e^2\left(\vec{r}\right)-\frac{Ze^2}{|r|}\right)\Psi_e\left(\vec{r}\right)=E_r\Psi_e\left(\vec{r}\right)$$

$$\Psi_e\left(\vec{r}\right)\Rightarrow\Psi_e\left(x,y,z\right)\Leftrightarrow\Psi\left(x,y,z\right):\quad \text{3 variables}$$

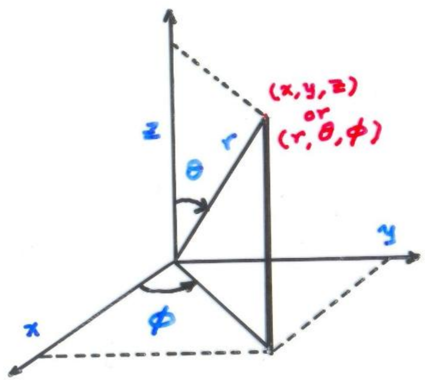
$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}\Psi\left(x,y,z\right)+\frac{\partial^2}{\partial y^2}\Psi\left(x,y,z\right)+\frac{\partial^2}{\partial z^2}\Psi\left(x,y,z\right)\right)$$

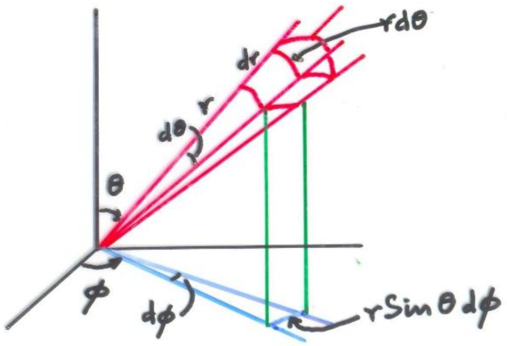
$$-\frac{Ze^2}{\sqrt{x^2+y^2+z^2}}\Psi\left(x,y,z\right)=E.\Psi\left(x,y,z\right)$$

Road-Block: This 2nd order PDE with ***3 variables…***

Can not be separated!!!

Spherical Polar Coordinates





Conversion from
Cartesian coordinates

$x = r \sin\theta \cos\phi$

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$

$dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$

$$\nabla^2_{x,y,z} = \left(\frac{\partial^2}{\partial x^2}\Psi(x,y,z) + \frac{\partial^2}{\partial y^2}\Psi(x,y,z) + \frac{\partial^2}{\partial z^2}\Psi(x,y,z) \right)$$

$$\equiv$$

$$\boxed{\nabla^2_{r\theta\phi} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial\phi^2}}$$

Hamiltonian: Spherical Polar Coordinates

Schrödinger eq. in spherical polar coordinates

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi(r,\theta,\phi)$$

Looks can be deceiving!

$$-\frac{Ze^2}{r}\Psi(r,\theta,\phi)=E\Psi(r,\theta,\phi)$$

Solve this PDE →need to separate variables **r**, θ, φ: **POSSIBLE**

$$\textit{Special solution if } \widehat{H}=\widehat{H}(r)+\widehat{H}(\theta)+\widehat{H}(\phi): \quad \Psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$$

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)}=\beta(const.)$$

$$\boxed{\frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)}=\beta(const.)$$

$$\widehat{H}(r)R(r)=E_nR(r)$$

$$\widehat{H}(\theta)\Theta(\theta)=E_l\Theta(\theta)$$

$$\therefore\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+m^2=0$$

$$\widehat{H}(\phi)\Phi(\phi)=E_{m_l}\Phi(\phi)$$

H-Atom: Three Quantum Numbers

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)} = \beta(const.)$$

n = principle quantum no

$$\boxed{\frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)} = \beta(const.)$$

l = Azimuthal quantum no

$$\therefore \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+m^2=0$$

m_l = magnetic quantum no

The three quantum numbers are not independent to each other; There are restrictions (Unlike particle in 3-D Box)

How to obtain normalized $\Psi_{n,l,m}(r,\theta,\pi)$?

$$\left|\Psi\left(r,\theta,\phi\right)\right|^2 r^2 dr\ Sin\theta\, d\theta\ \ d\phi$$

$$\int_0^\infty r^2 dr \int_0^\pi Sin\theta\, d\theta \int_0^{2\pi} d\phi\ \left|\Psi\left(r,\theta,\phi\right)\right|^2 = 1$$

Normalization:

Spherical harmonics $\int_0^{2\pi} d\phi \int_0^\pi d\theta\ \sin\theta\ Y_l^{m*}\left(\theta,\phi\right) Y_l^m\left(\theta,\phi\right) = 1$

Radial wavefunctions $\int_0^\infty dr\ r^2 R_{nl}^*\left(r\right) R_{nl}\left(r\right) = 1$

Loose Meaning of Quantum Numbers

n specifies the energy of the electron

l specifies the magnitude of the electron's orbital angular momentum

m_l specifies the orientation of the electron's orbital angular momentum

L=0 → s-orbital
L=1 → p-orbital
L=2 → d-orbital
L=3 → f-orbital

Radial Solutions depend on n and l (l=n-1)

$$R_{nl} = A(n,l).\boxed{r^l}.\boxed{L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)}.\boxed{e^{\left(-Zr/na_0\right)}}$$

$$\underbrace{r^l \cdot L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)}_{f(r,n,l,Z)} \qquad \underbrace{e^{\left(-Zr/na_0\right)}}_{g(r,Z)}$$

Exponential Decay g(r)

where $L_{n+l}^{2l+1}\left(2Zr/na_0\right)$ are the *associated Laguerre functions,*

$n=1 \quad l=0 \quad L_1^1 = -1$

$n=2 \quad l=0 \quad L_2^1 = -2!\left(2 - Zr/a_0\right)$

$l=1 \quad L_3^3 = -3!$

$n=3 \quad l=0 \quad L_3^1 = -3!\left(3 - 2Zr/a_0 + 2Z^2r^2/9a_0^2\right)$

$l=1 \quad L_4^3 = -4!\left(4 - 2Zr/3a_0\right)$

$l=2 \quad L_5^5 = -5!$

Note: $R_{nl} \rightarrow 0$ as $r \rightarrow$ infinity

Additional restrictions on l: n ≥ l+1 arise when DE is solved

Complete Wavefunction of H-Atom

$$\psi(r,\theta,\phi) = R(r)\,Y_l^m(\theta,\phi)$$

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

where $L_{n+l}^{2l+1}(2Zr/na_0)$ are the *associated Laguerre functions*, th

$$Y_\ell^m(\theta,\varphi) = (-)^m \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\,P_\ell^m(\cos\theta)\,e^{im\varphi}$$

Lets not get intimidated: Please do not even try to remember

H-Atom Complete $\Psi(r,\theta,\phi)$ for n=1,2

$\sigma \rightarrow r/a_0$

1s $n=1 \quad l=0 \quad m=0 \quad \psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma} = \psi_{1s}$ **F(r) only**

2s $n=2 \quad l=0 \quad m=0 \quad \psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma) e^{-\sigma/2} = \psi_{2s}$ **F(r) only**

$2p_z$ $l=1 \quad m=0 \quad \psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta = \psi_{2p_z}$ **F(r,θ)**

$2p_{x,y}$ $l=1 \quad m=\pm 1 \quad \psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \, e^{\pm i\phi}$ **F(r,θ,φ)**

or the alternate linear combinations

Linear combination Of two solutions is Also a solution

$$\psi_{2p_x} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \, \cos\phi = \frac{1}{\sqrt{2}}\left(\psi_{21+1} + \psi_{21-1}\right)$$

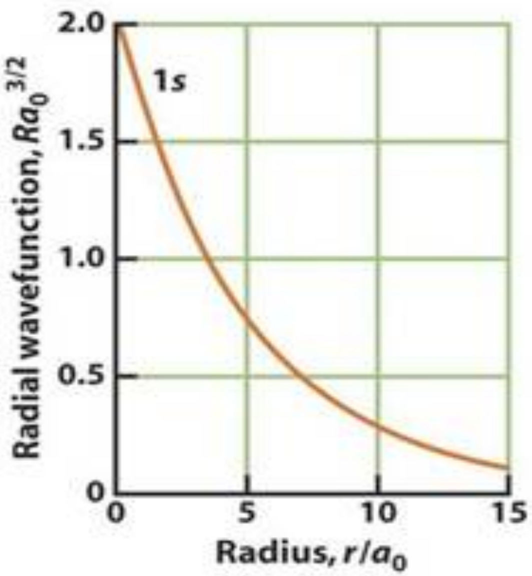
$$\psi_{2p_y} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \, \sin\phi = \frac{1}{\sqrt{2i}}\left(\psi_{21+1} - \psi_{21-1}\right)$$

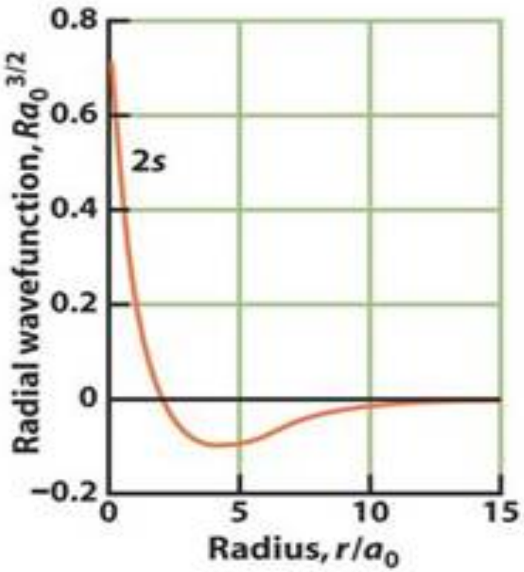
S-Orbitals ($l=0, m_l=0$)" R_{nl} and R_{nl}^2

