Complete Wave function of H-Atom
(Take home messages from last class)

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

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

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

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

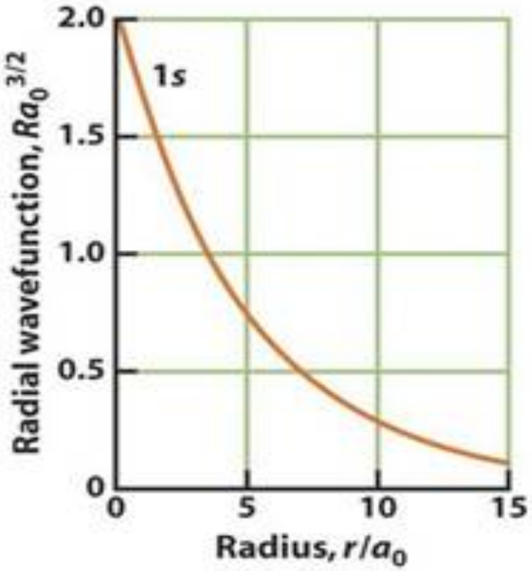
$$\psi_{2p_y} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \sin\phi = \frac{1}{\sqrt{2i}}\left(\psi_{21+1} - \psi_{21-1}\right)$$

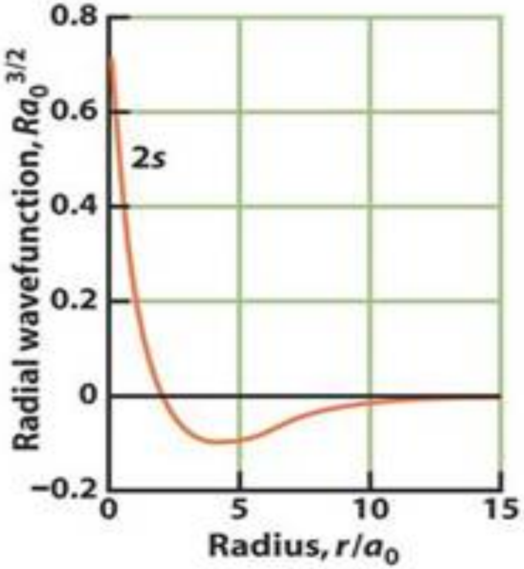
S-Orbitals ($l=0, m_l=0$)" R_{nl} and R_{nl}^2

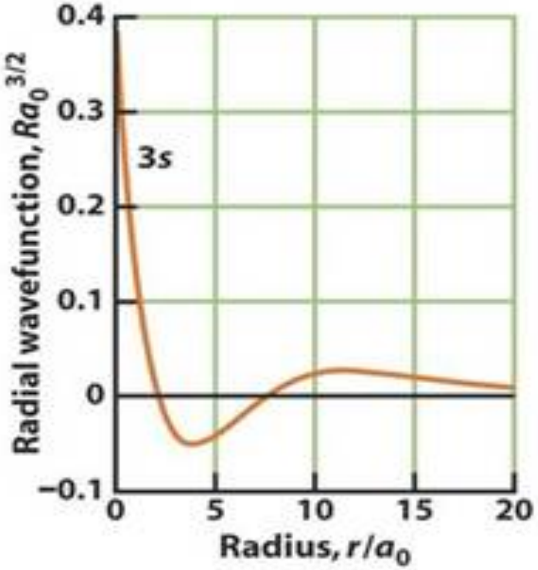
$$\Psi_{1S}^{100} = N' e^{-\rho/2}$$

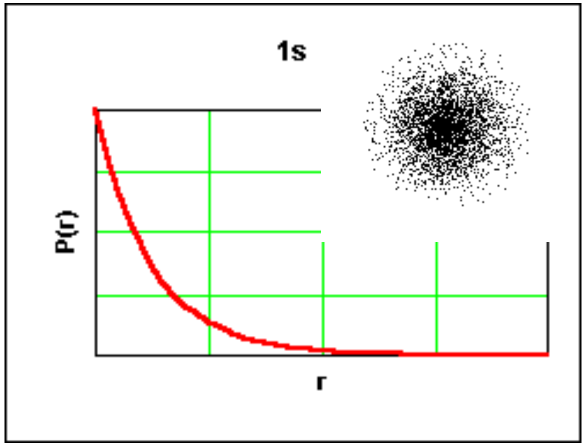
$$\Psi_{2S}^{200} = N'' (2-\rho) e^{-\rho/2}$$

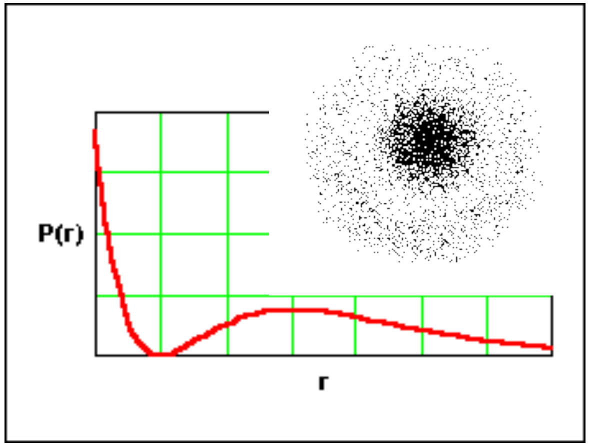
$$\Psi_{3S}^{300} = N''' (27 - 18\rho + 2\rho^2) e^{-\rho/3}$$

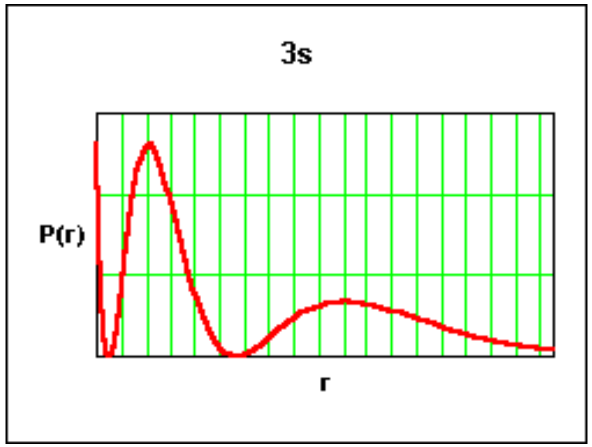




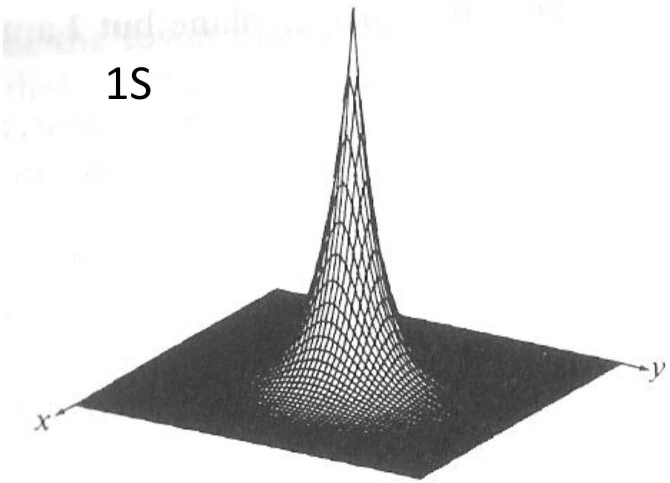


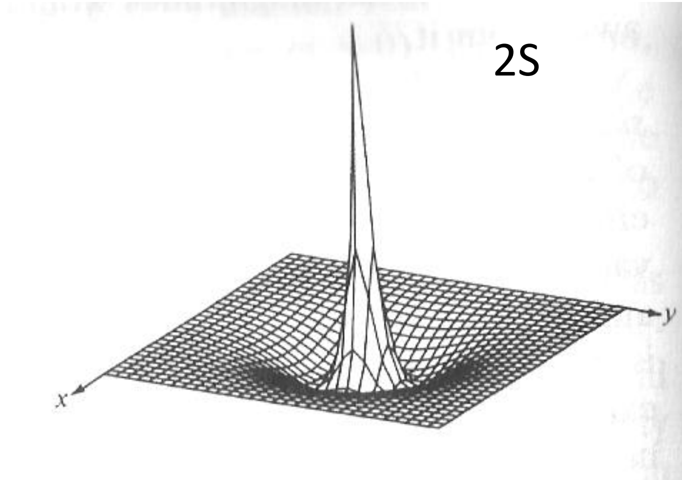


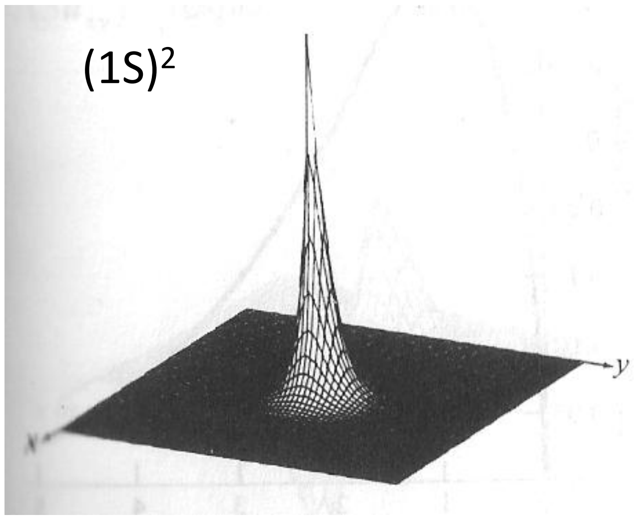


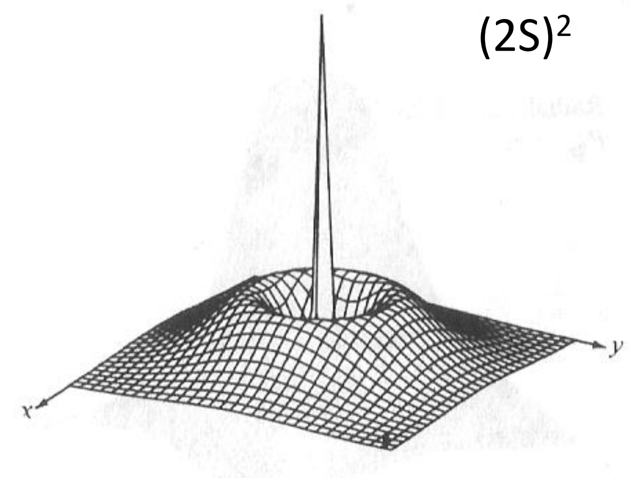


Surface plot of Ψ and Ψ^2 for S









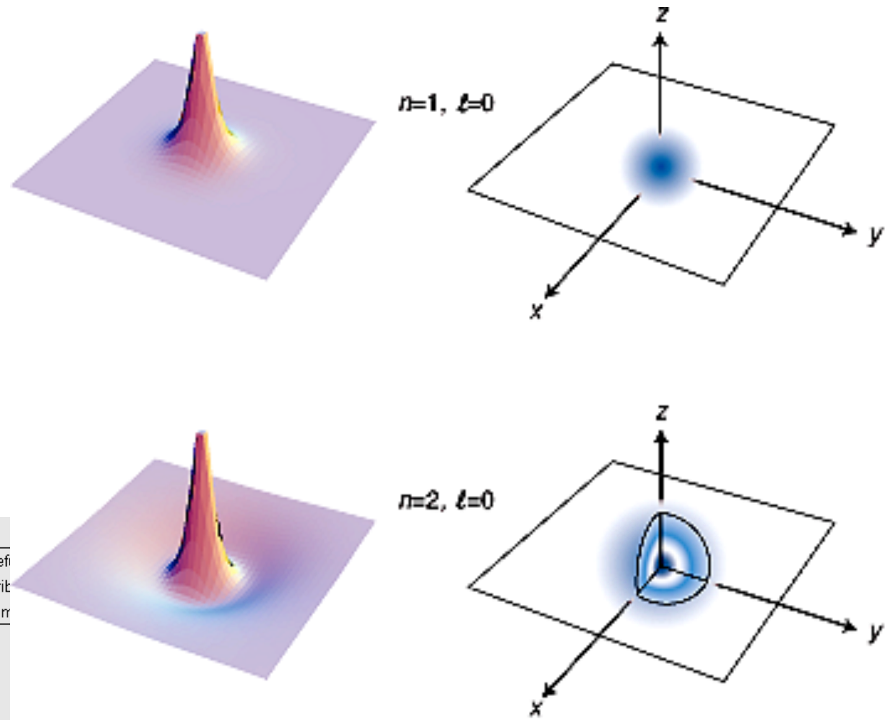
Maximum probability of finding the electron on the nucleus?

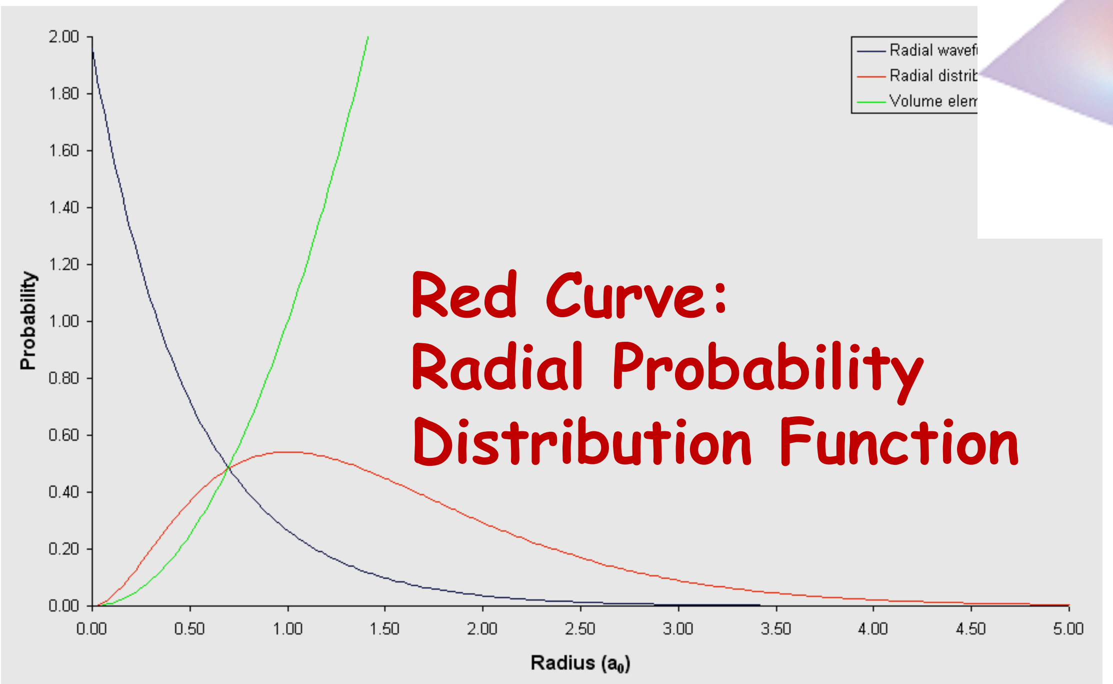
$R^2(r)$ predicts maximum probability at the center of the atom (for s)!!!