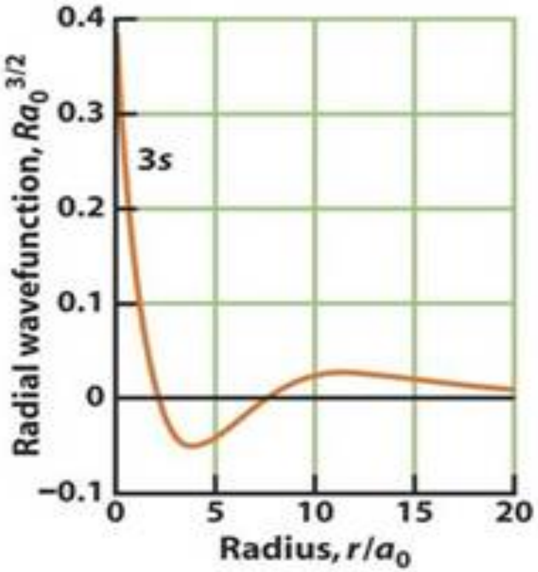
$$\Psi_{1S}^{100} = N' e^{-\rho/2}$$

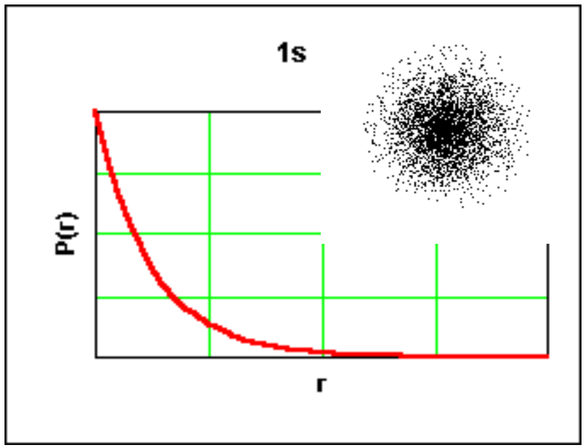
$$\Psi_{2S}^{200} = N'' (2-\rho) e^{-\rho/2}$$

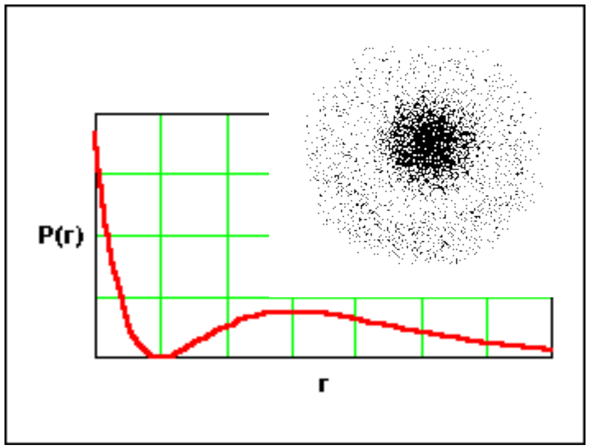
$$\Psi_{3S}^{300} = N''' (27 - 18\rho + 2\rho^2) e^{-\rho/3}$$

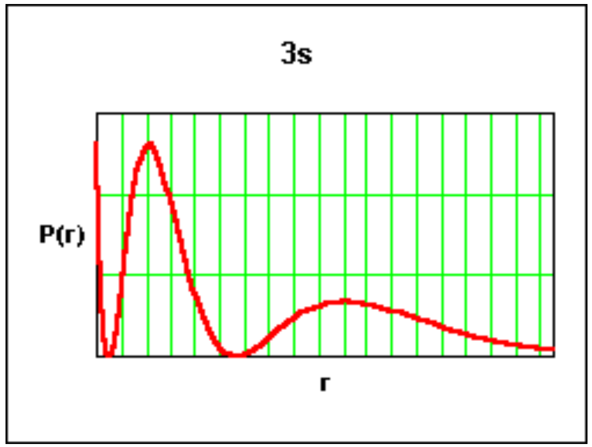




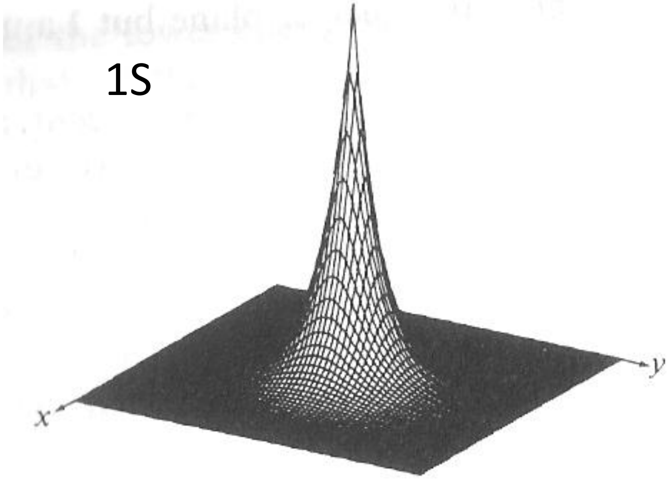


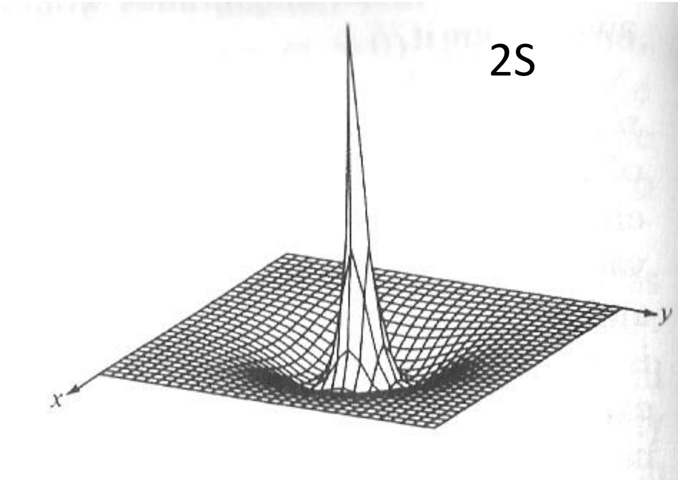


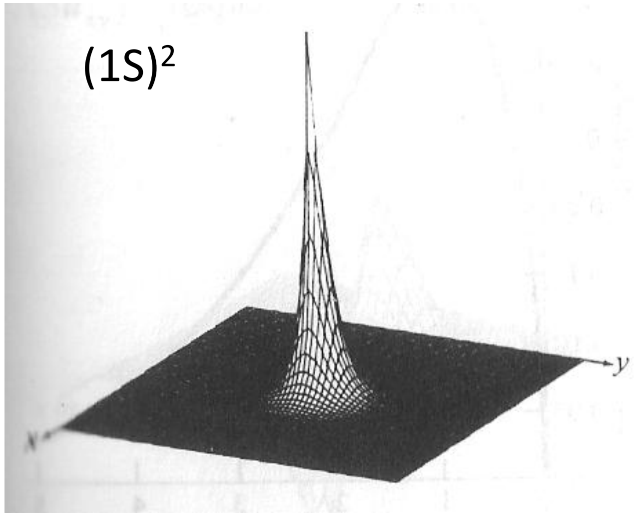


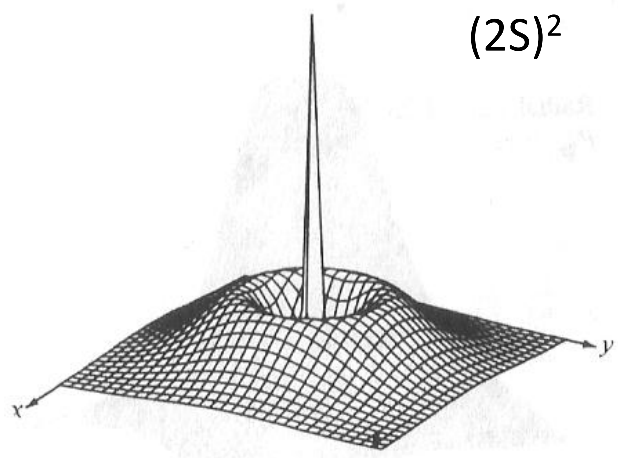


Surface plot of Ψ and Ψ^2 for S









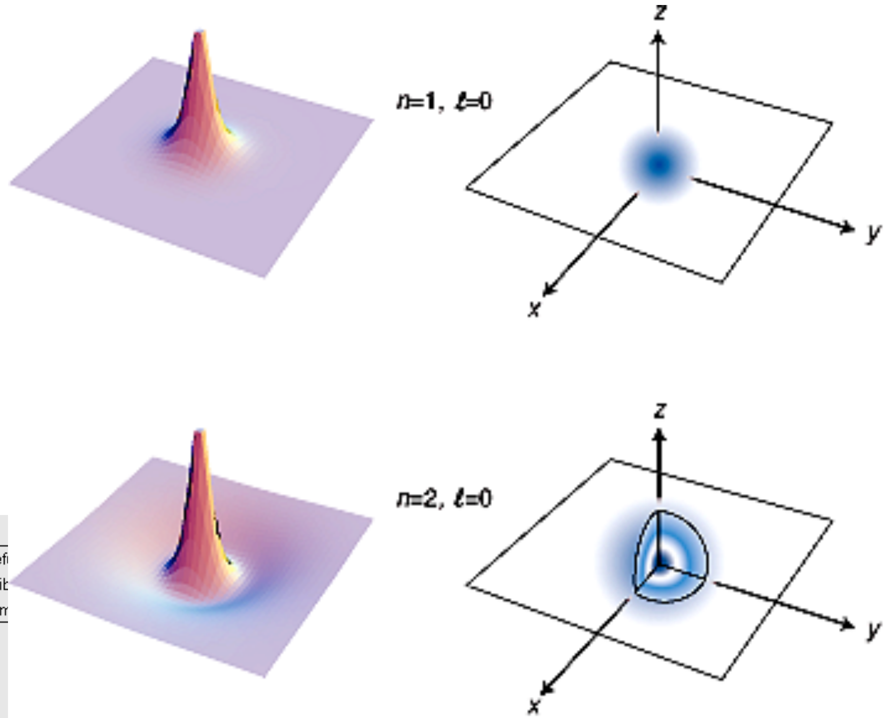
Maximum probability of finding the electron on the nucleus?