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*

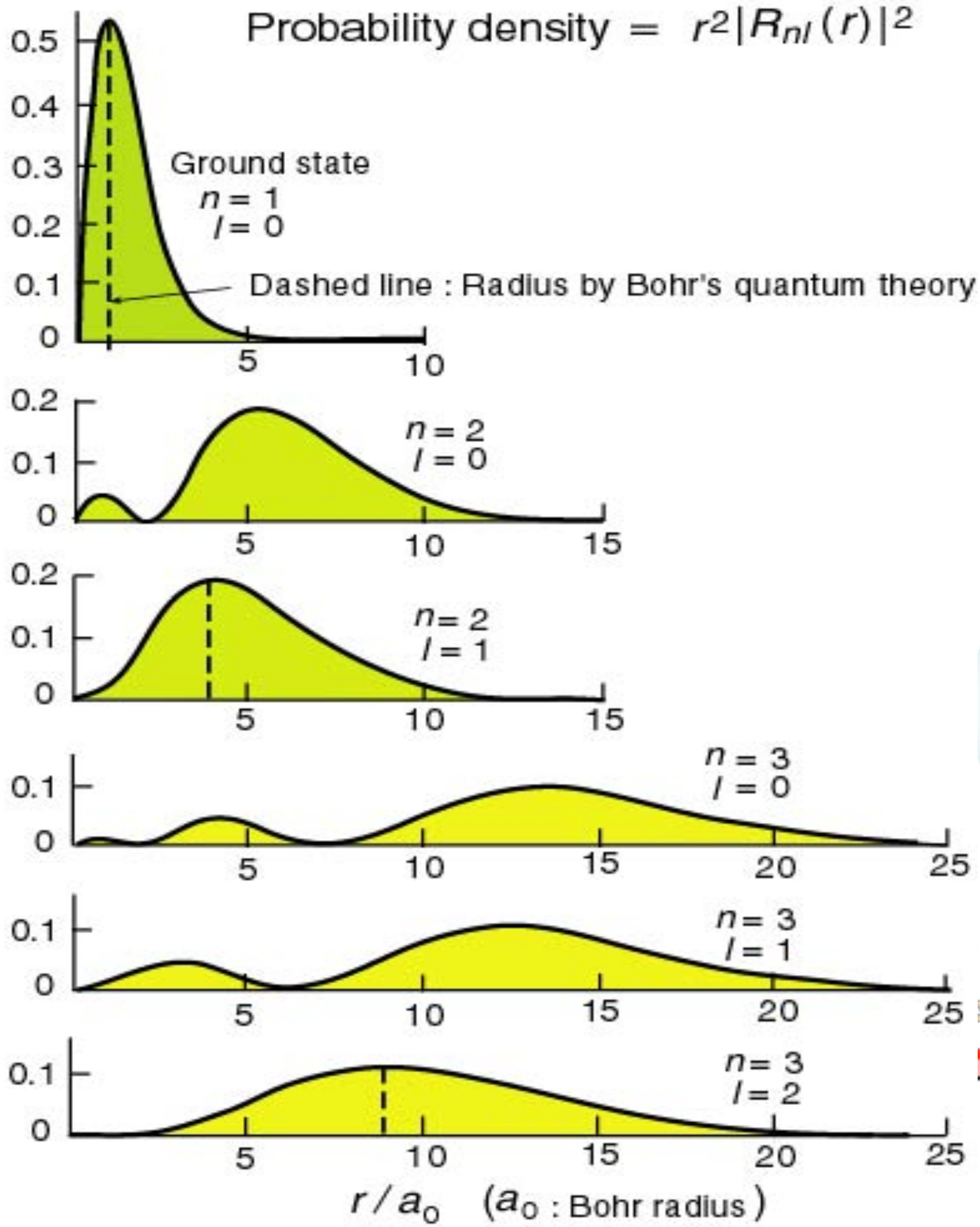
$4\pi r^2 R_{nl}^2(r)dr \rightarrow 0$ *as* $4\pi r^2 dr \rightarrow 0$

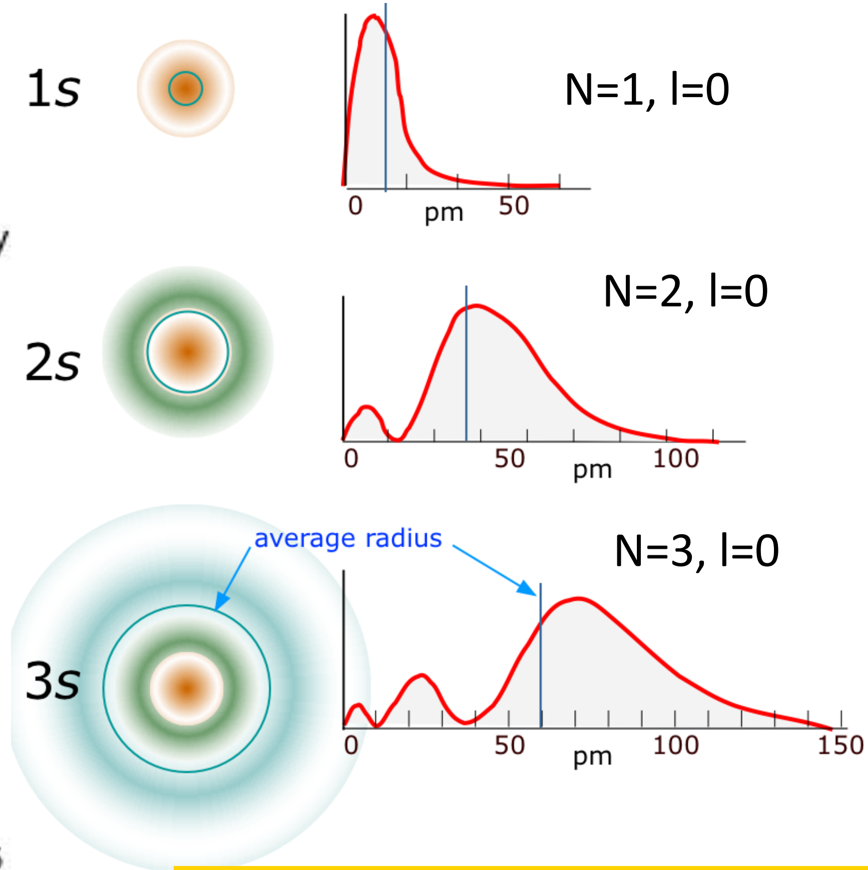




Product of an increasing function and a decreasing function: MAXIMUM

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





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

SHAPES AND SYMMETRIES OF THE ORBITALS

S ORBITALS

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

$l = 0$ 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

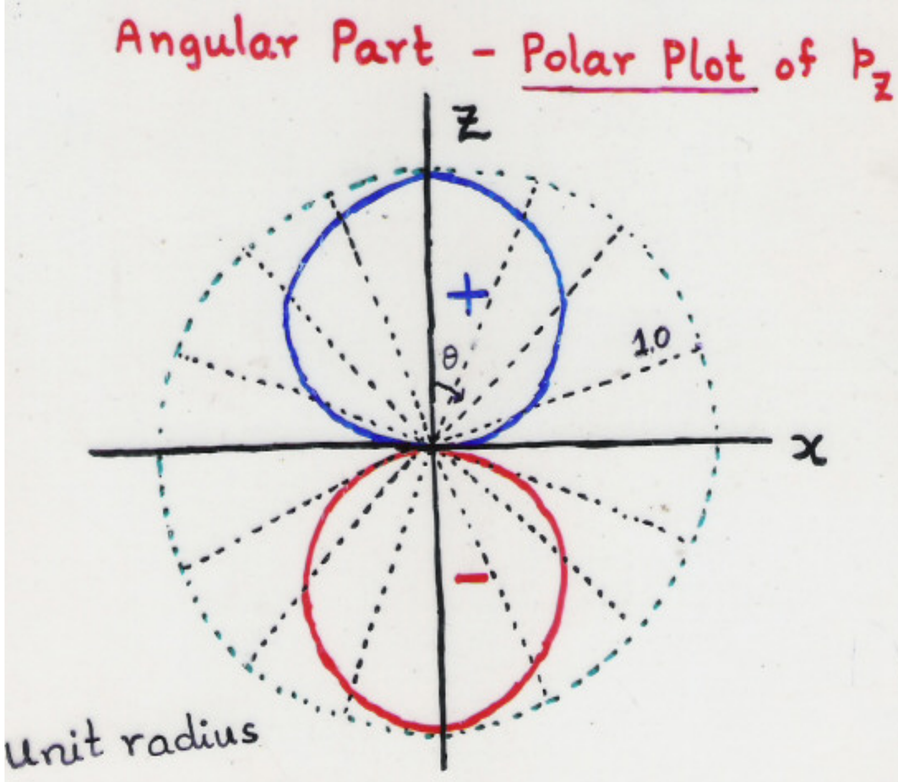
xy nodal plane - zero amplitude at nucleus

Angular part of Wave Functions

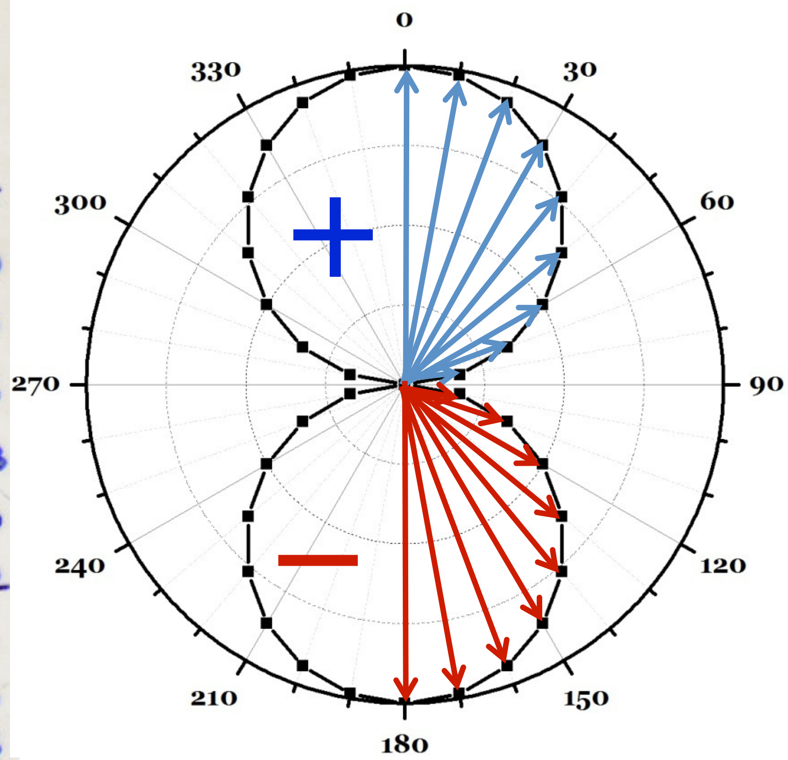
m = 0 case: $\psi_{210} = \psi_{2p_z} = \left(32\pi a_0^3\right)^{-1/2}\left(r/a_0\right)e^{-r/2a_0}\cos\theta$

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

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



θ	$\cos\theta$
10	0.985
20	0.940
30	0.866
40	0.766
50	0.643
60	0.500
70	0.342
80	0.174
120	−0.500
150	−0.866
210	−0.866
240	−0.500



Basis of Nomenclature of orbitals

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

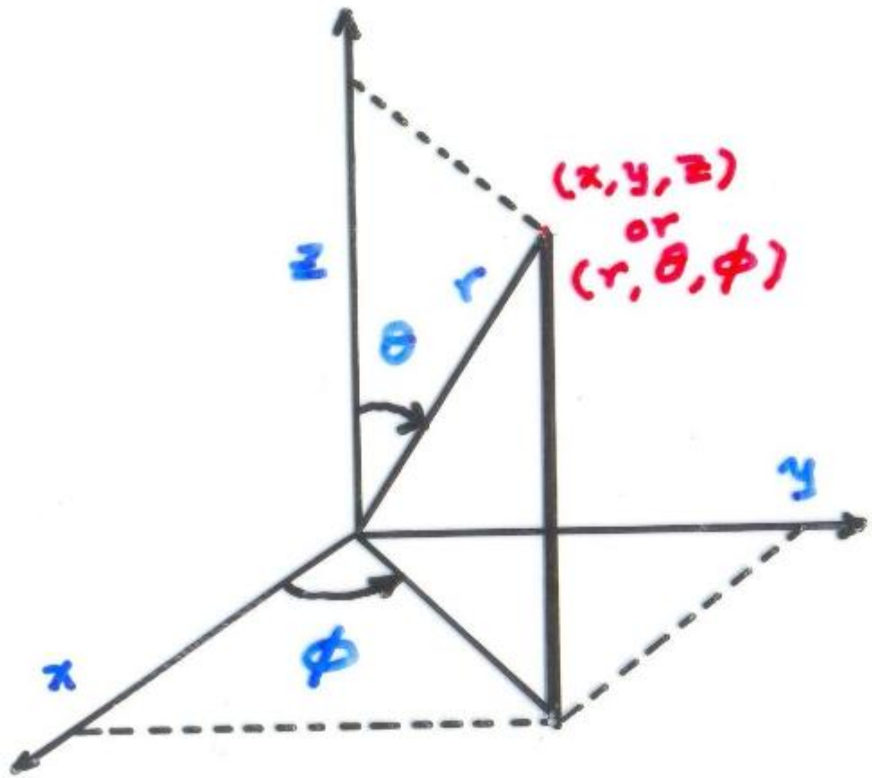
$$\Psi(2p_x) = N'\rho e^{-\rho/2}.\sin\theta.\cos\phi$$

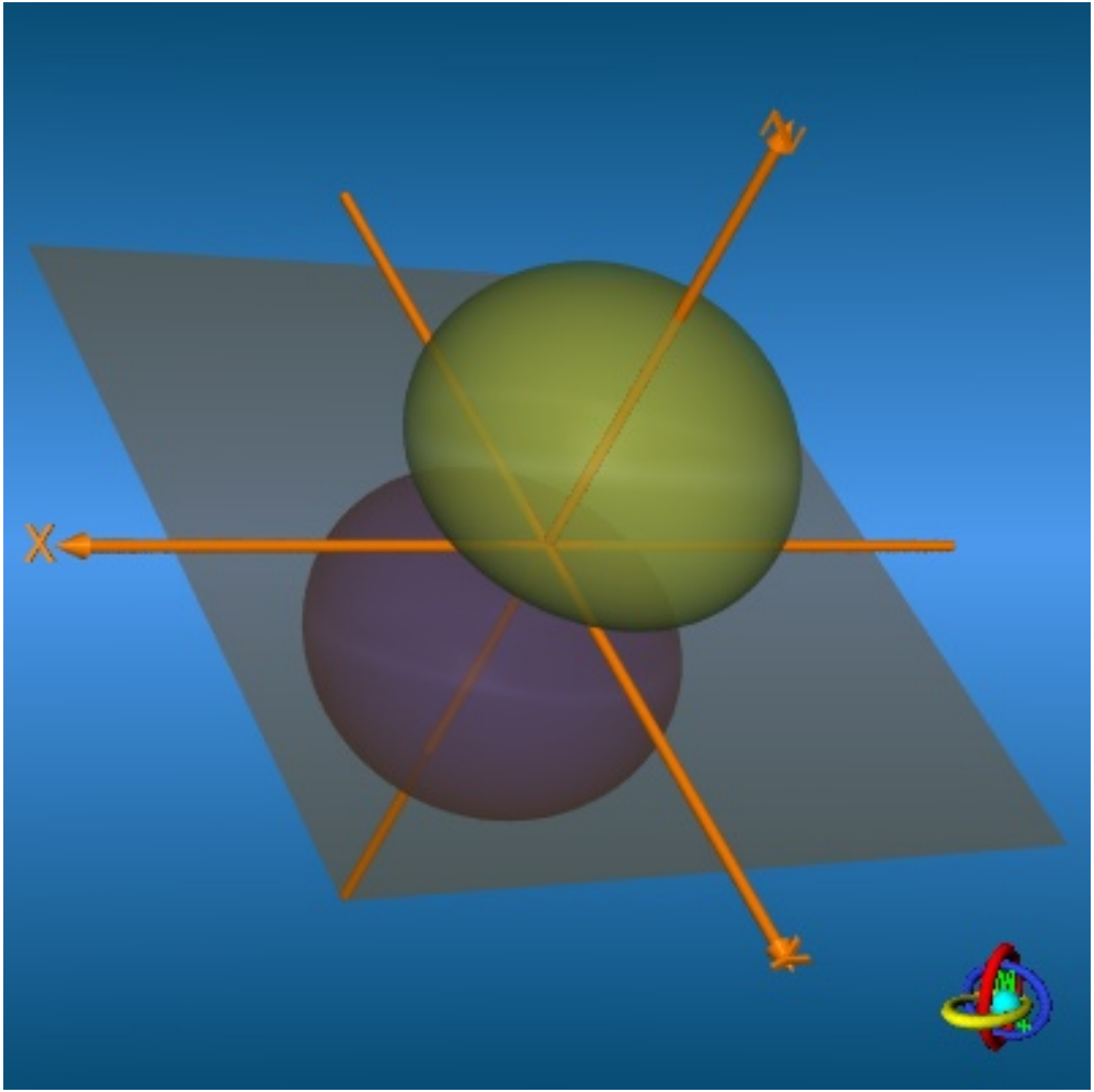
$$\Psi(2p_y) = N''\rho e^{-\rho/2}.\sin\theta.\sin\phi$$

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

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

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




X

Surface plot of Ψ and Ψ² for 2p

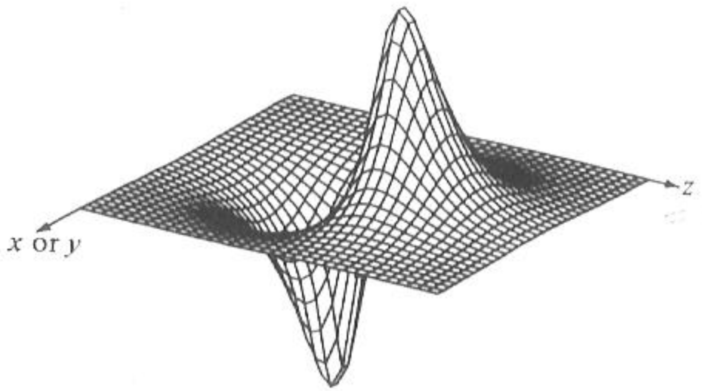


FIGURE 5-10
Surface plot of the $2p_z$ wavefunction (orbital) in the xz (or yz) plane for the hydrogen atom. The "pit" represents the negative lobe and the "hill" the positive lobe of a $2p$ orbital.