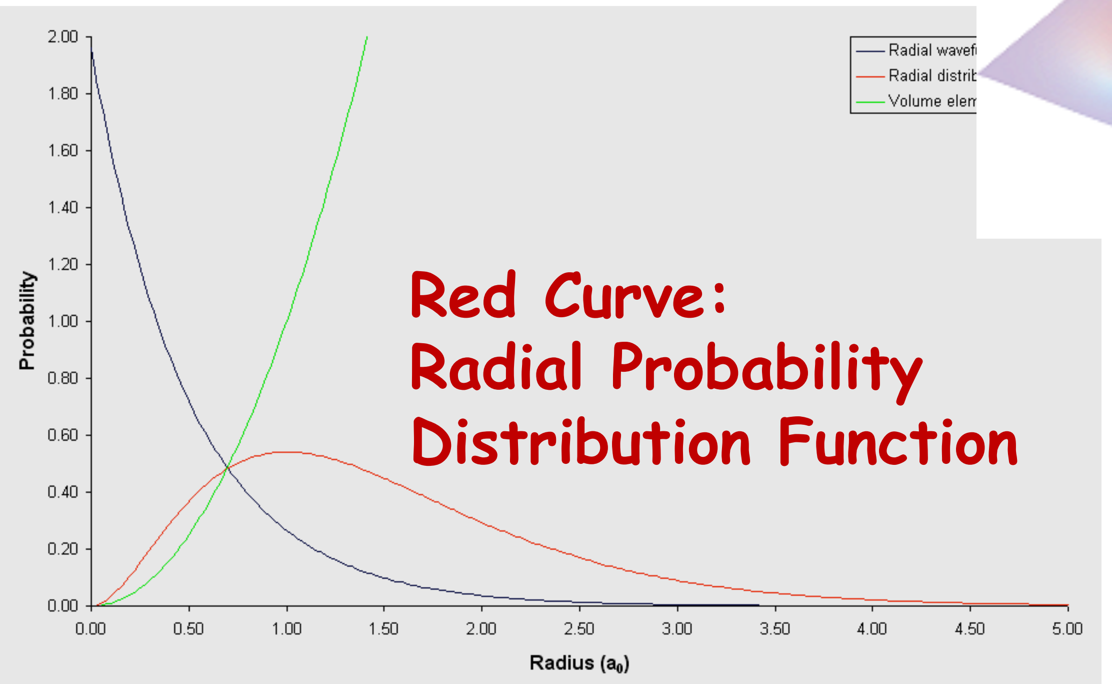
$R^2(r)$ predicts maximum probability at the center of the atom (for s)!!!

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

$r^2 \rightarrow$ increasing *function*

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





Red Curve: Radial Probability Distribution Function

Product of an increasing function and a decreasing function: MAXIMUM

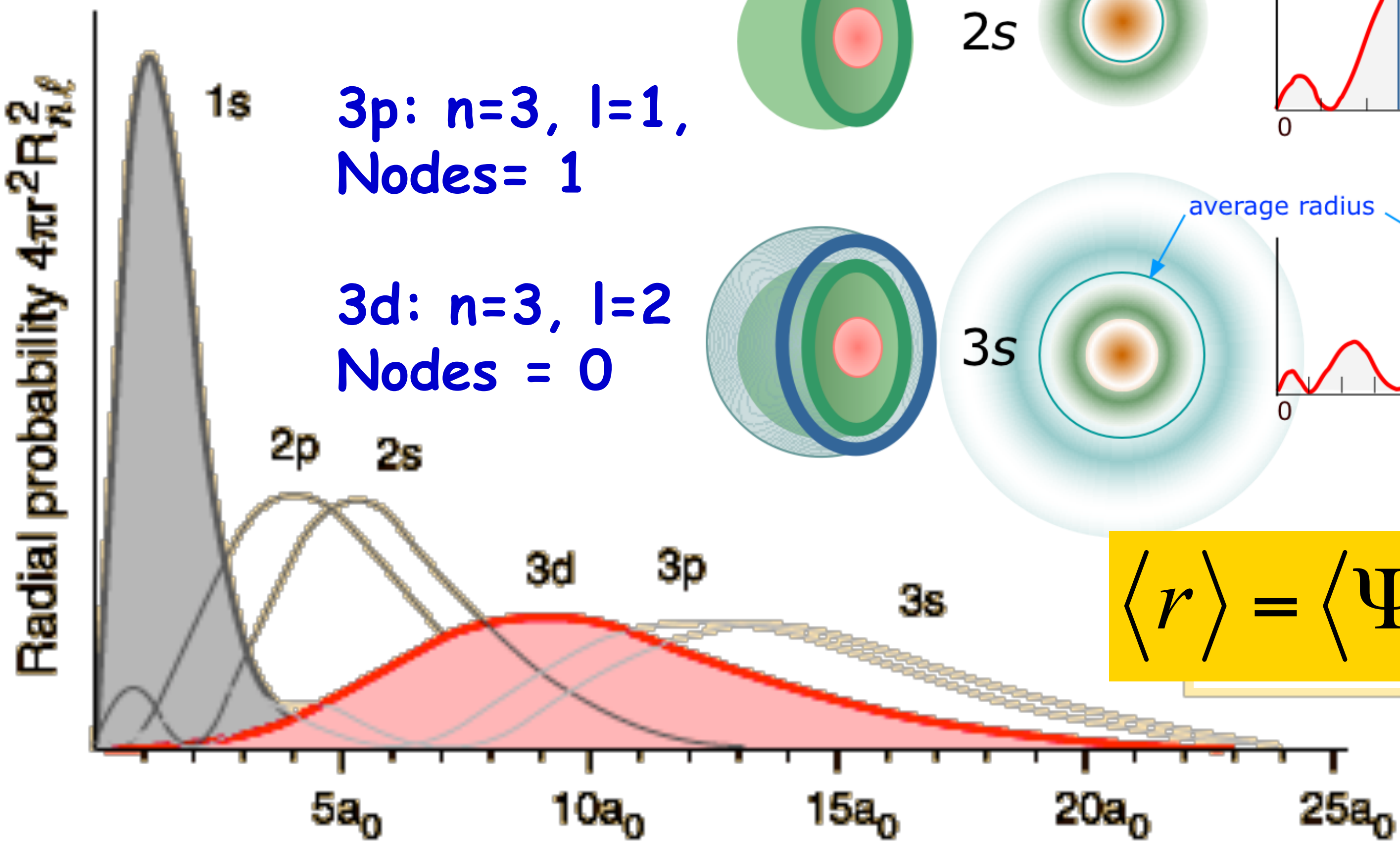
Radial Distribution Functions: $4\pi r^2 R_{nl}^2(r)$

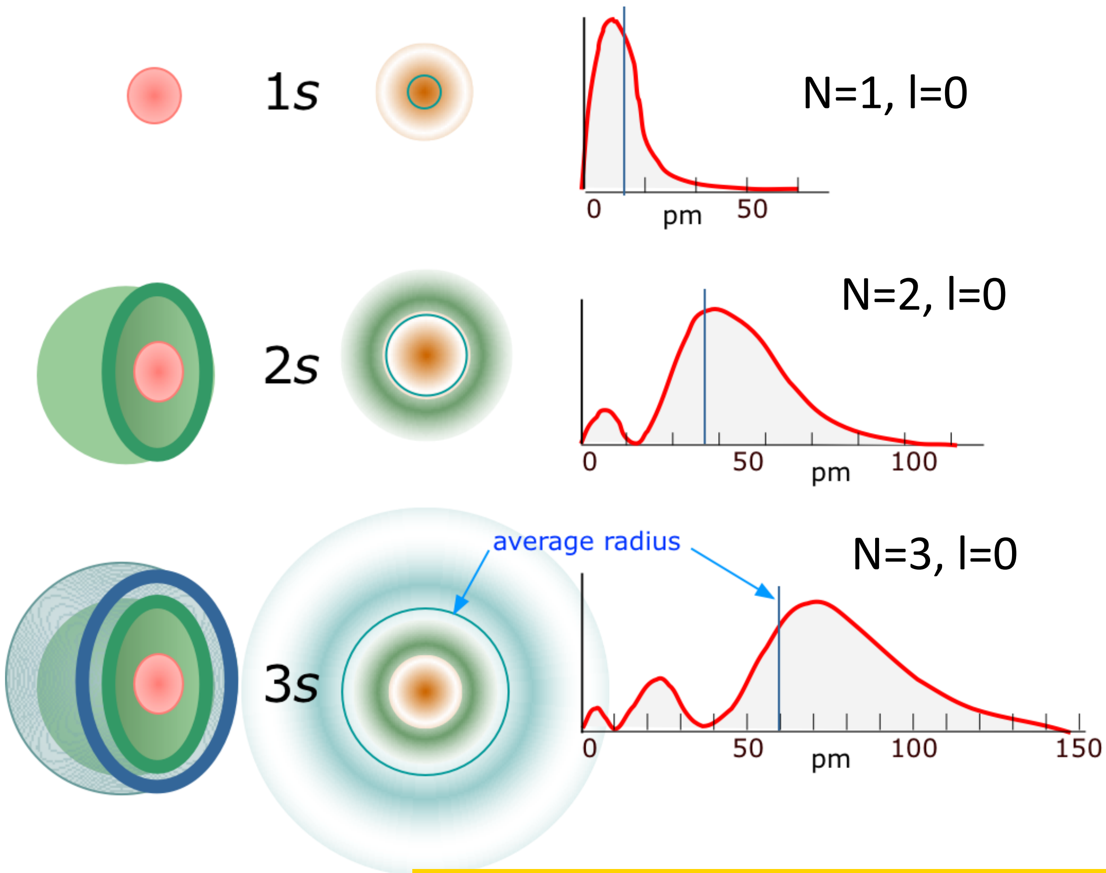
Number of Radial Nodes
is always n-l-1

3s: n=3, l=0
Nodes= 2

3p: n=3, l=1,
Nodes= 1

3d: n=3, l=2
Nodes = 0





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

SHAPES AND SYMMETRIES OF THE ORBITALS

S ORBITALS

$$\psi_{1s} = \left(\pi a_0^3\right)^{-1/2} e^{-r/a_0} \qquad\qquad \psi_{2s} = \left(32\pi a_0^3\right)\left(2 - r/a_0\right) e^{-r/2a_0}$$

$l = 0$ spherically symmetric

$n - l - 1 = 0$	radial nodes	$n - l - 1 = 1$
$l = 0$	angular nodes	$l = 0$
$n - 1 = 0$	total nodes	$n - 1 = 1$

P ORBITALS: wavefunctions

"Shapes" of orbitals depend on Orbital quantum number l and Magnetic quantum no. m_l

Not spherically symmetric: depend on θ, ϕ

m = 0 case: $\psi_{210} = \psi_{2p_z} = \left(32\pi a_0^3\right)^{-1/2} \left(r/a_0\right) e^{-r/2a_0} \cos\theta$

ψ_{2p_z} independent of ϕ symmetric about z axis

radial nodes	$n - l - 1 = 0$	(note difference from 2s: $R_{nl}(r)$ depends on l as well as n)
angular nodes	$l = 1$	
total nodes	$n - 1 = 1$	