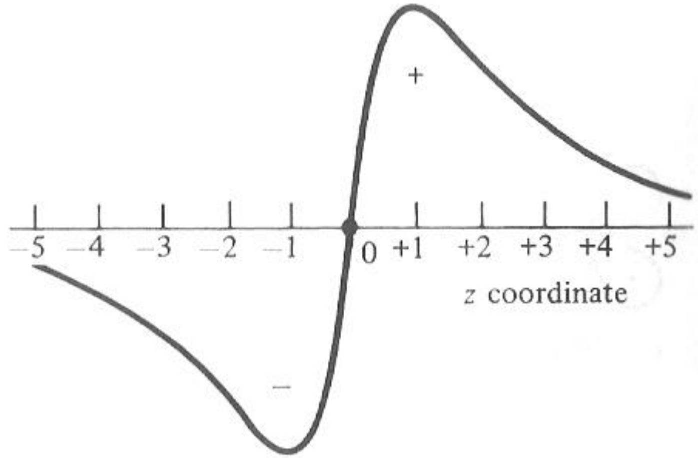


FIGURE 5-11
Profile of the $2p_z$ orbital along the z axis.

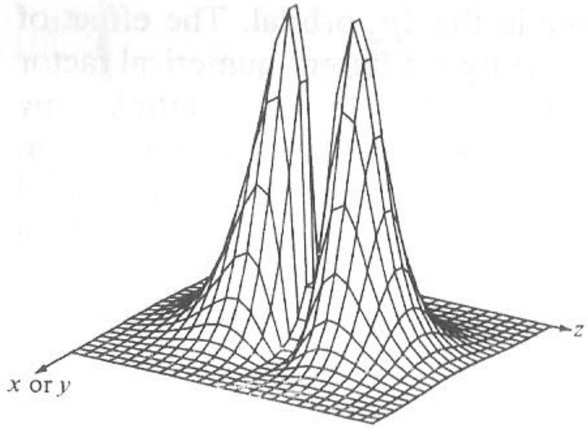
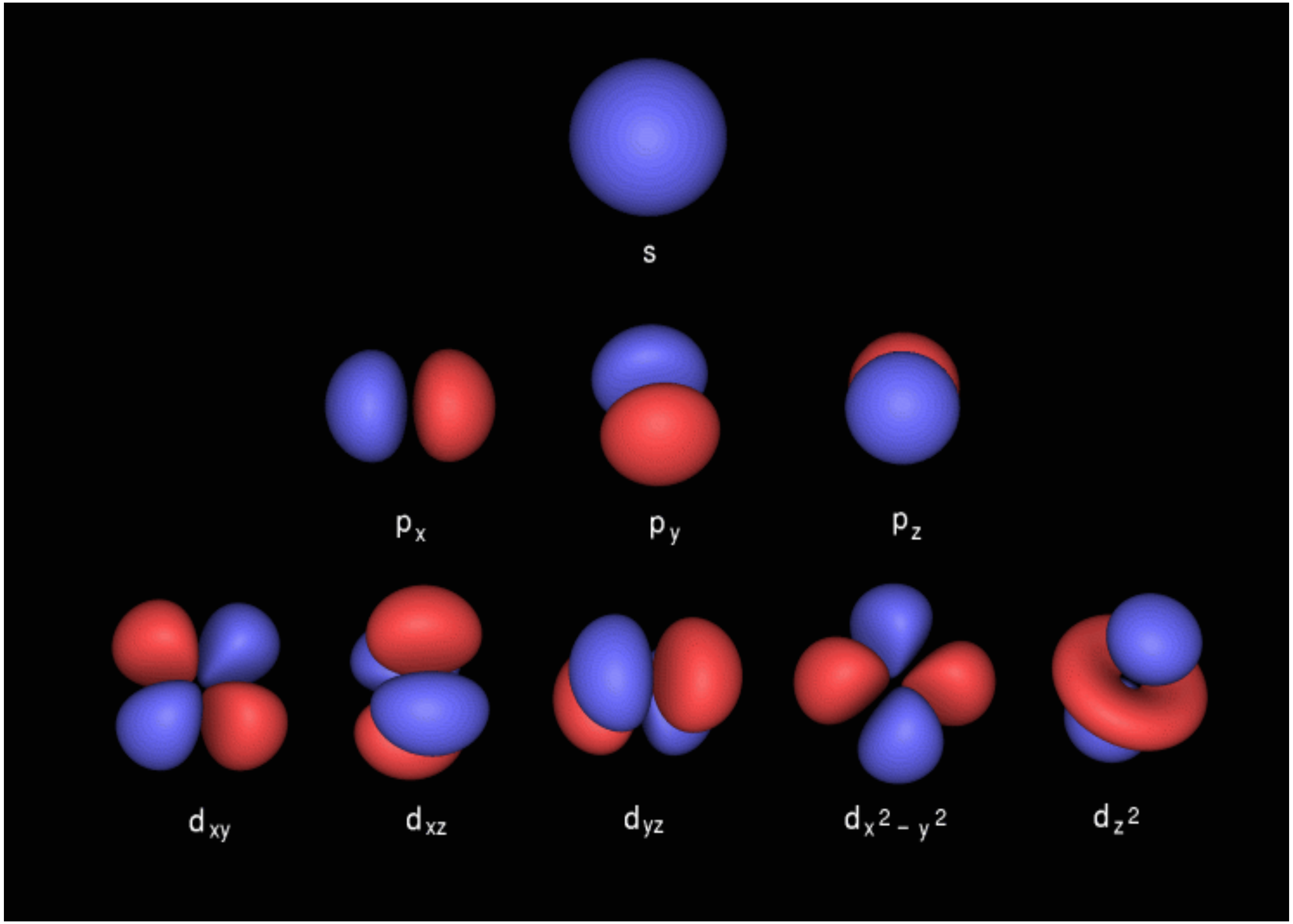


FIGURE 5-12
Surface plot of $(2p_z)^2$; the probability density represented by the $2p_z$ wavefunction of the hydrogen atom. Each of the hills represents an area in the xz (or yz) plane where the probability density is the highest. The probability density along the x (or y) axis passing through the nucleus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

So what is an orbital?



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

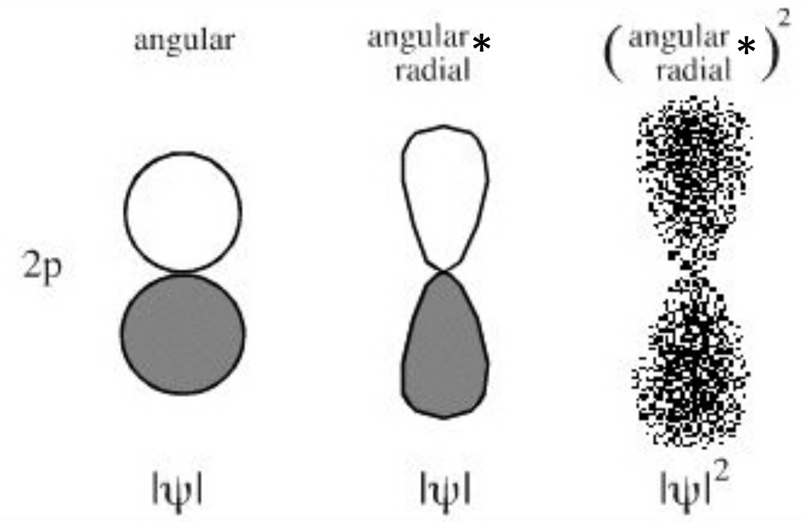
Misinterpretation of Orbital pictures

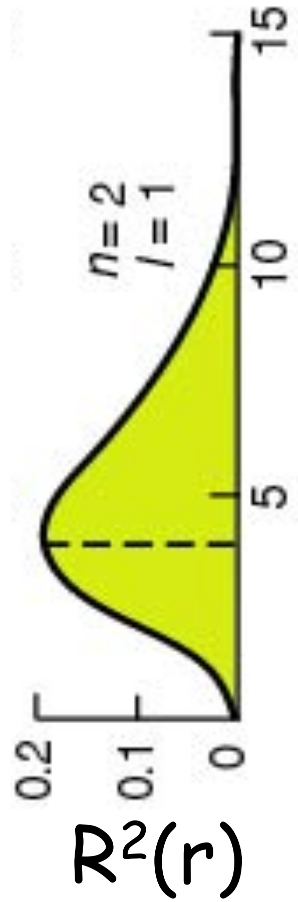
Angular plots of $\Psi(r,\theta,\phi)$ has no physical meaning – just mathematical functions - may be used to obtain information about probable electron distribution.

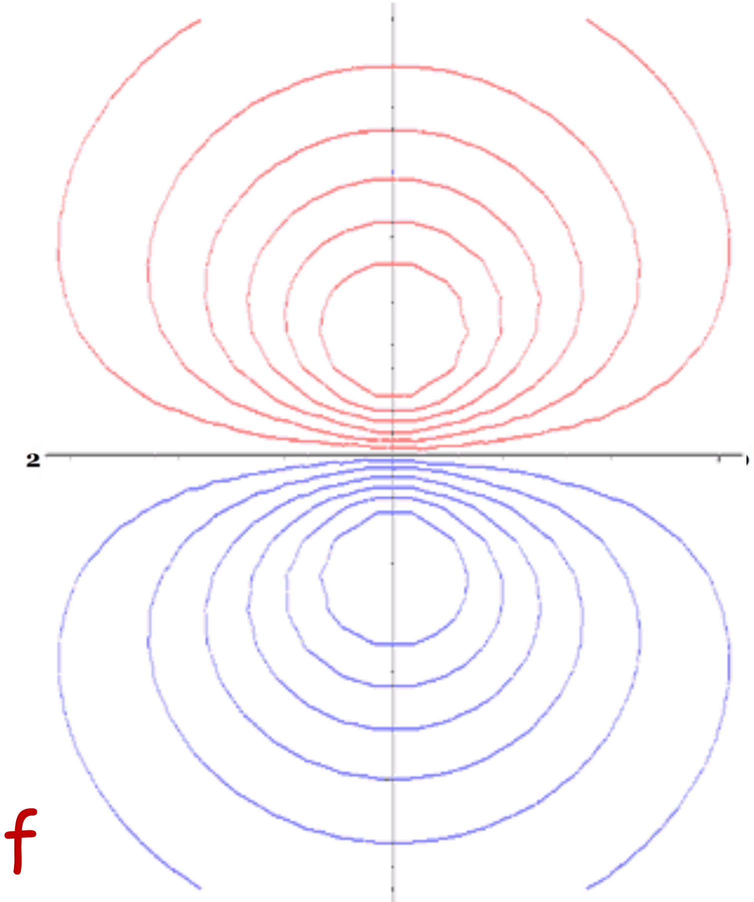
But can not be, in any way, regarded as the "picture" of an orbital. It is unfortunate that fuzzy drawings like these are often represented as "orbitals"