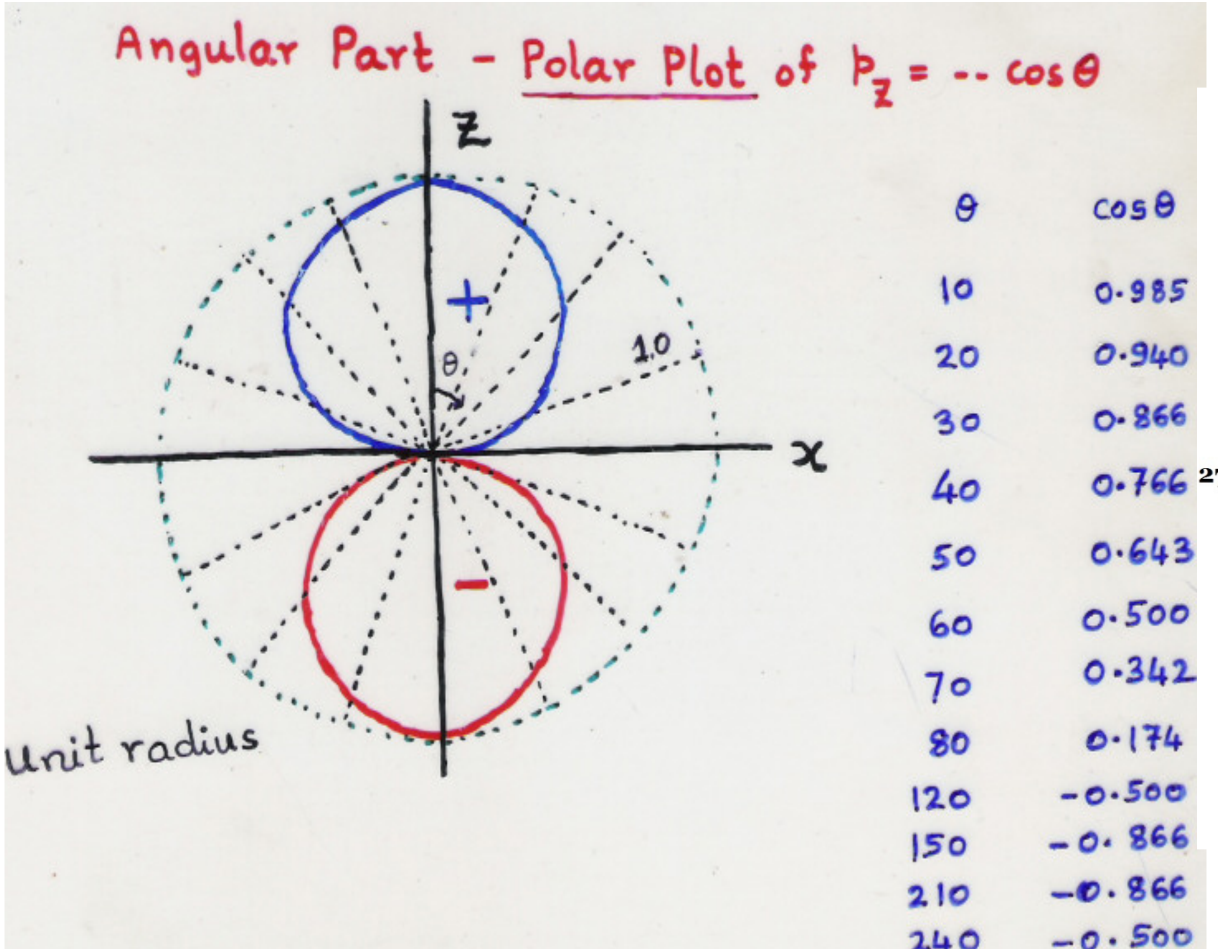
No ϕ dependence: symmetric around z axis

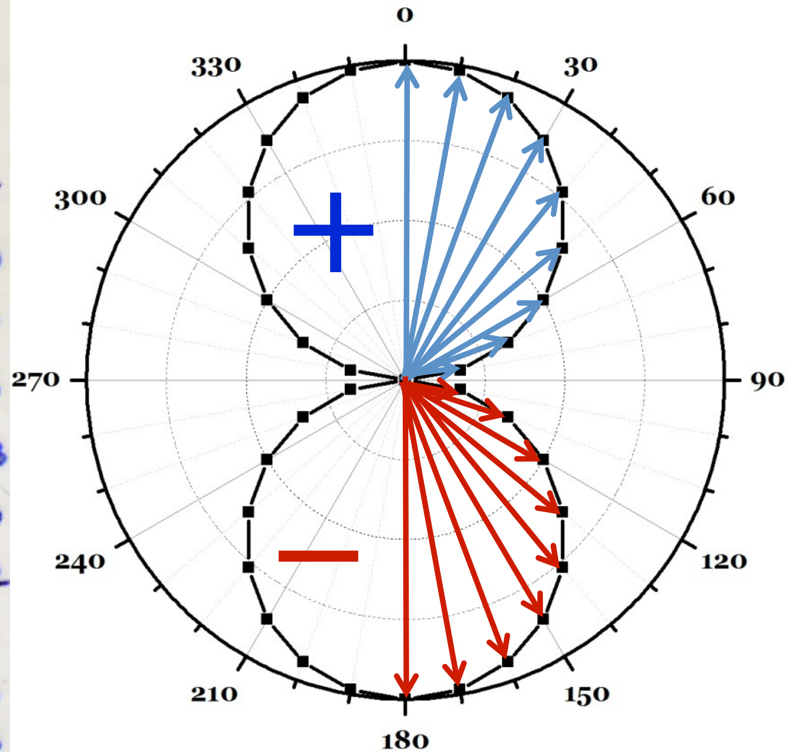
xy nodal plane - zero amplitude at nucleus

Angular part of Wave Functions

m = 0 case: $\psi_{210} = \psi_{2p_z} = \left(32\pi a_0^3\right)^{-1/2}\left(r/a_0\right)e^{-r/2a_0}\cos\theta$

ψ_{2p_z} independent of ϕ symmetric about z axis $\Psi_{210}(2p_z) = N\rho e^{-\rho/2}.\cos\theta$





Basis of Nomenclature of orbitals

$$\Psi_{210}(2p_z) = N\rho e^{-\rho/2}.\cos\theta$$

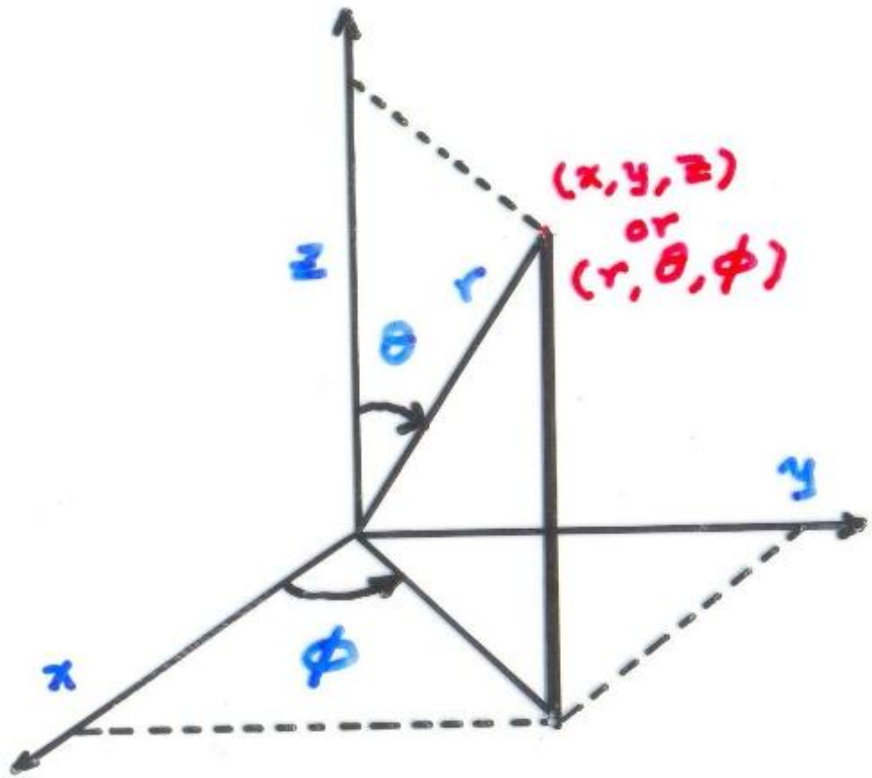
$$\Psi(2p_x) = N'\rho e^{-\rho/2}.\sin\theta.\cos\phi$$