However, ψ^2 might provide a better intuitive picture

Angular + Radial Electron Density

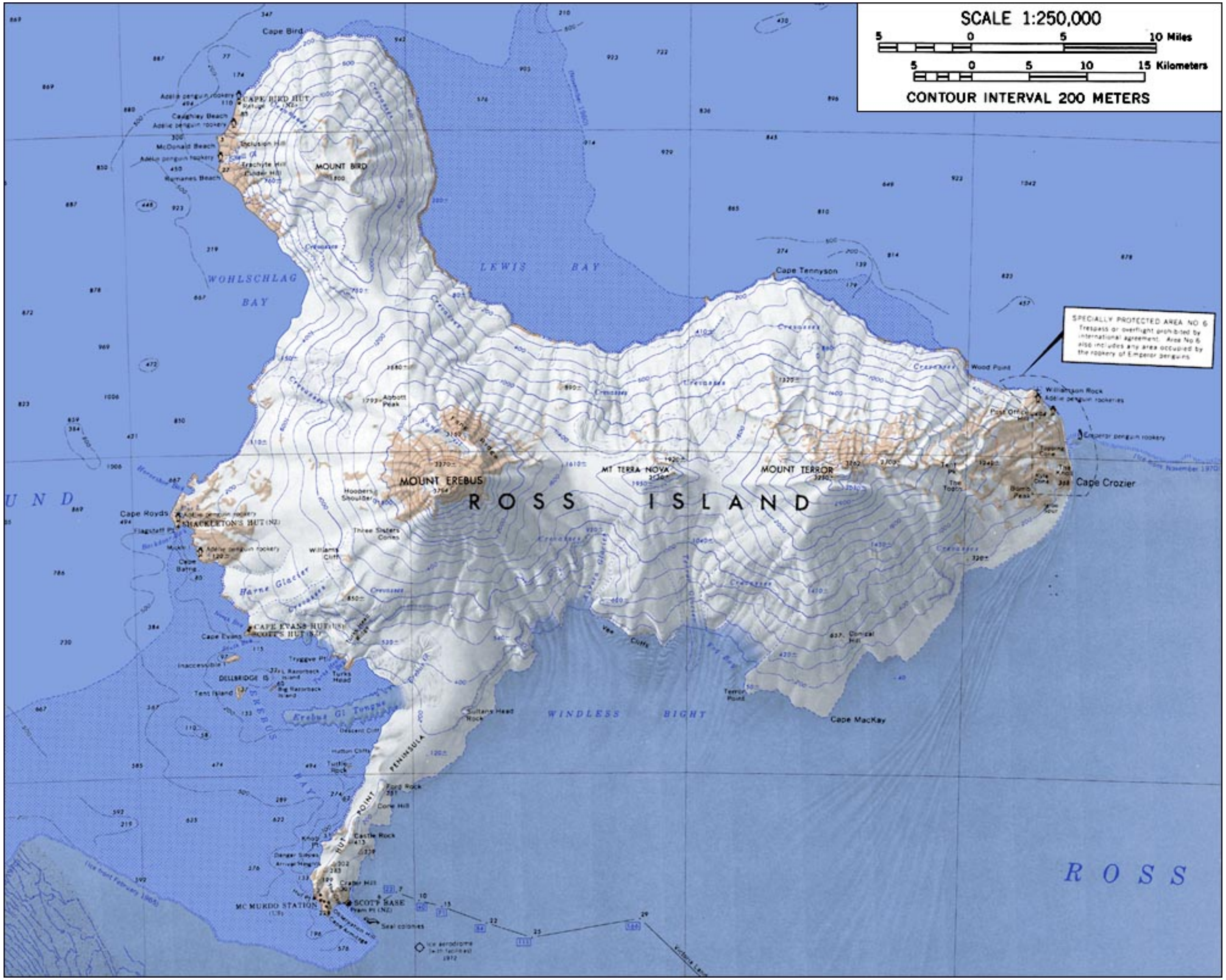




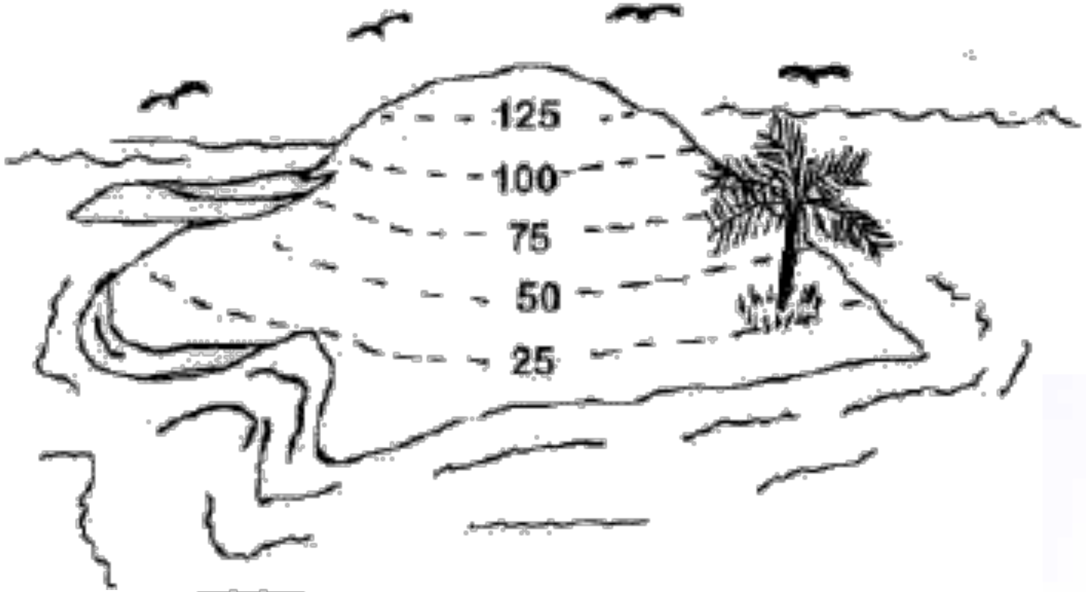


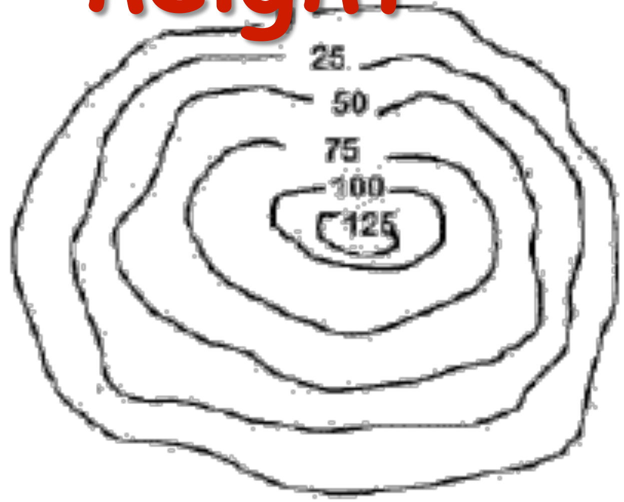
Contours of
Constant or
equal Probability/density