$$\Psi(2p_y) = N''\rho e^{-\rho/2}.\sin\theta.\sin\phi$$

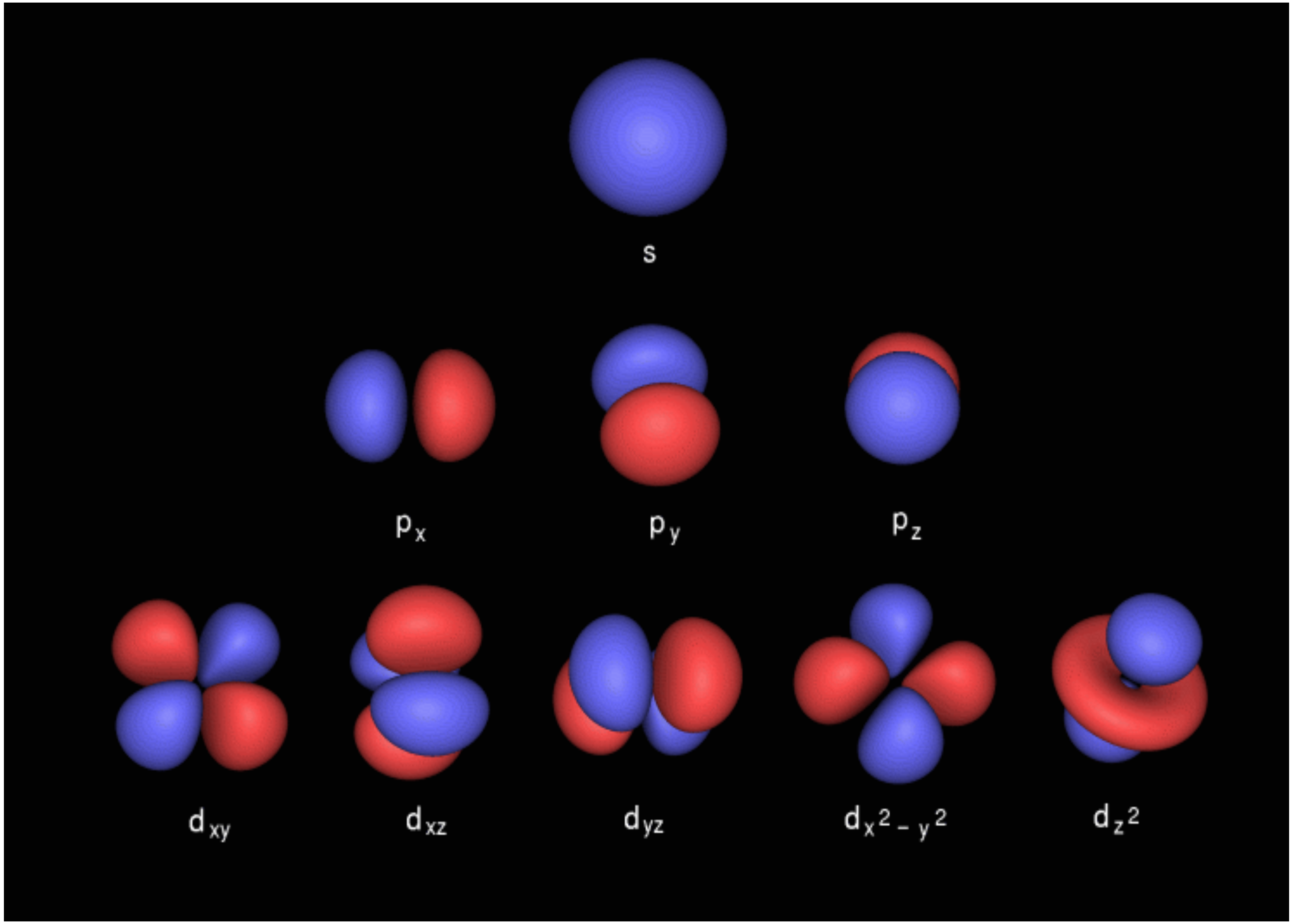
$$z = r\boxed{\cos\theta}$$

$$x = r\boxed{\sin\theta.\cos\phi}$$

$$y = r\boxed{\sin\theta.\sin\phi}$$



So what is an orbital?



Are these what chemists refer to as pictures of "Orbitals"?

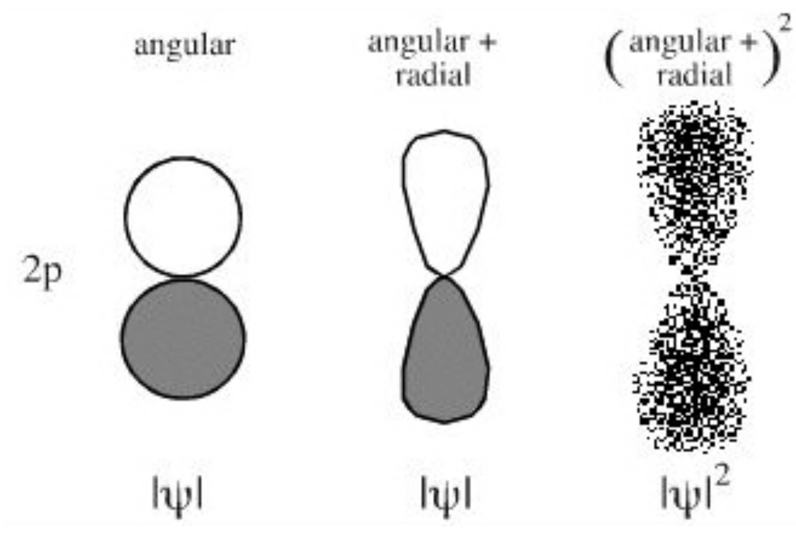
Misinterpretation of Orbital pictures

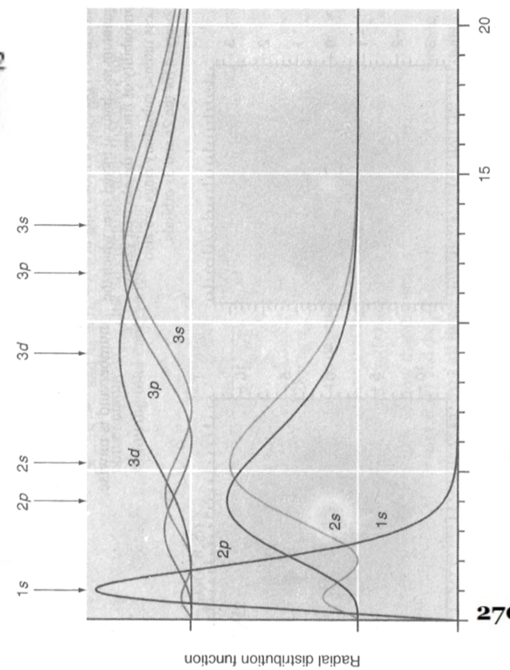
Angular plots of $\Psi(r,\theta,\phi)$ has no physical meaning – just mathematical functions - may be used to obtain information about probable electron distribution.

But can not be, in any way, regarded as the "picture" of an orbital. It is unfortunate that fuzzy drawings like these are often represented as "orbitals"

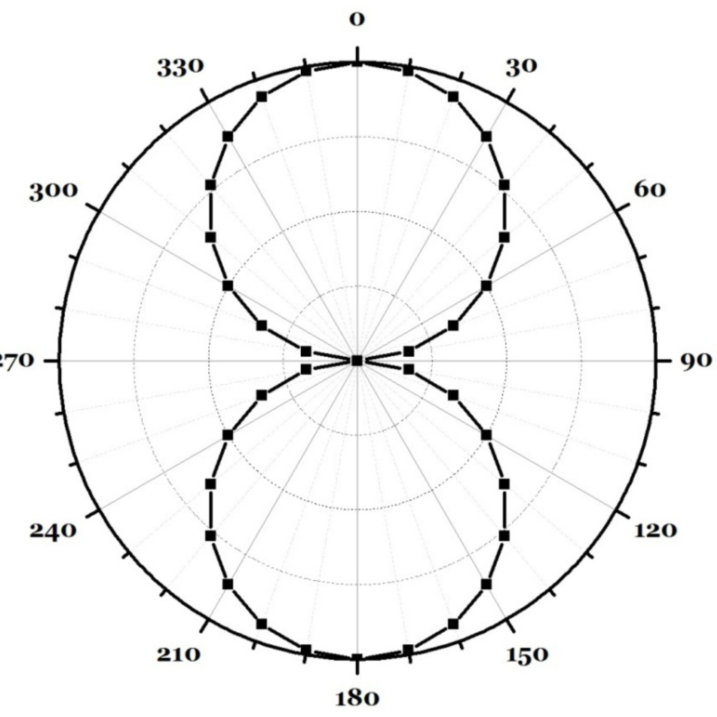
However, ψ^2 might provide a better intuitive picture