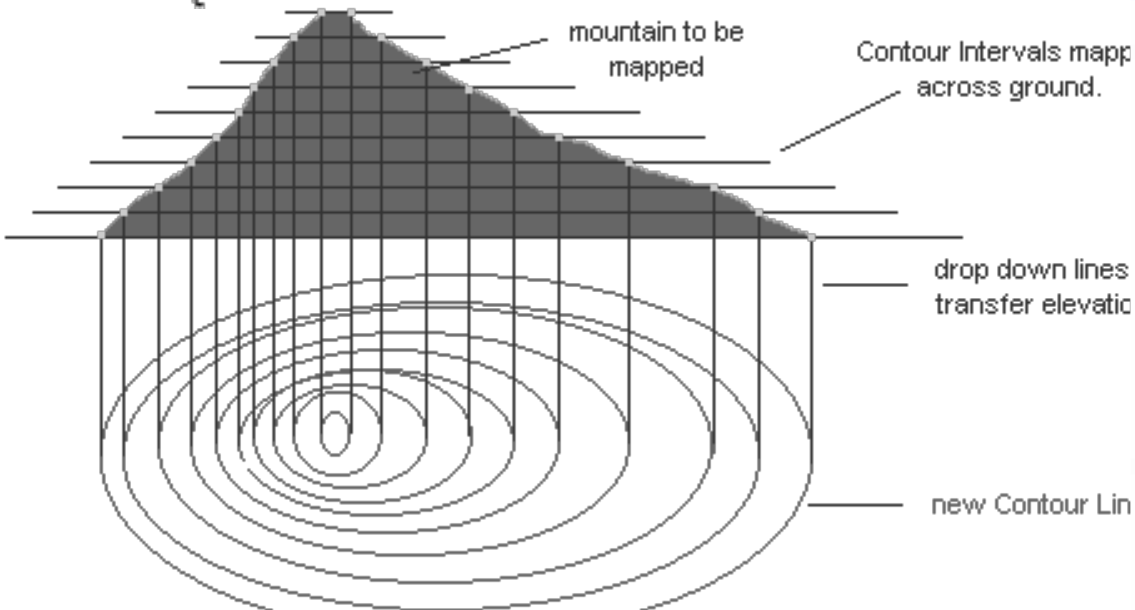
Let's look at some islands in Ocean



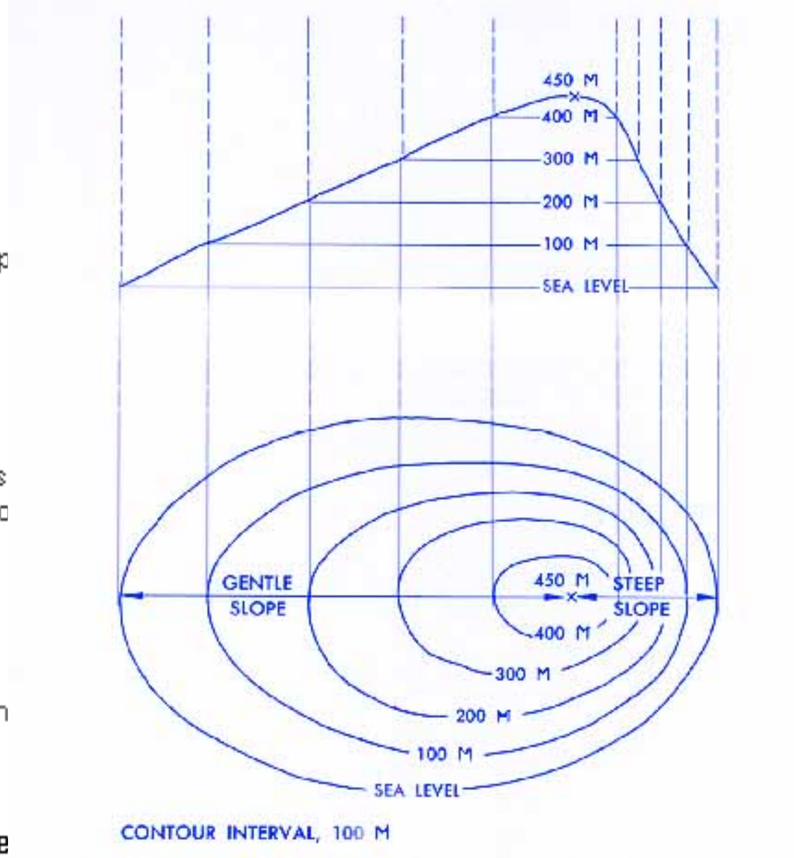
Topographic Contours - height





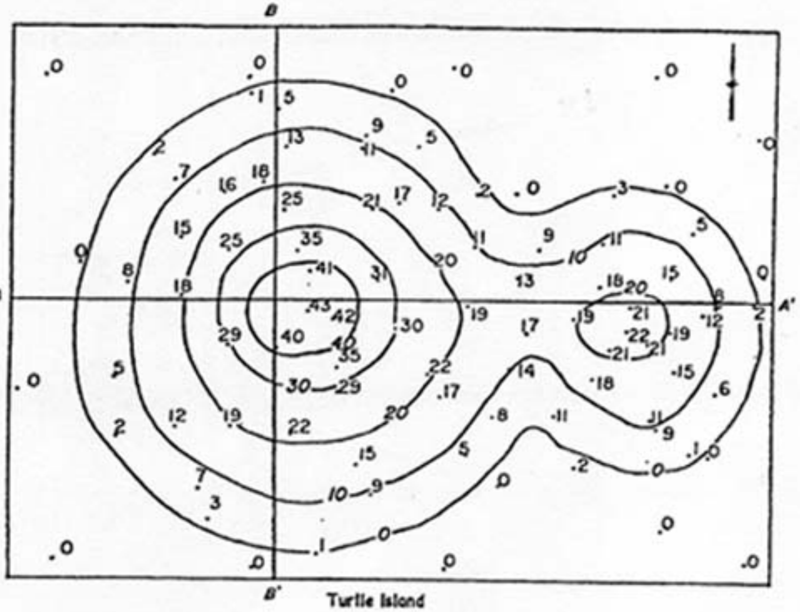


Figure

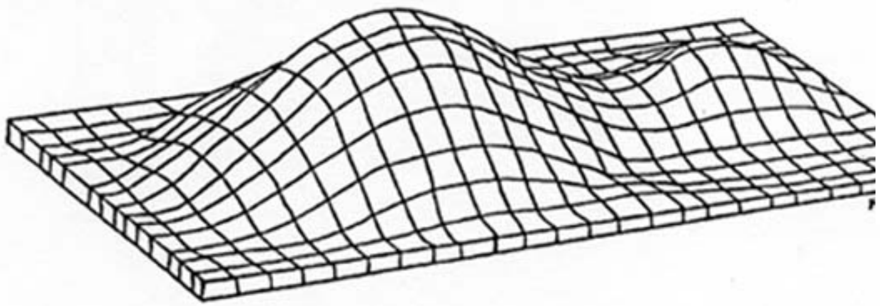


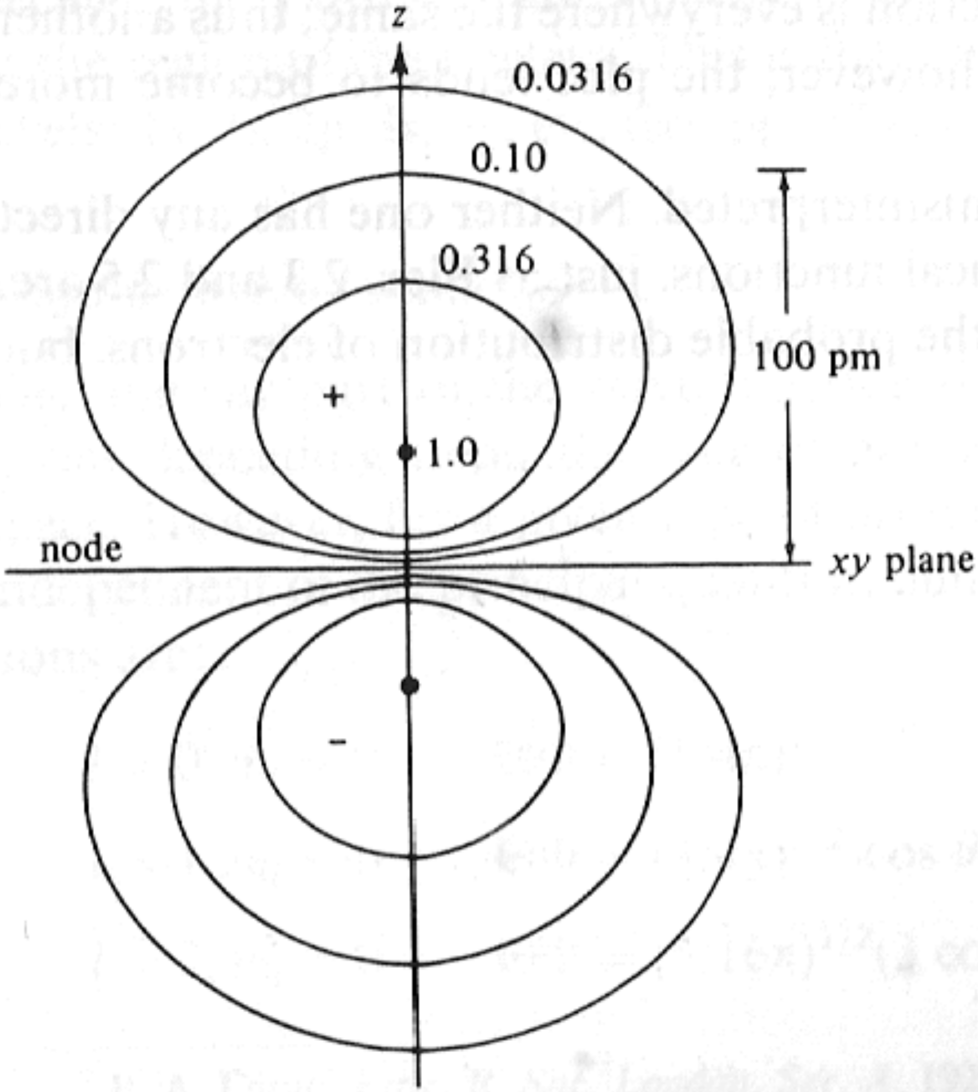
Contours of Equal probability density

Contour Map of Turtle Island



Three Dimensional Model of Turtle Island

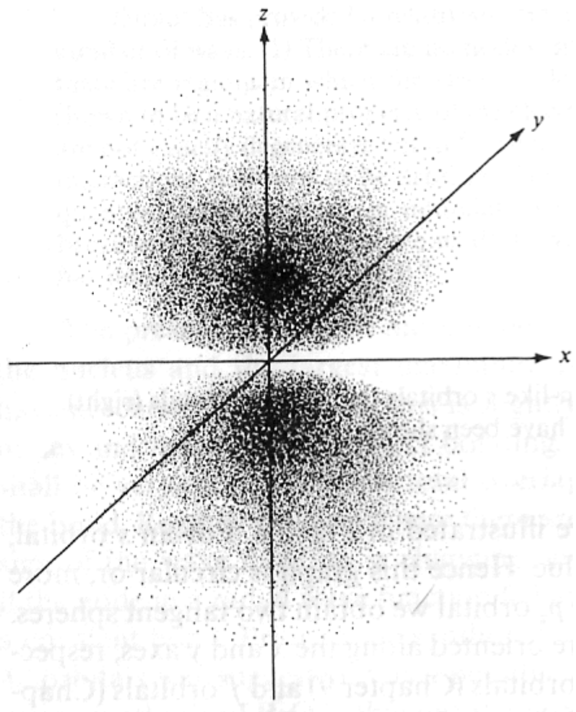




Actual Electronic Distribution

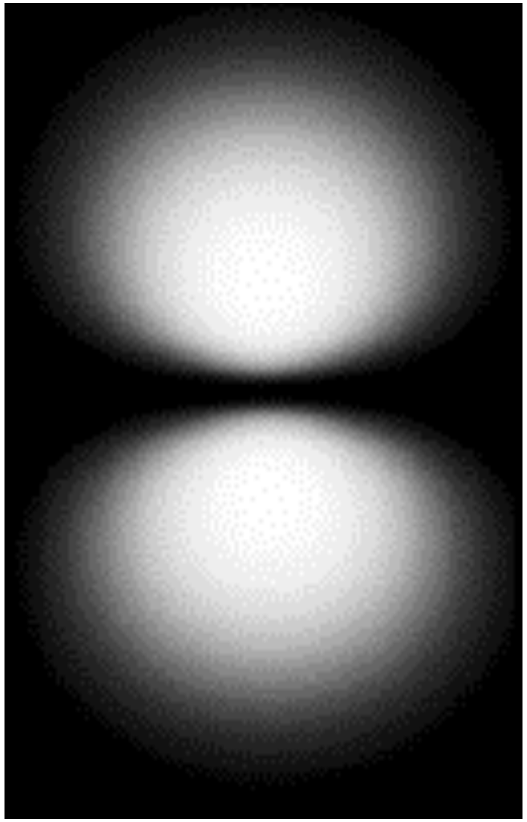
$$\Psi^2(r,\theta,\phi)dv$$

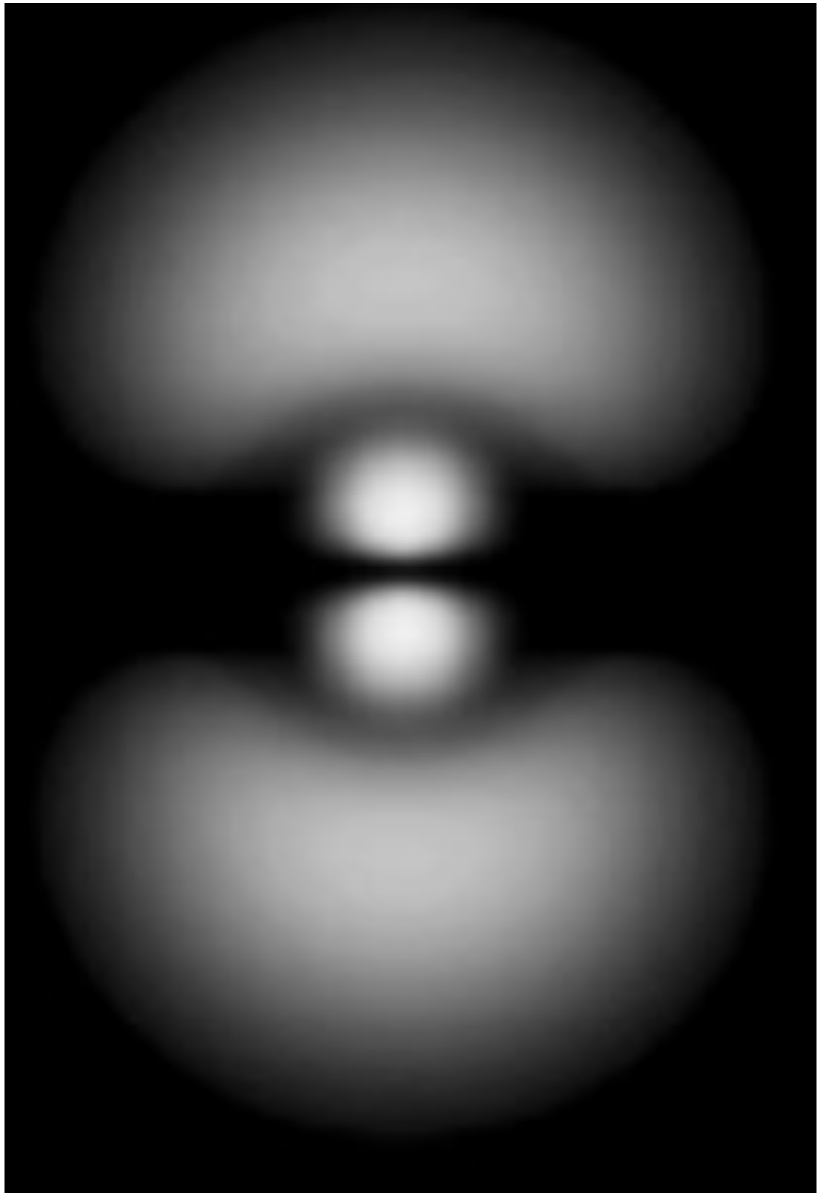
$$\Rightarrow r^2 R_{n,l}^2(r)dr \otimes Y_{l,m}^2(\theta,\phi)\, Sin\theta\, d\theta\, d\phi$$



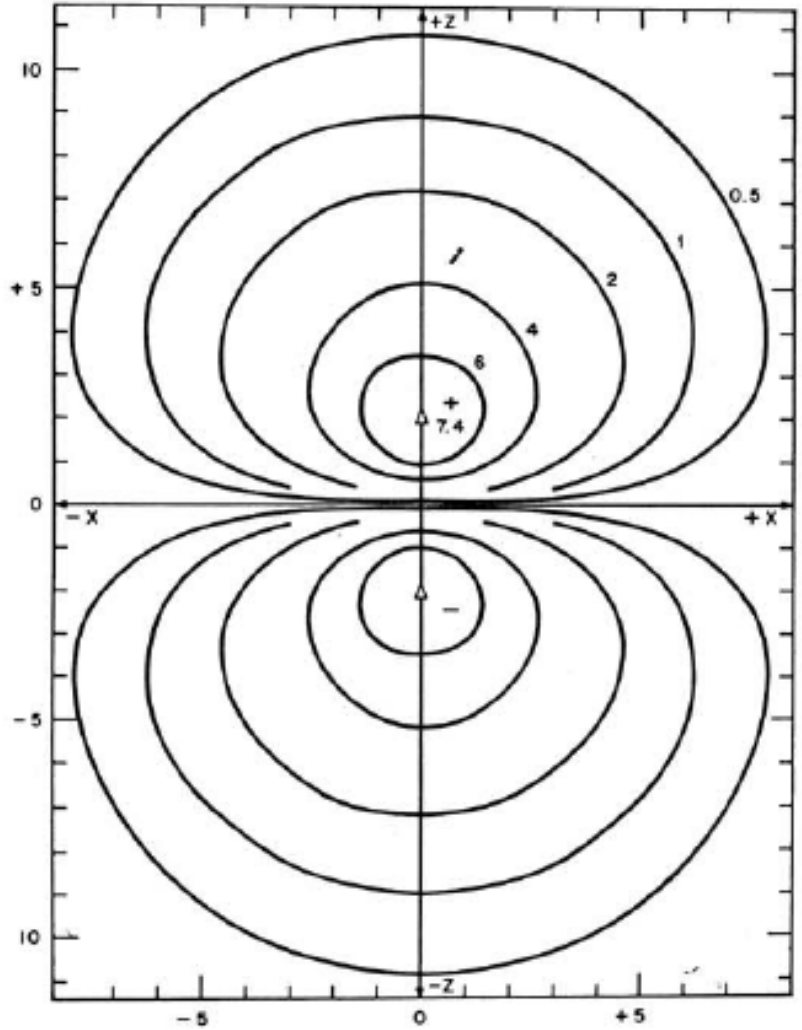
But, an "Orbital" is just a 1-e wavefunction

Angular+Radial Electron Density $2p_z$ & $3p_z$ Size and Shape!





Probability density contours: $2p_z$ & $3p_z$



. Contour lines of the normalized wave function

$\psi_{2p_z} = (1/4\sqrt{2\pi})\rho e^{-\rho/2}\cos\theta = (1/4\sqrt{2\pi})ze^{-\rho/2}$

ıbers in the figure refer to $\psi \times 10^2$. The points where ψ is at its
n are indicated by a triangle. The numbers on the coordinate

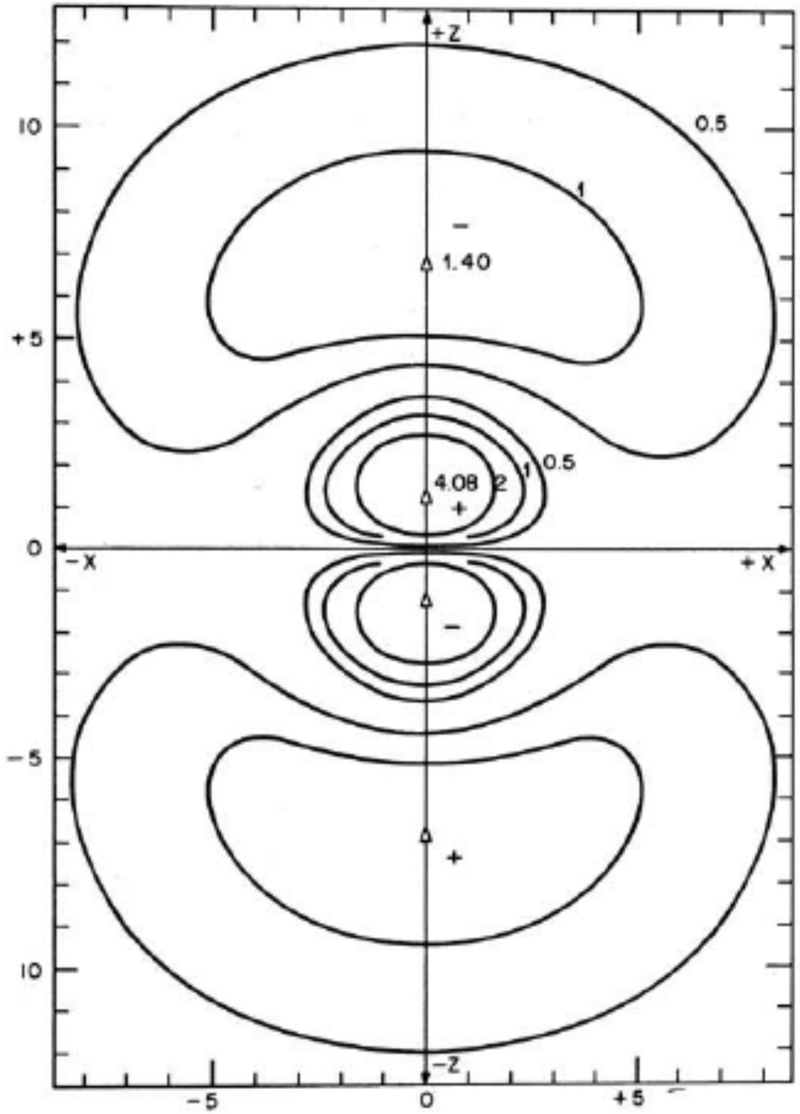


Figure 2. Contour lines of the normalized wave function

$\psi_{3p_z} = (\sqrt{2}/36\sqrt{\pi})(4-\rho)\rho e^{-\rho/2}\cos\theta = (\sqrt{2}/36\sqrt{\pi})(4-\rho)$

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

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

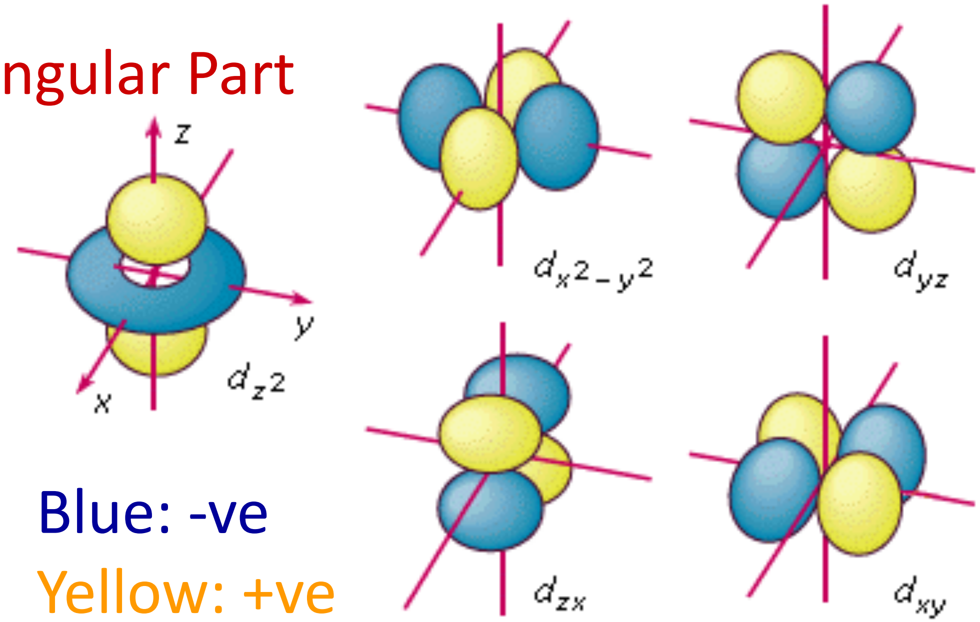
$$3d_{xz} = N_2\rho^2 \sin\theta\cos\theta\cos\phi e^{-\rho/3}$$

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

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

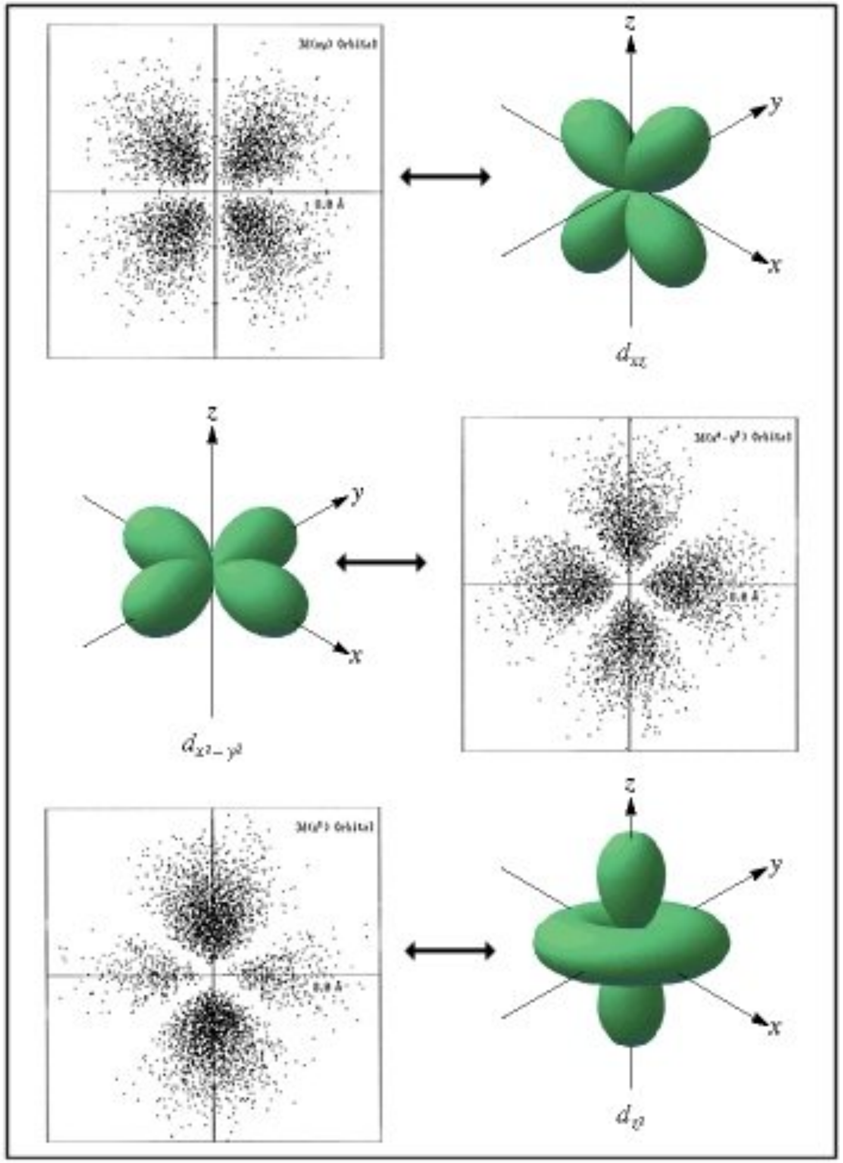
$$3d_{xy} = N_5\rho^2 \sin^2\theta\sin 2\phi e^{-\rho/3}$$