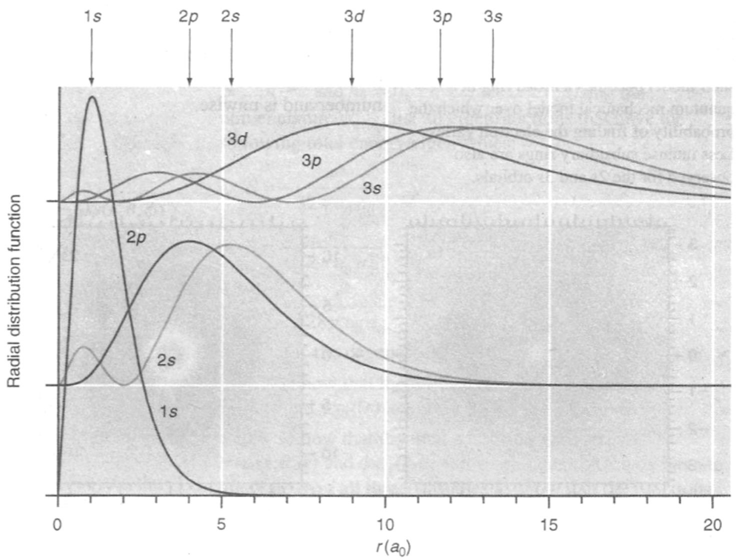
Angular + Radial Electron Densities



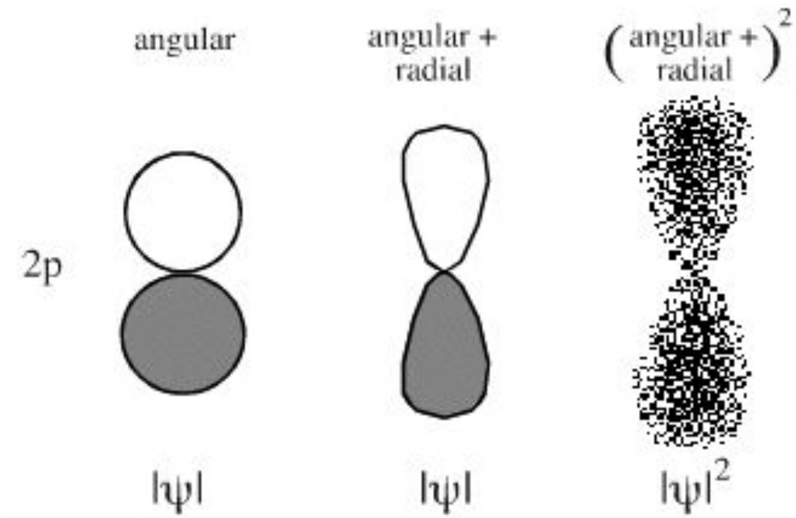


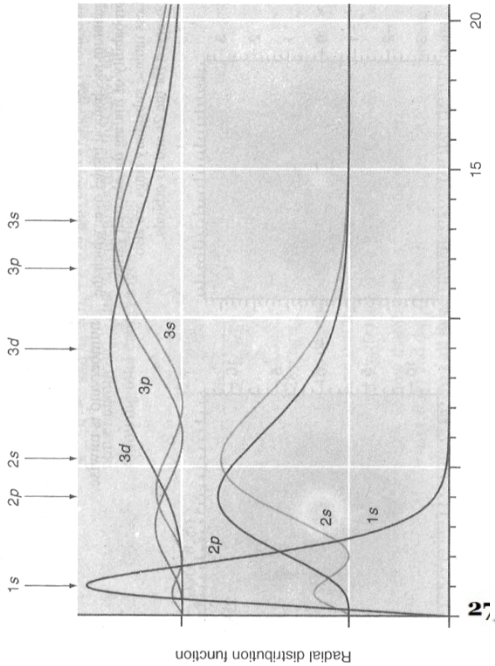
$r^2R^2(r)$





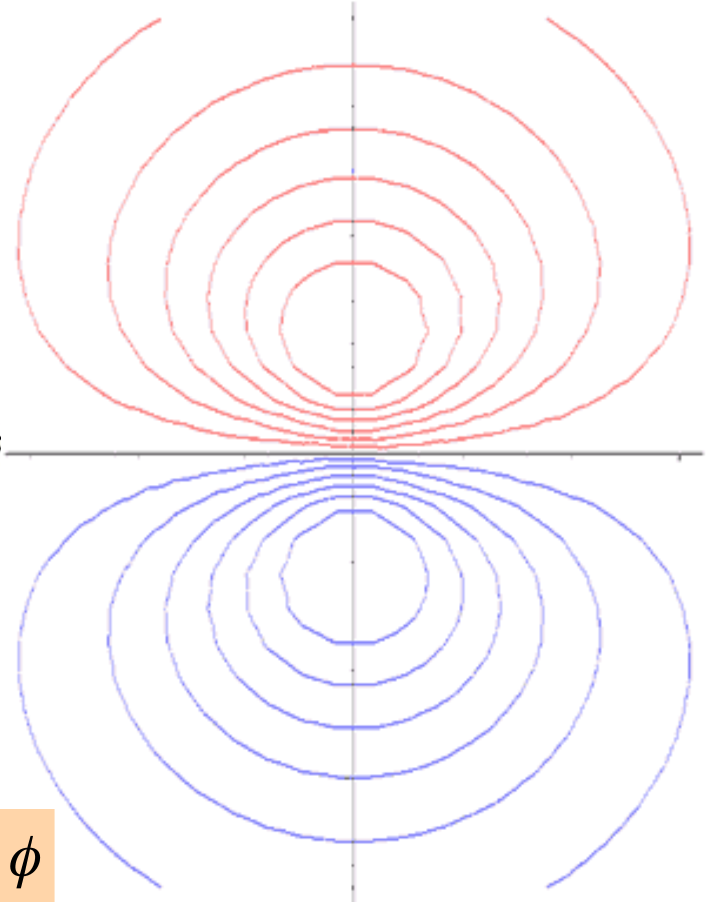
Angular + Radial Electron Densities

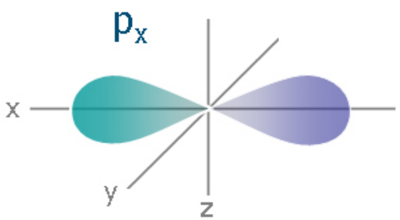


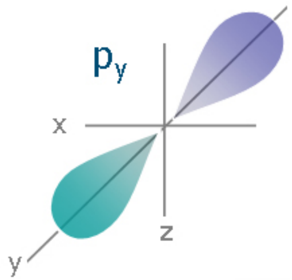


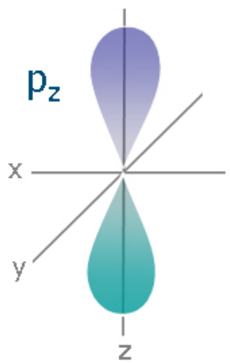
$r^2R^2(r)$

Contours of constant Prob.









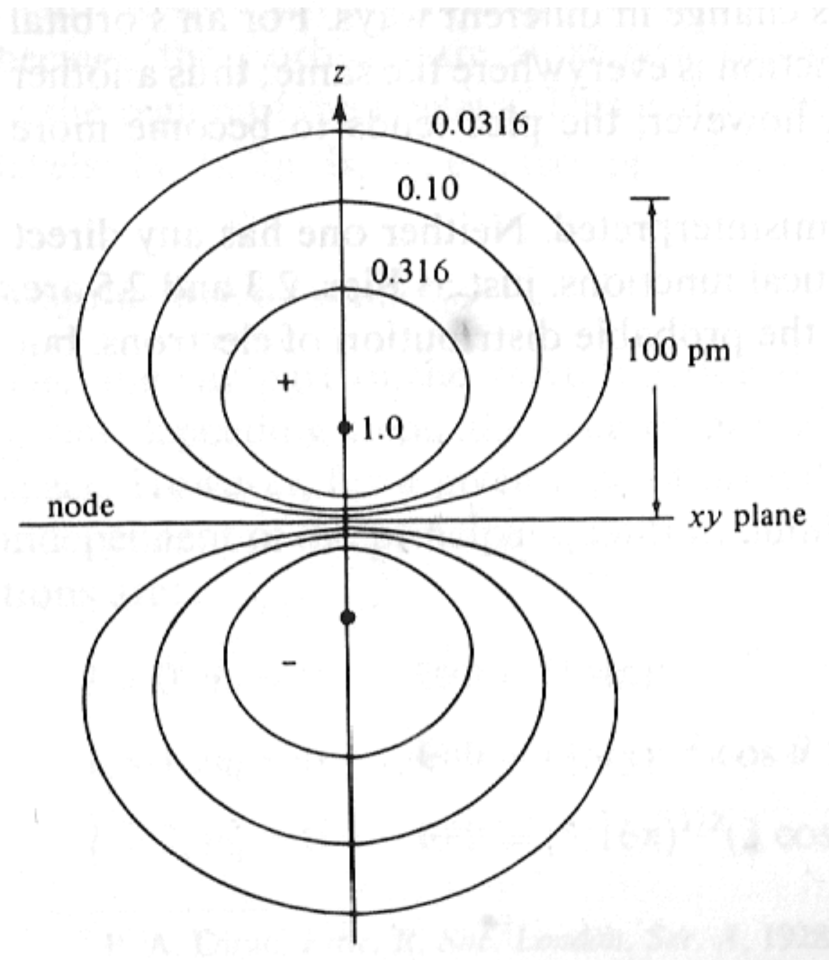
$$\Psi(2p_x) = N\rho e^{-\rho/2}.\sin\theta.\cos\phi$$

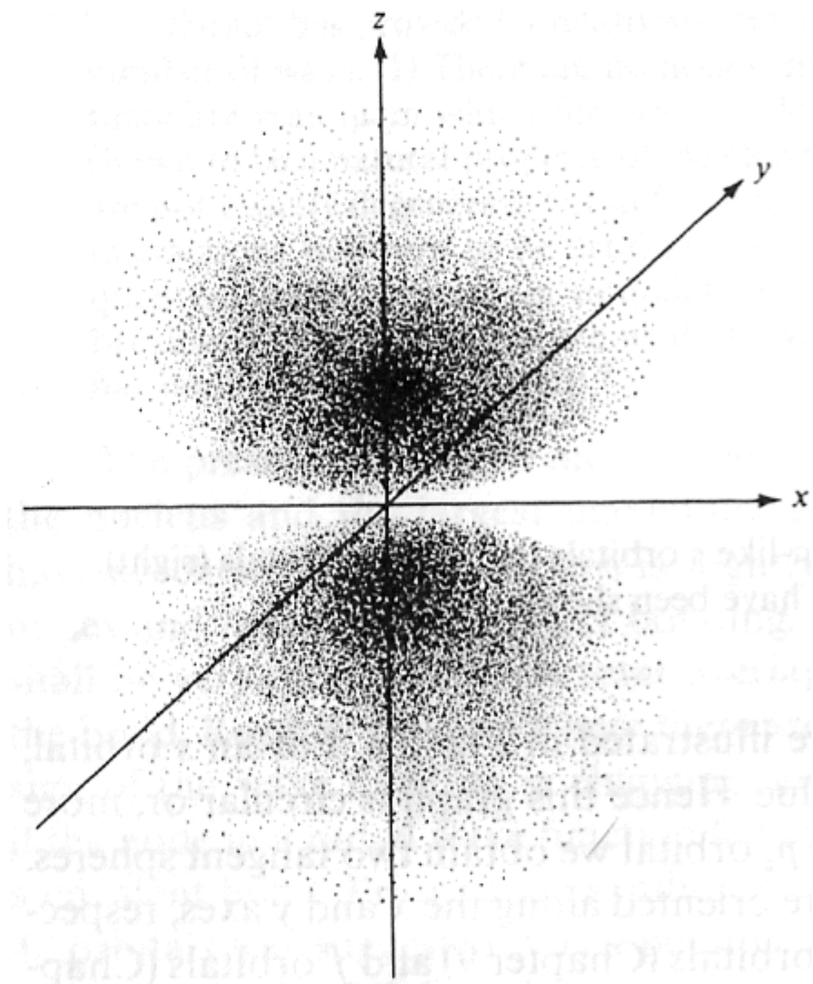
$$\Psi(2p_y) = N\rho e^{-\rho/2}.\sin\theta.\sin\phi$$

"Orbital" is a 1-e wavefunction

Contours of constant probability → Distribution of electron density

$$Maximise\ \Psi^2(r,\theta,\phi)dv \Rightarrow r^2 R_{n,l}^2(r)dr \otimes Y_{l,m}^2(\theta,\phi)Sin\theta d\theta d\phi$$





An "Orbital" is a 1-e wavefunction

Surface plot of Ψ and Ψ² for 2p

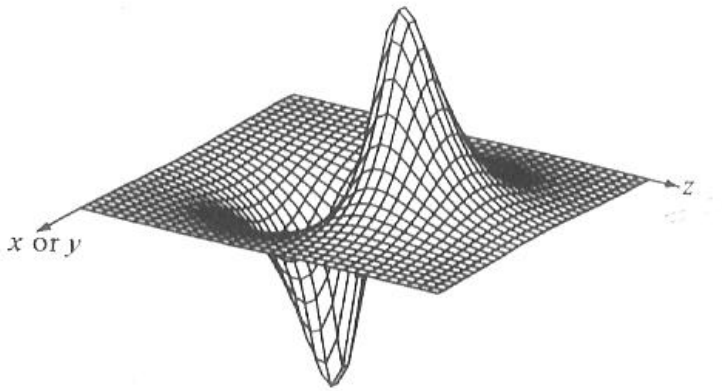


FIGURE 5-10
Surface plot of the $2p_z$ wavefunction (orbital) in the xz (or yz) plane for the hydrogen atom. The "pit" represents the negative lobe and the "hill" the positive lobe of a $2p$ orbital.

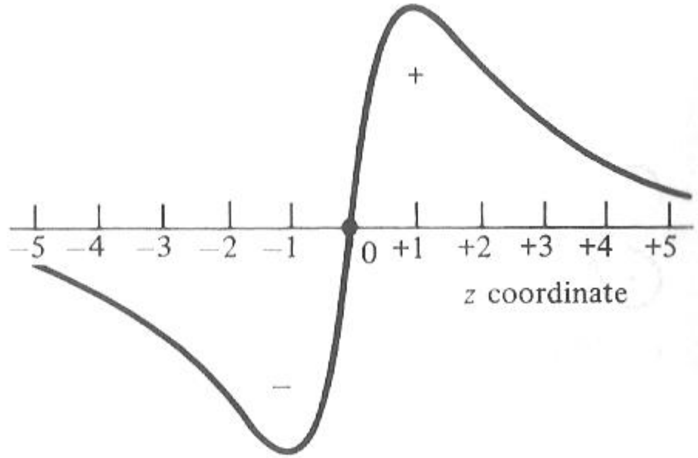


FIGURE 5-11
Profile of the $2p_z$ orbital along the z axis.

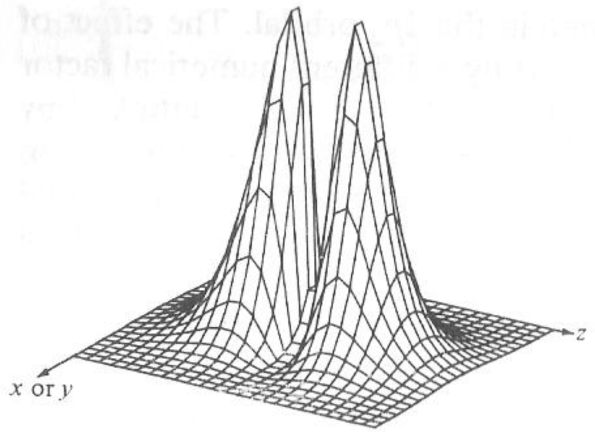


FIGURE 5-12
Surface plot of $(2p_z)^2$; the probability density represented by the $2p_z$ wavefunction of the hydrogen atom. Each of the hills represents an area in the xz (or yz) plane where the probability density is the highest. The probability density along the x (or y) axis passing through the nucleus $(0, 0)$ is everywhere zero.

d-orbitals: n=3, l=2, m_l=-2,-1,0,1,2

$$3d_{z^2} = N_1\rho^2(3\cos^2\theta - 1)e^{-\rho/3}$$

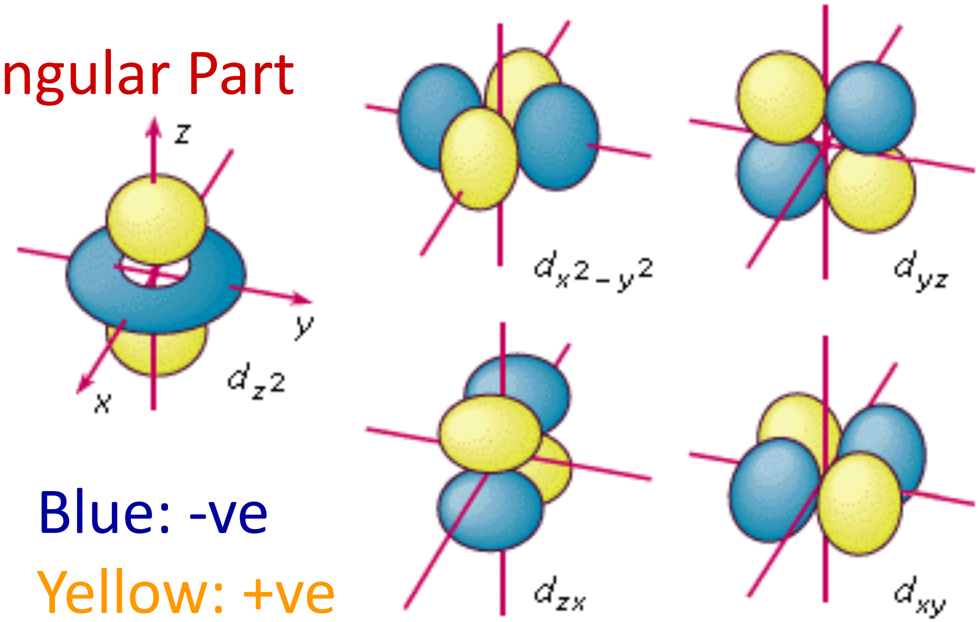
$$3d_{xz} = N_2\rho^2 \sin\theta\cos\theta\cos\phi e^{-\rho/3}$$

$$3d_{yz} = N_3\rho^2 \sin\theta\cos\theta\sin\phi e^{-\rho/3}$$

$$3d_{x^2-y^2} = N_4\rho^2 \sin^2\theta\cos 2\phi e^{-\rho/3}$$

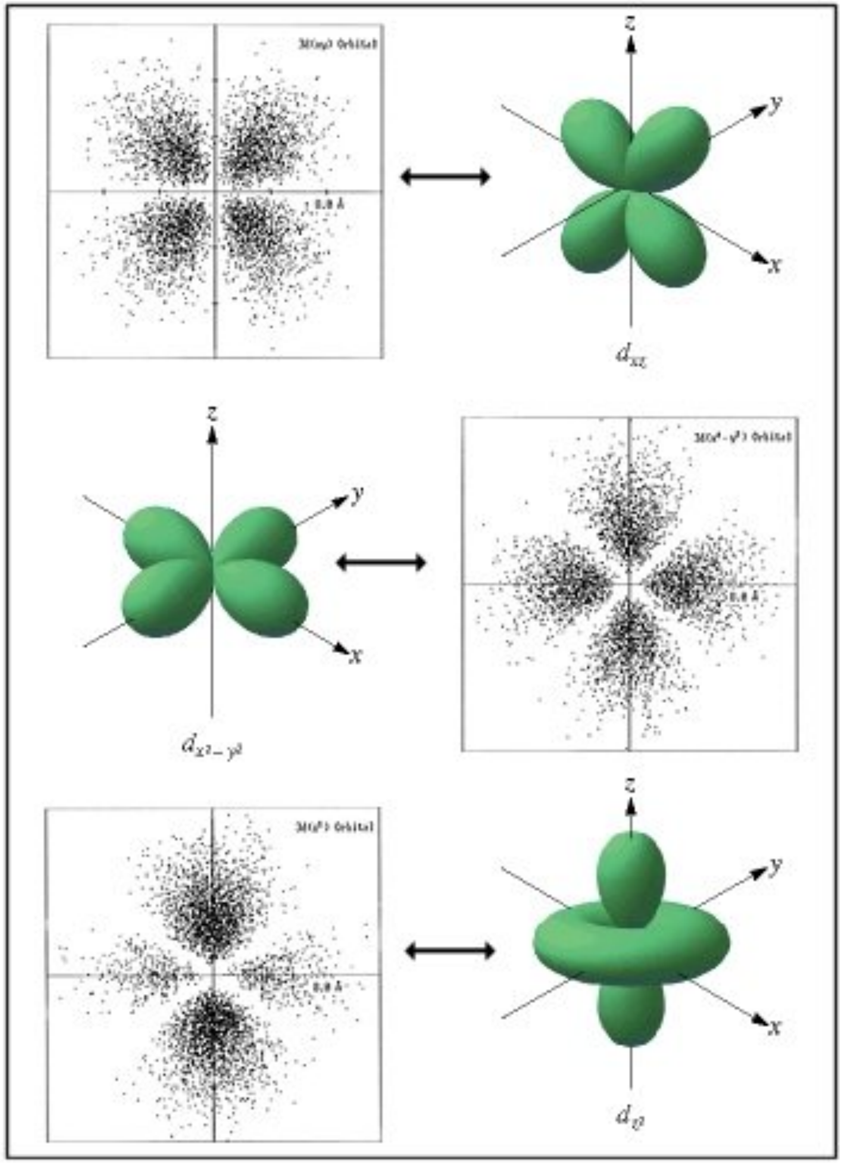
$$3d_{xy} = N_5\rho^2 \sin^2\theta\sin 2\phi e^{-\rho/3}$$