Angular Part



Blue: -ve

Yellow: +ve



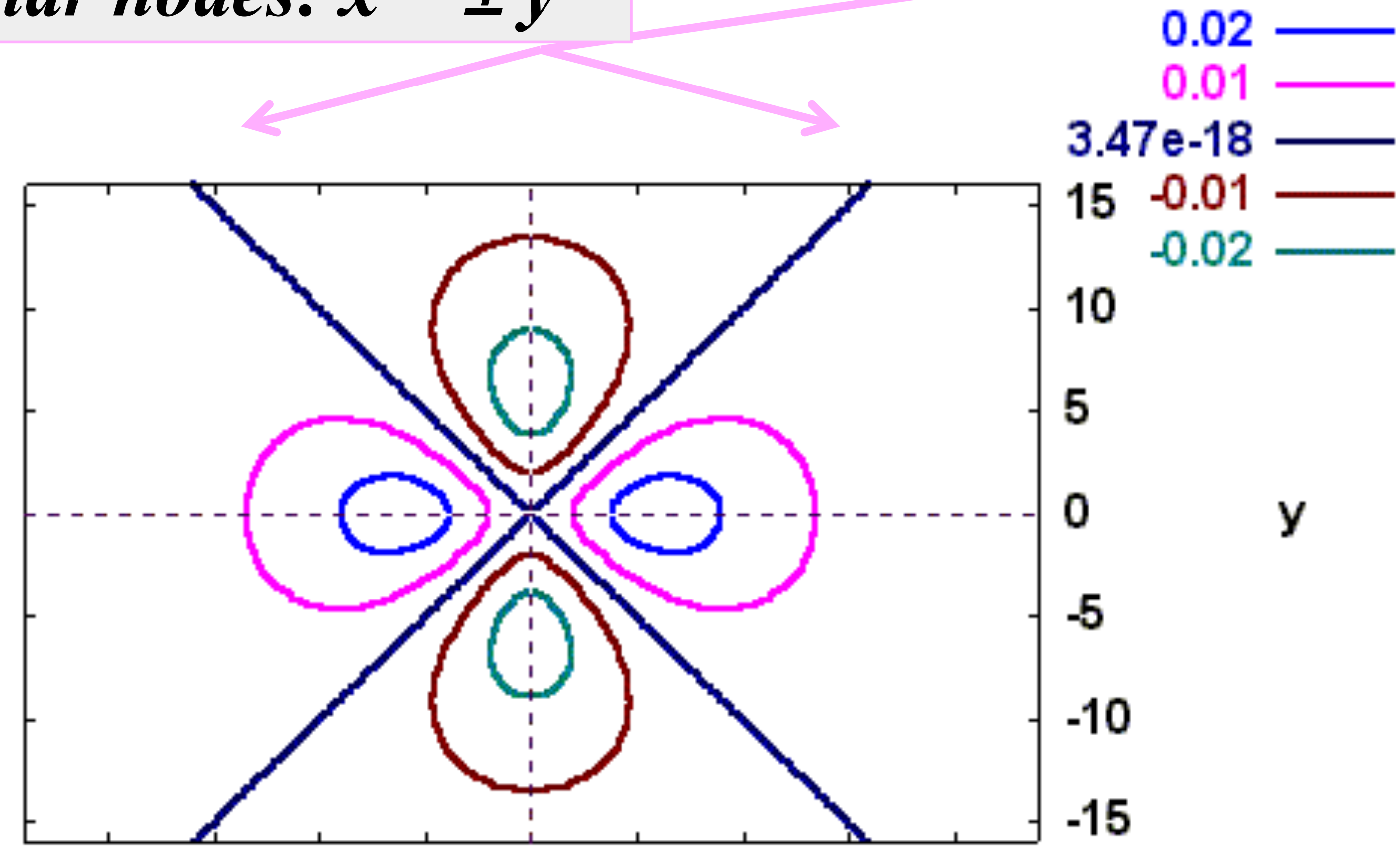
Angular + Radial

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

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

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

Angular nodes: $x = \pm y$



y/a

x/a

Surface plot of Ψ and Ψ^2 for 3d

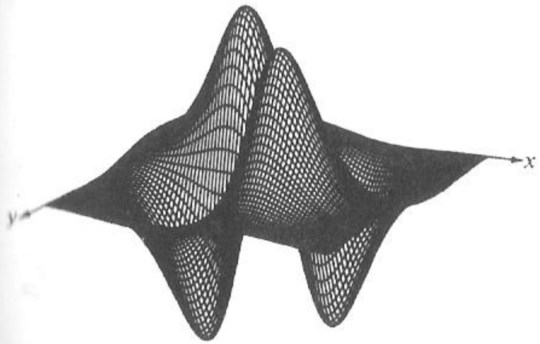


FIGURE 5-16
Surface plot of the $3d_{xy}$ wavefunction (orbital) in the xy plane for the hydrogen atom. Compare the hills and pits of this figure with the positive and negative lobes shown in Fig. 5-13.

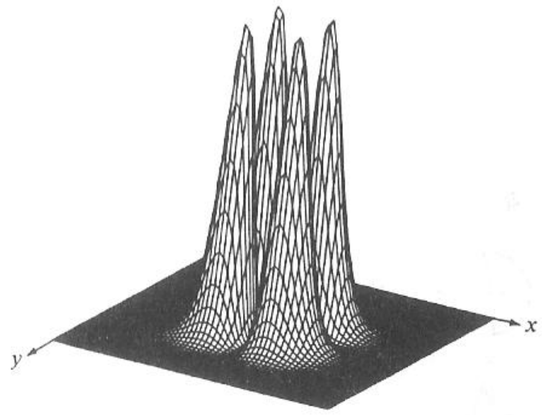


FIGURE 5-17
Surface plot of $(3d_{xy})^2$, the probability density associated with the $3d_{xy}$ wavefunction of the hydrogen atom. Note that the pits of Fig. 5-16 now appear as hills.

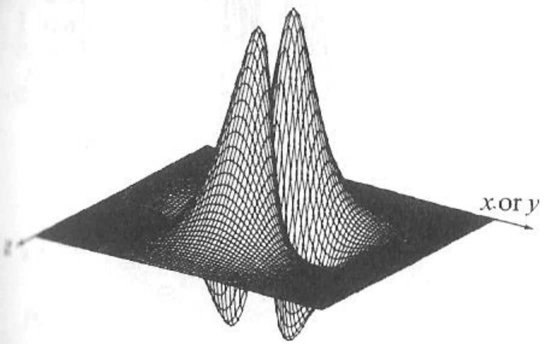


FIGURE 5-14
Surface plot of the $3d_{z^2}$ wavefunction (orbital) in the yz plane for the hydrogen atom. The large hills correspond to the positive lobes of Fig. 5-13 and the small pits correspond to the negative lobes of Fig. 5-13.

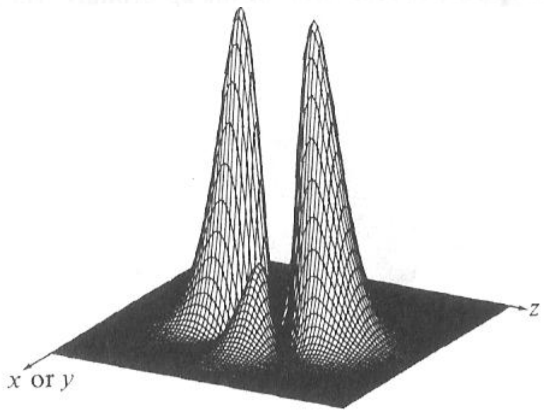
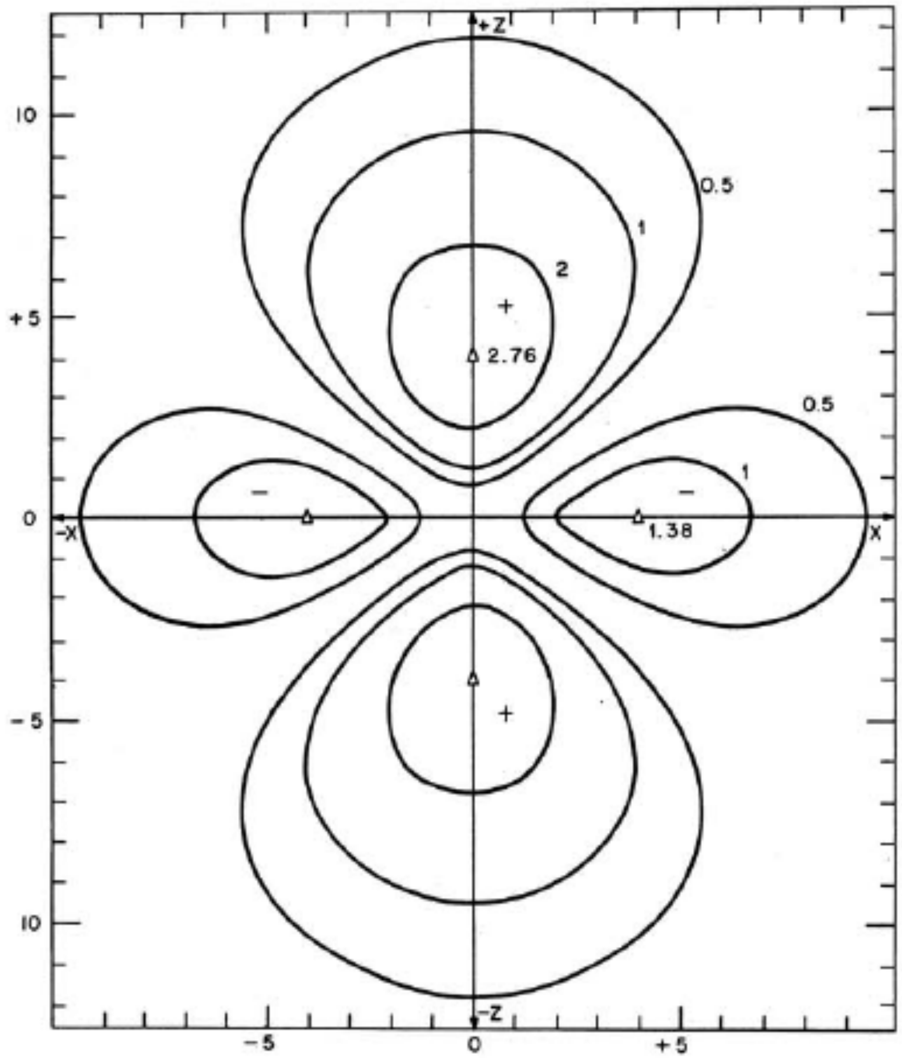


FIGURE 5-15
Surface plot of $(3d_{z^2})^2$, the probability density associated with the $3d_{z^2}$ orbital of the hydrogen atom. The figure has been rotated 90° from that of Fig. 5-14 in order to show the small hill more clearly; the second hill is hidden behind the right-hand large hill.

Probability density contours $3d_{zz}$,$3d_{xz}$



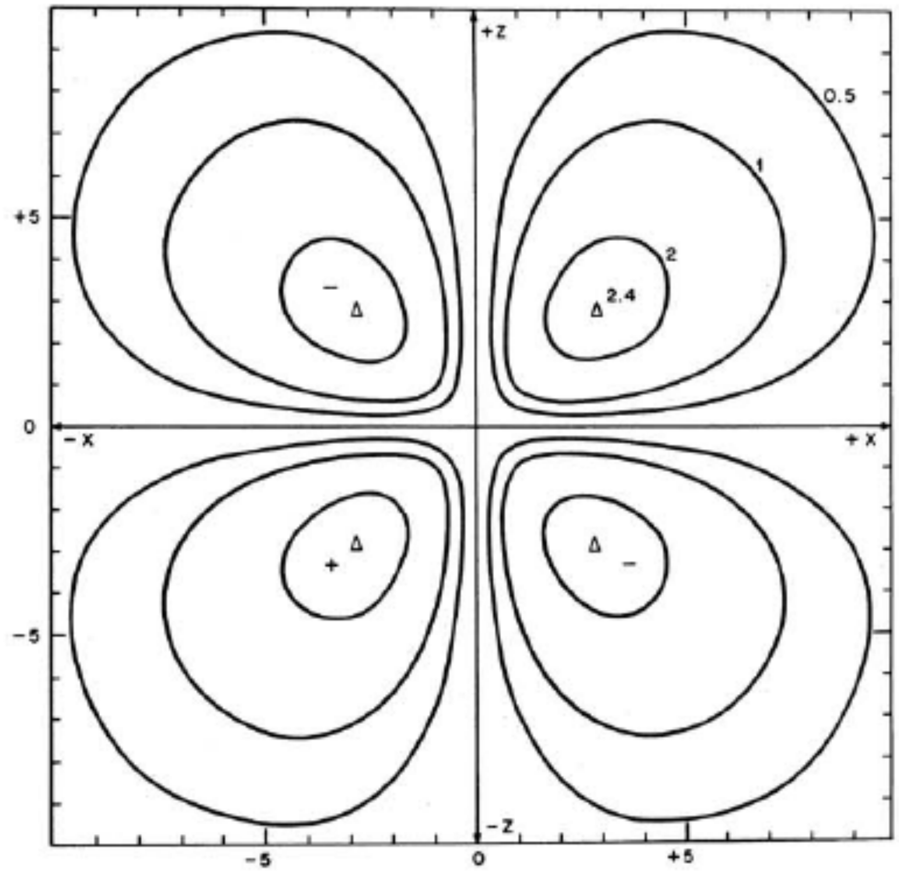
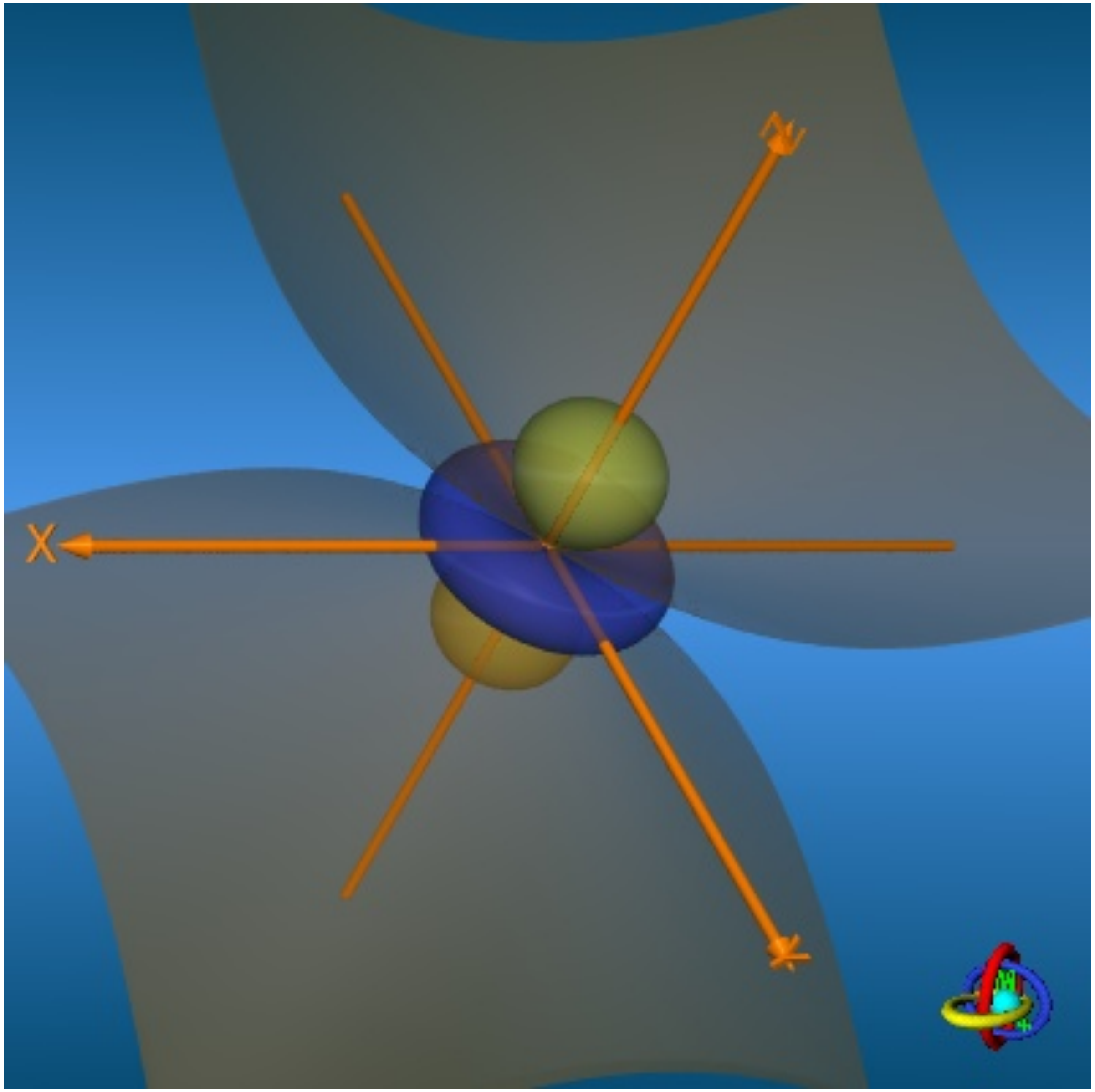


Figure 4. Contour lines of the normalized wave function

$\psi_{3d_{zz}} = (\sqrt{2}/36\sqrt{\pi})\rho^2 e^{-\rho/2} \sin\theta \cos\theta \cos\phi = (\sqrt{2}/36\sqrt{\pi})\, zx -$

The meaning of the numbers is explained in Figure 1. The three-dimensio contour surfaces each consist of 4 lobes which do not have a circular cro section (11).