Angular Part



Blue: -ve

Yellow: +ve



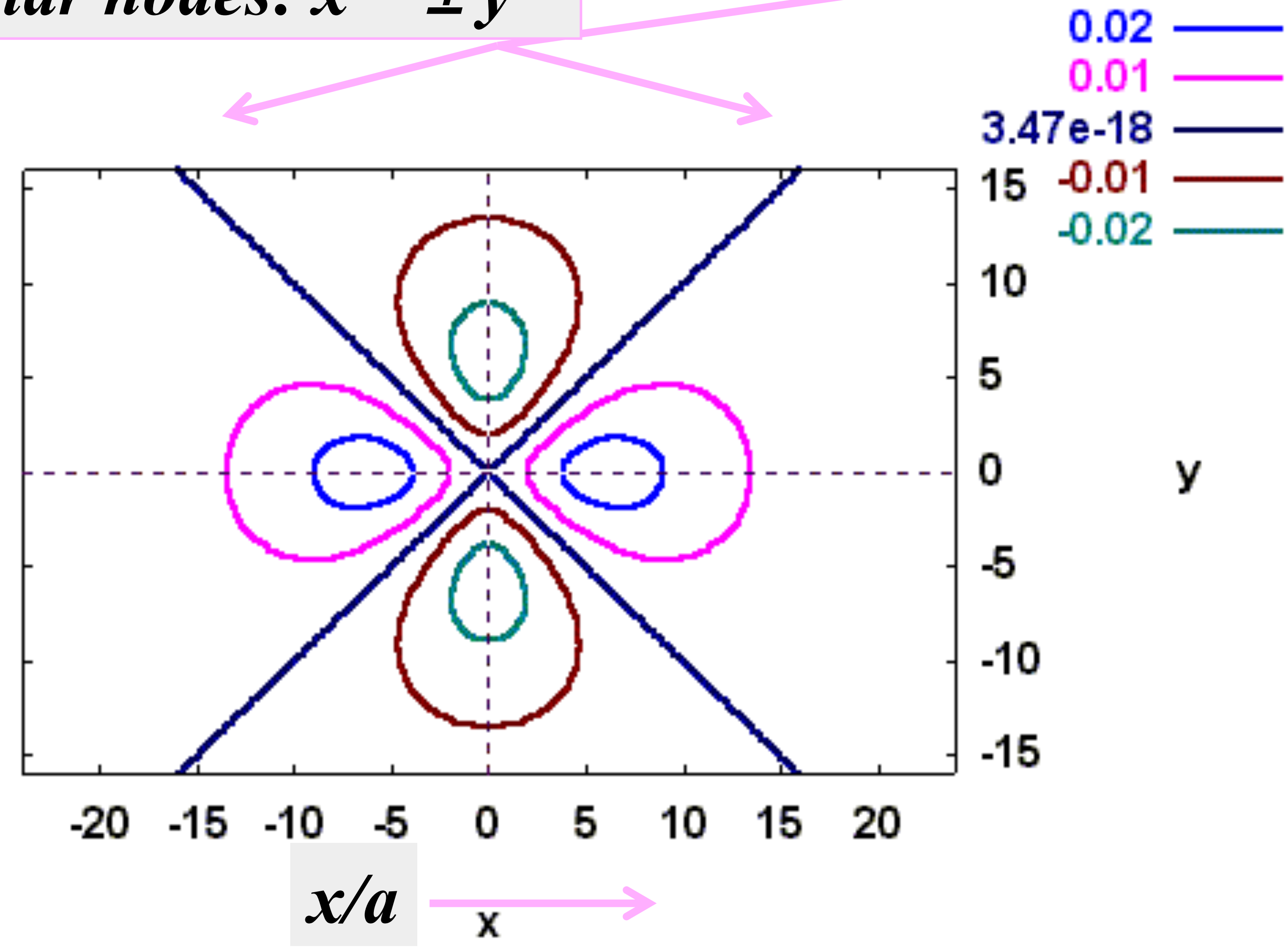
Angular + Radial

Why we called it $\Psi_{3d_{x^2-y^2}}$?

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

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

Angular nodes: $x = \pm y$



y/a

x/a

Surface plot of Ψ and Ψ^2 for 3d

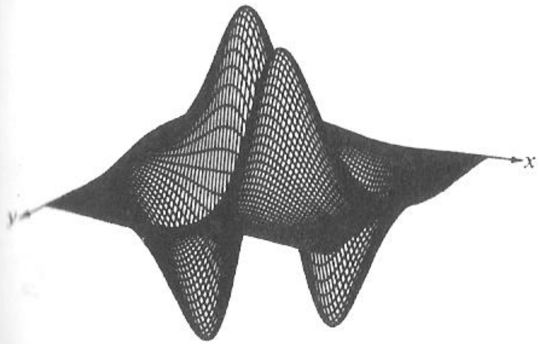


FIGURE 5-16
Surface plot of the $3d_{xy}$ wavefunction (orbital) in the *xy* plane for the hydrogen atom. Compare the hills and pits of this figure with the positive and negative lobes shown in Fig. 5-13.

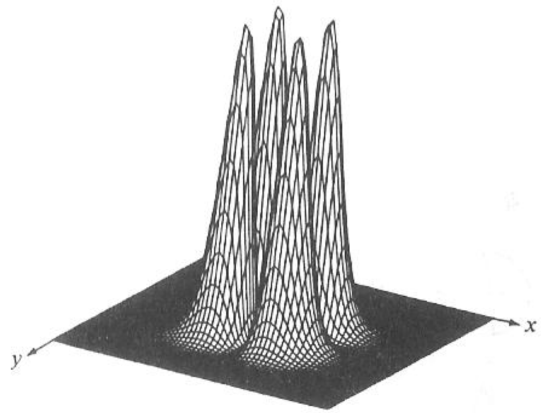


FIGURE 5-17
Surface plot of $(3d_{xy})^2$, the probability density associated with the $3d_{xy}$ wavefunction of the hydrogen atom. Note that the pits of Fig. 5-16 now appear as hills.

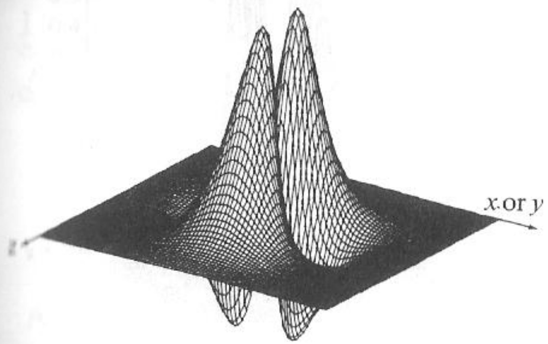


FIGURE 5-14
Surface plot of the $3d_{z^2}$ wavefunction (orbital) in the *yz* plane for the hydrogen atom. The large hills correspond to the positive lobes of Fig. 5-13 and the small pits correspond to the negative lobes of Fig. 5-13.

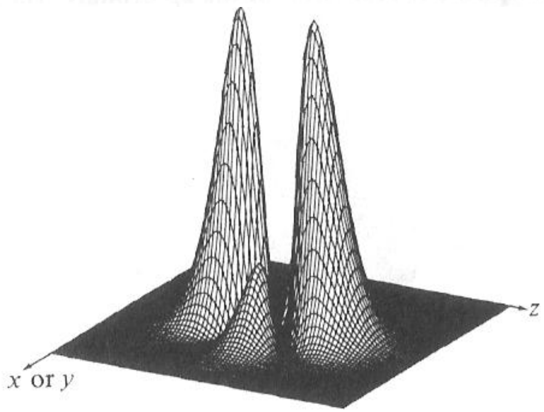
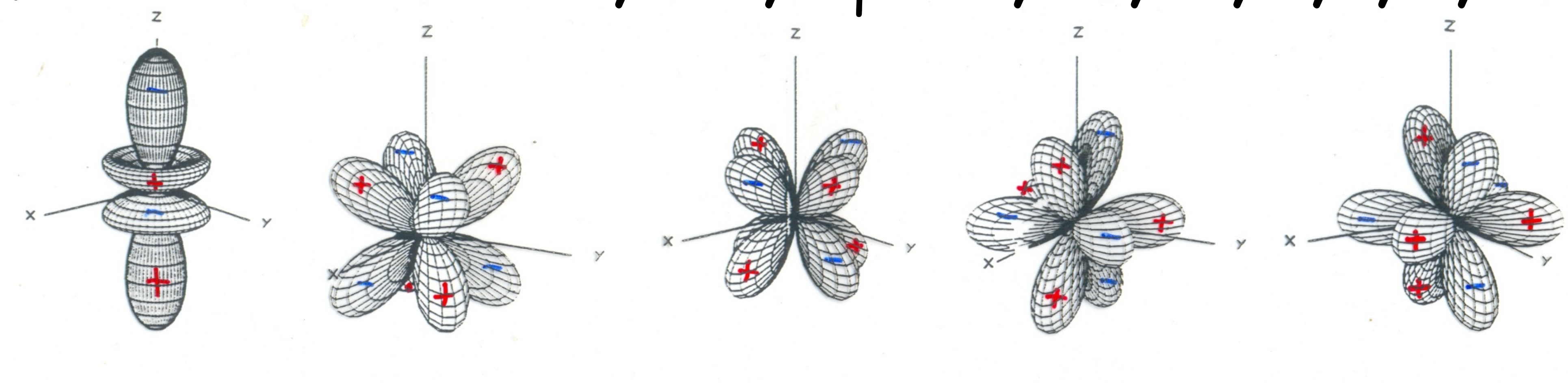
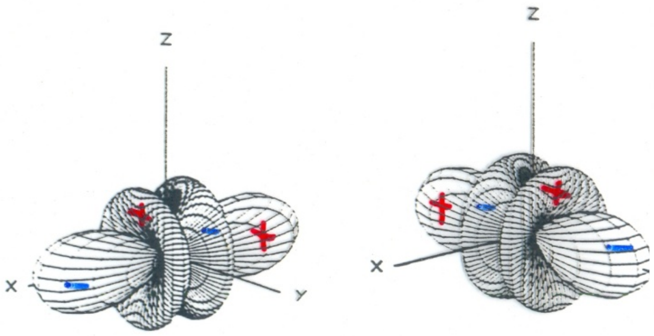


FIGURE 5-15
Surface plot of $(3d_{z^2})^2$, the probability density associated with the $3d_{z^2}$ orbital of the hydrogen atom. The figure has been rotated 90° from that of Fig. 5-14 in order to show the small hill more clearly; the second hill is hidden behind the right-hand large hill.

f-orbitals: n=4, l=3, m_l=-3,-2,-1,0,1,2,3



f_{z^3} f_{xyz} $f_{z(x^2-y^2)}$ $f_{x(y^2-z^2)}$ $f_{y(z^2-x^2)}$



f_{x^3} f_{y^3}

$$f_{x^3}: \sqrt{\frac{7}{16\pi}}\sin\theta\cos\phi\,(5\sin^2\theta\cos^2\phi-3);\ \gamma(X,39.23^o),\sigma(Y,Z),\gamma(-X,39.23^o)$$

$$f_{y^3}: \sqrt{\frac{7}{16\pi}}\sin\theta\ \sin\phi(5\sin^2\theta\ \sin^2\phi-3);\quad \gamma(Y,39.23^o),\sigma(X,Z),\gamma(-Y,39.23^o)$$

$$f_{z^3}: \sqrt{\frac{7}{16\pi}}\cos\theta(5\cos^2\theta-3);\quad \gamma(Z,39.23^o),\sigma(X,Y),\gamma(-Z,39.23^o)$$

$$f_{z(x^2-y^2)}: \sqrt{\frac{105}{16\pi}}\sin^2\theta\cos\theta\cos2\phi;\quad \phi=45^o,\sigma(X,Y),\ \phi=135^o$$

$$f_{y(z^2-x^2)}: \sqrt{\frac{105}{16\pi}}\sin\theta\sin\phi\,(\cos^2\theta-\sin^2\theta\cos^2\phi);\sigma(Y,d(Z,X)),\sigma(X,Z),\sigma(Y,d(-Z,X$$

$$f_{x(y^2-z^2)}: \sqrt{\frac{105}{16\pi}}\sin\theta\cos\phi(-\cos^2\theta+\sin^2\theta\sin^2\phi);\sigma(X,d(Y,Z)),\sigma(Y,Z),\sigma(X,d(-Y,Z$$

$$f_{xyz}: \sqrt{\frac{105}{16\pi}}\sin^2\theta\sin2\phi\cos\theta;\ \sigma(X,Y),\sigma(Y,Z),\sigma(X,Z)$$

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