Nodal planes and/or Surface(s)



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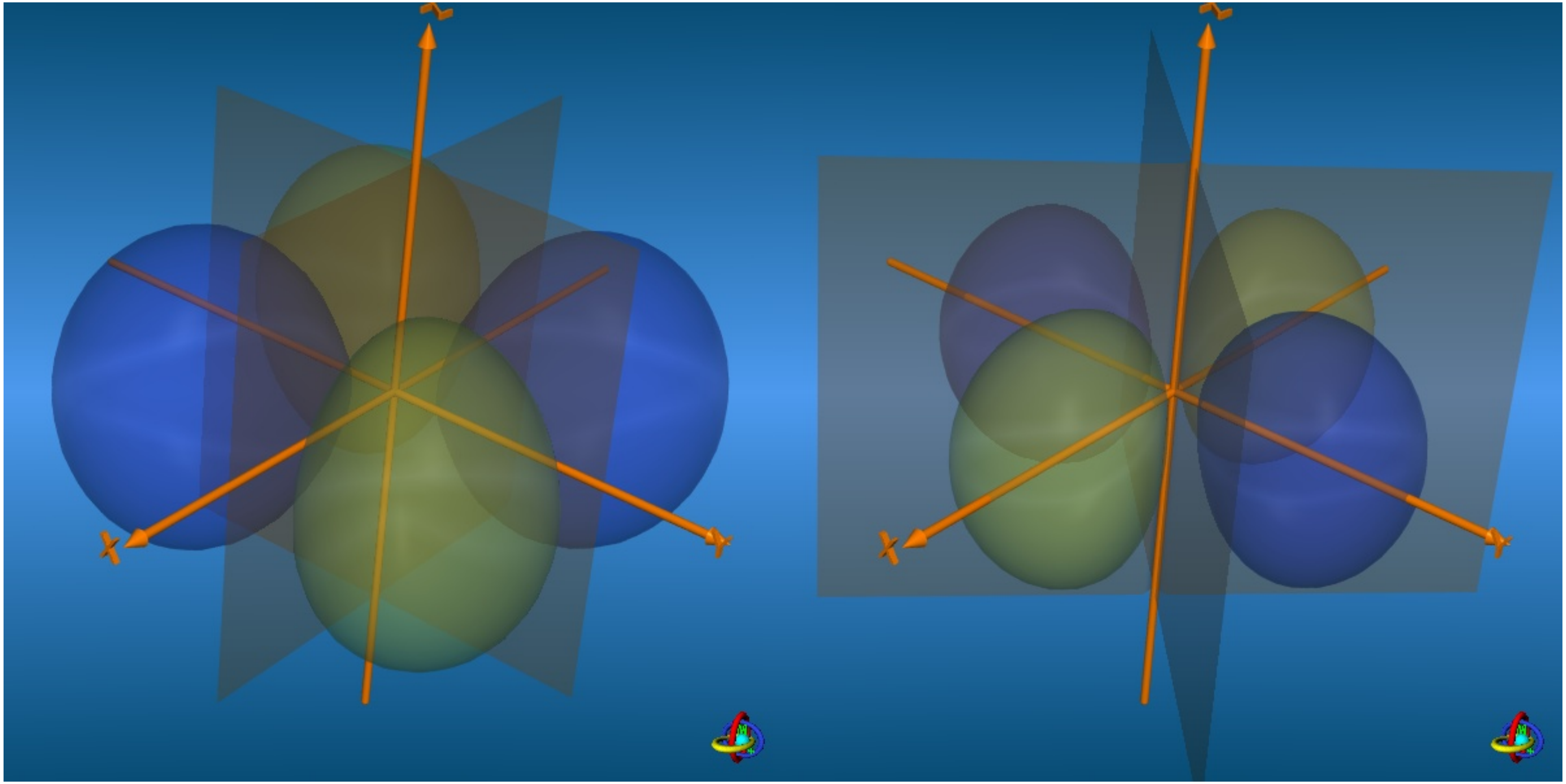
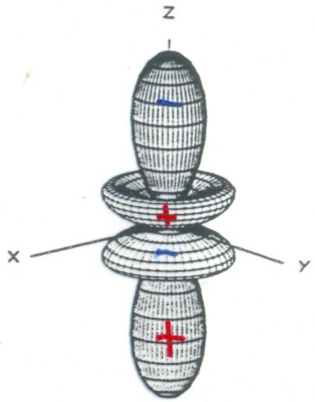
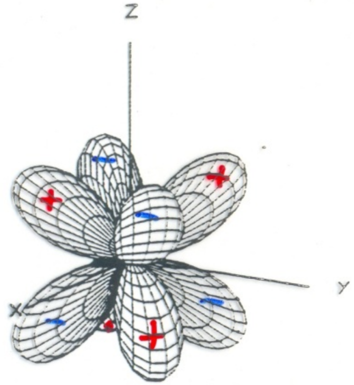


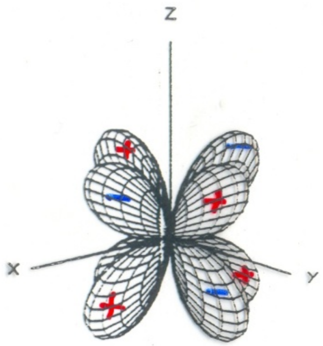
f-orbitals: n=4, l=3, m_l=-3,-2,-1,0,1,2,3



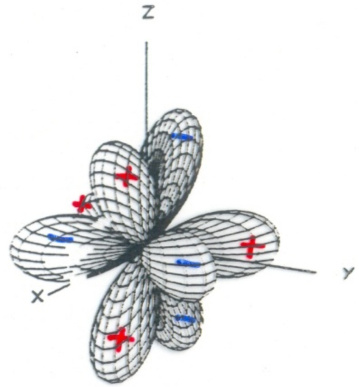
f_{z^3}



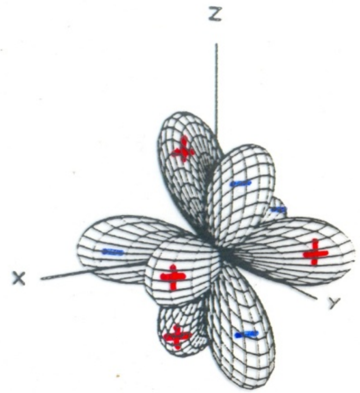
f_{xyz}



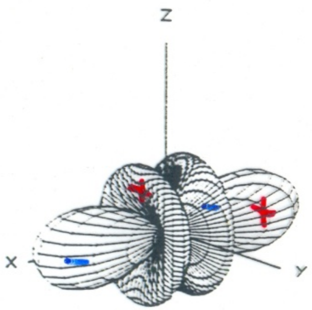
$f_{z(x^2-y^2)}$



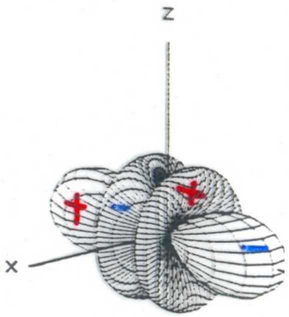
$f_{x(y^2-z^2)}$



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



f_{x^3}



f_{y^3}

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

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

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

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

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

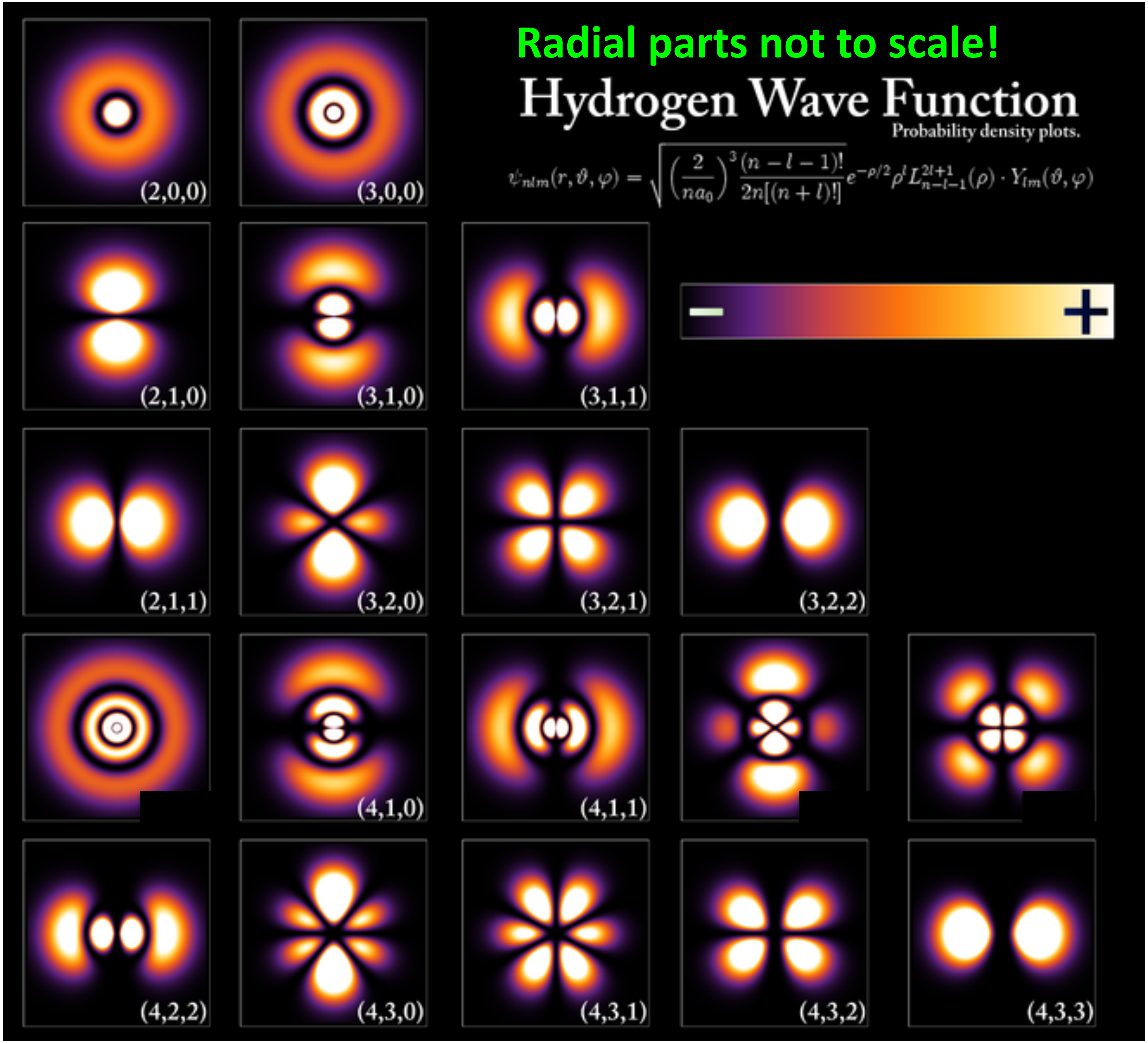
$f_{xyz}: \sqrt{\frac{105}{16\pi}} \sin^2\theta \sin 2\phi \cos\theta$; $\sigma(X,Y), \sigma(Y,Z), \sigma(X,Z)$

Designed by

K L Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 560 012, India.

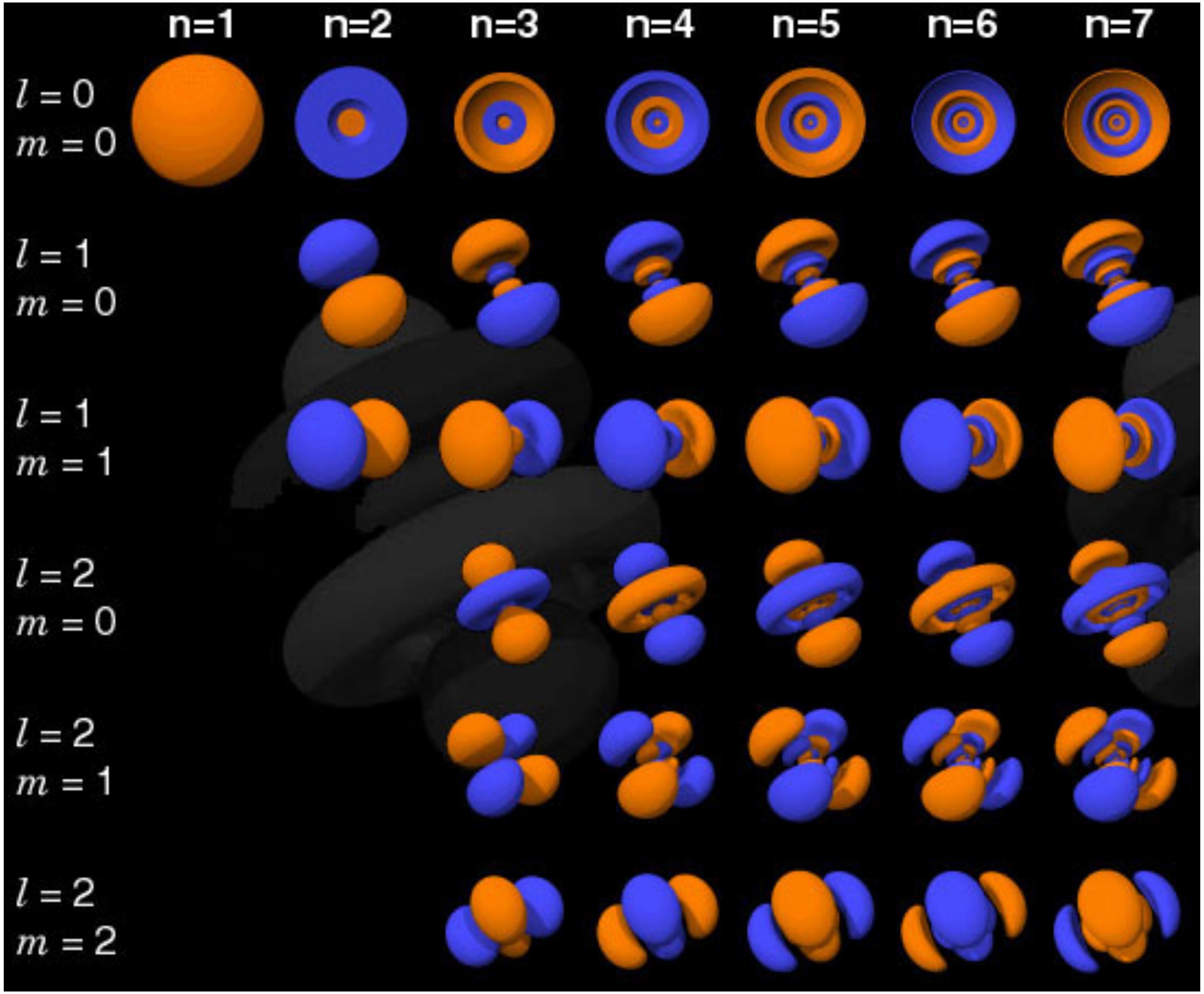
Resonance

Resonance – December 1997



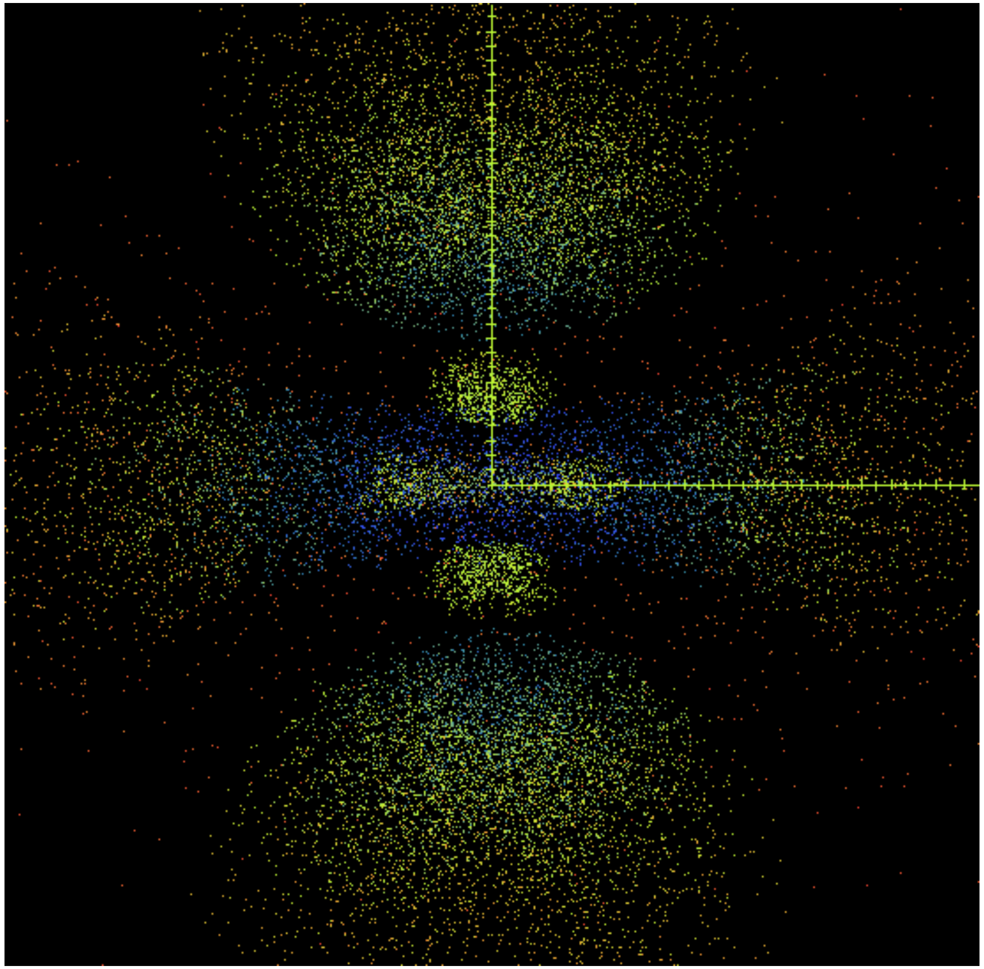
Radial parts not to scale!
Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}}\, e^{-\rho/2}\rho^l L^{2l+1}_{n-l-1}(\rho)\cdot Y_{lm}(\vartheta,\varphi)$
−
+
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
(2,1,1)
(3,2,0)
(3,2,1)
(3,2,2)
(4,1,0)
(4,1,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

How do they look from *inside* in 3D?



Radial parts not to scale!

Can you guess what orbital this is?
What are the quantum numbers?



Probably a tough question to ask, but look into it carefully…

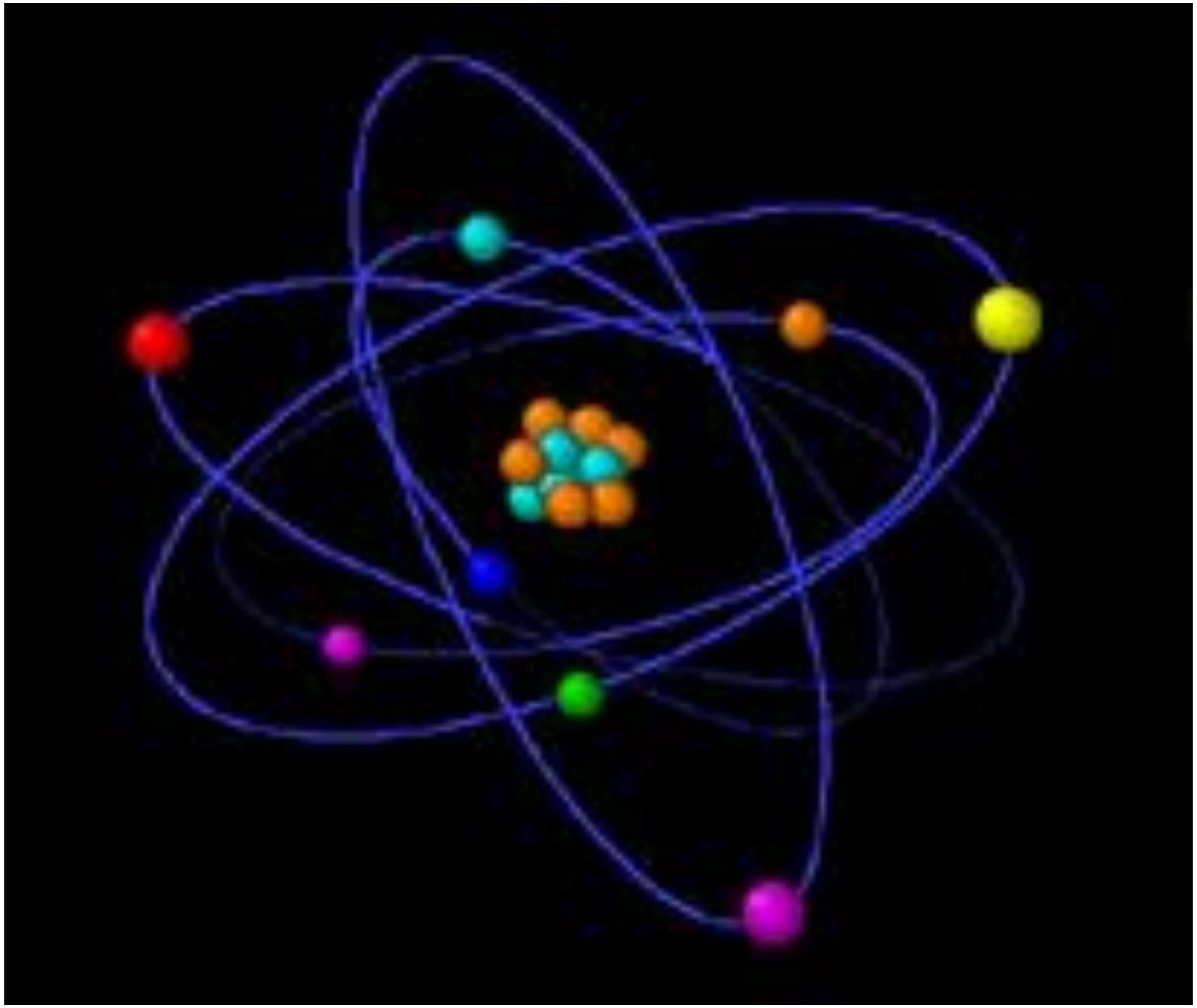
Why did we talk about all these complex orbitals when there is only one electron in H-atom?

Excited Electronic States!

Basis for all kinds of spectroscopy!

Multi electron systems: Orbitals are *not that different*!

Multi-Electronic Atoms



More than 1e: Can not be solved exactly!

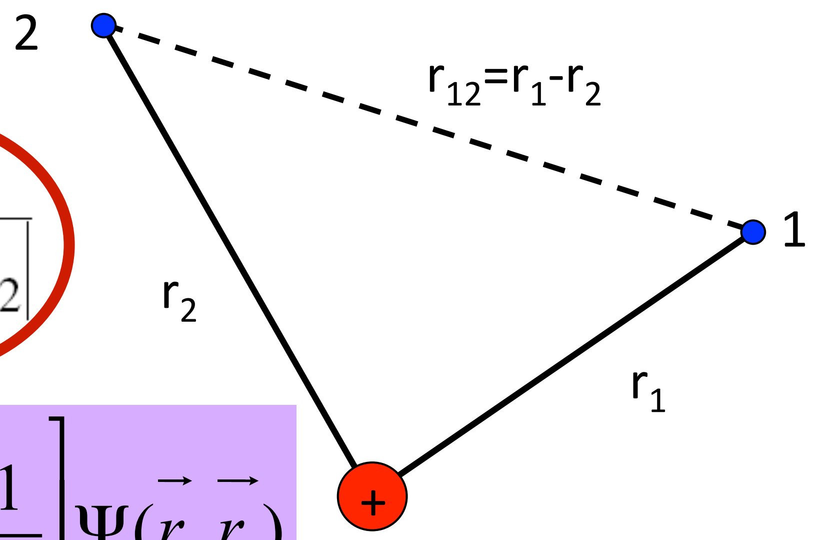
(Assume same symmetry as H-atom)

He-atom (2e): 3-particle system!

Kinetic Energy Of Electron 1 — Nucleus-Electron 1 Attraction — Electron-Electron Repulsion

$$\hat{H} \equiv \frac{\hat{\mathbf{p}}_1^2}{2m_e} + \frac{\hat{\mathbf{p}}_2^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{\hat{r}_1} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{\hat{r}_2} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\left|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2\right|}$$

Kinetic Energy Of Electron 2 — Nucleus-Electron 2 Attraction



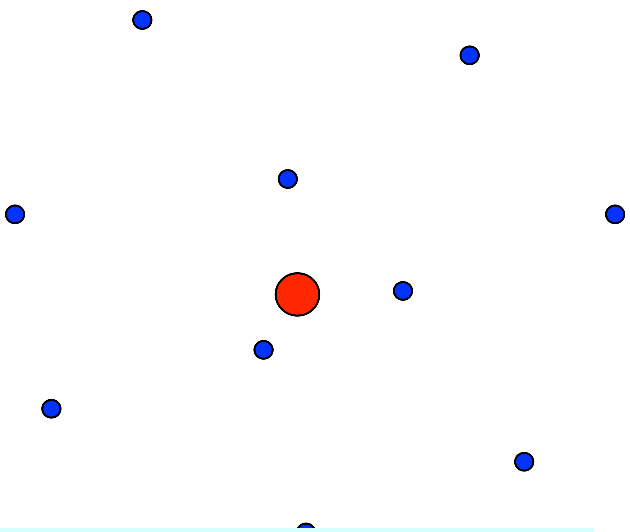
$$\widehat{H}\Psi(\vec{r}_1,\vec{r}_2) \equiv \left[\boxed{\left(-\nabla_{r_1}^2 - \frac{Z}{r_1}\right)} + \boxed{\left(-\nabla_{r_2}^2 - \frac{Z}{r_2}\right)} + \frac{1}{r_{12}}\right]\Psi(\vec{r}_1,\vec{r}_2)$$

$$\widehat{H}_{He}^{electronic} = \widehat{H}_1\left(\vec{r}_1\right) + \widehat{H}_2\left(\vec{r}_2\right) + \frac{1}{r_{12}}$$

$$\Rightarrow \widehat{H}_{He}\Psi\left(\vec{r}_1,\vec{r}_2\right) = \widehat{H}_1\left(\vec{r}_1\right)\Psi\left(\vec{r}_1,\vec{r}_2\right) + \widehat{H}_2\left(\vec{r}_2\right)\Psi\left(\vec{r}_1,\vec{r}_2\right) + \boxed{\frac{1}{r_{12}}\Psi\left(\vec{r}_1,\vec{r}_2\right)}$$

In atomic units (for convenience) constants m_e, e', $4\pi\varepsilon_0$, $h/2\pi$ → X

Multi-electron atoms



Assume nucleus to be STATIC

$$\widehat{H}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\ldots\ldots\vec{r}_N) \equiv -\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Z}{r_i} + \boxed{\sum_{i<j}^{N}\frac{1}{r_{ij}}}$$

$$\widehat{H}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2,\ldots\ldots r_N,\theta_N,\phi_N) \equiv \sum_{i=1}^{N}\widehat{H}_i(r_i,\theta_i,\phi_i) + \sum_{i<j}^{N}\frac{1}{r_{ij}}$$

$H_i \rightarrow$ 1 electron hydrogenic Hamiltonian for the i-th electron

$$\frac{1}{r_{ij}} \neq f\left(\frac{1}{r_i}\right) + g\left(\frac{1}{r_j}\right) \Rightarrow \textit{Not Separable}$$

Inter-electronic interaction terms mess things up!

Hamiltonian is no longer spherically symmetric due to $\Sigma\ (1/r_{12})$ term and therefore, numerical methods must be used to solve the TISE

Orbital Approximation for N electrons

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\ldots\ldots,\vec{r}_N)\approx\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\psi_3(\vec{r}_3)\ldots\ldots\psi_N(\vec{r}_N)$$

$$H_{Eff}^{(i)}\psi_i(\vec{r}_i)=\varepsilon_i\psi_i(\vec{r}_i)$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla_i^2+V_i^{eff}\left(r_i\right)\right)\psi_i(\vec{r}_i)=\varepsilon_i\psi_i(\vec{r}_i)$$

Many e Wave-F(n) is a product of 1e Wave-F(n)s;

Can solve numerically if V^{Eff} is spherically symmetric

1-e wavefunctions are orbitals: E_T = sum of ε_i (Orbital Energies)

TISE for He atom: 2 electron system

$$\widehat{H}_{He}\Psi_{He}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)=E_{He}\Psi_{He}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

$$\widehat{H}_{He}=\widehat{H}_1^{1e}(r_1,\theta_1,\phi_1)+\widehat{H}_2^{1e}(r_2,\theta_2,\phi_2)+\frac{1}{r_{12}}$$

$$\Psi_{He}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)\approx\Psi_1(r_1,\theta_1,\phi_1)\Psi_2(r_2,\theta_2,\phi_2)\ \ (product\ of\ 1e-\psi\ s)$$

Orbital Approximation (for He)

$$In\ order\ to\ solve\ for\ \mathrm{1}e\ (orbital)\ energies: NEGLECT\ \ Electron-Electron\ REPULSION$$

$$\widehat{H}_{He}\Psi = \left[\boxed{\widehat{H}_1^{1e}\Psi_1(r_1,\theta_1,\phi_1)}\right]\Psi_2(r_2,\theta_2,\phi_2) + \Psi_1(r_1,\theta_1,\phi_1)\left[\boxed{\widehat{H}_2^{1e}\Psi_2(r_2,\theta_2,\phi_2)}\right] + \boxed{\cancel{\frac{1}{r_{12}}\Psi_1(r_1)\Psi_2(r_2)}}$$

$$\widehat{H}_{He}\Psi = \left[\boxed{\varepsilon_1^{1e}\Psi_1(r_1,\theta_1,\phi_1)}\right]\Psi_2(r_2,\theta_2,\phi_2) + \Psi_1(r_1,\theta_1,\phi_1)\left[\boxed{\varepsilon_2^{1e}\Psi_2(r_2,\theta_2,\phi_2)}\right]$$

$$\widehat{H}_{He}\Psi = \varepsilon_1^{1e}\left[\Psi_1(r_1,\theta_1,\phi_1)\Psi_2(r_2,\theta_2,\phi_2)\right] + \varepsilon_2^{1e}\left[\Psi_1(r_1,\theta_1,\phi_1)\Psi_2(r_2,\theta_2,\phi_2)\right]$$

$$\widehat{H}_{He}\Psi = \left(\varepsilon_1^{1e} + \varepsilon_2^{1e}\right)\left[\Psi_1(r_1,\theta_1,\phi_1)\Psi_2(r_2,\theta_2,\phi_2)\right] = E_{He}\Psi \Rightarrow E_{He} = \varepsilon_1^{1e} + \varepsilon_2^{1e}$$

Hydrogenic orbitals → both electrons will be in the 1s orbital!

$$\Psi_{He} \approx \sqrt{\frac{1}{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_1/a_0} \cdot \sqrt{\frac{1}{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_2/a_0} \Rightarrow \boxed{\Psi \approx 1s(1)1s(2)}$$

Effective Nuclear Charge

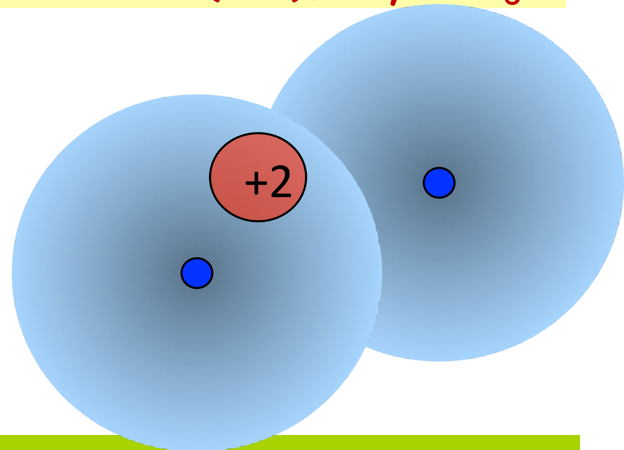
Let us find out what the ionization energies come out to be:

$$E_1(Theory) = -\frac{Z^2 \mu e^4}{n^2 \hbar^2} = -13.6\frac{Z^2}{n^2} eV = 4(-13.6)eV = E_2 \Leftrightarrow E = E_1 + E_2 = -108.8eV$$

$$Exp.\ Ionization\ Energies:\ E_1^{IE} = -24.6eV \quad E_2^{IE} = -54.4eV$$

For He: Z=2, n=1 (GS), say $a=a_0$

Electrons must be shielding each other!!!
Outer electrons feel that the net charge on the nucleus is less than what is expected:
Screening of Z
"Effective Nuclear Charge"



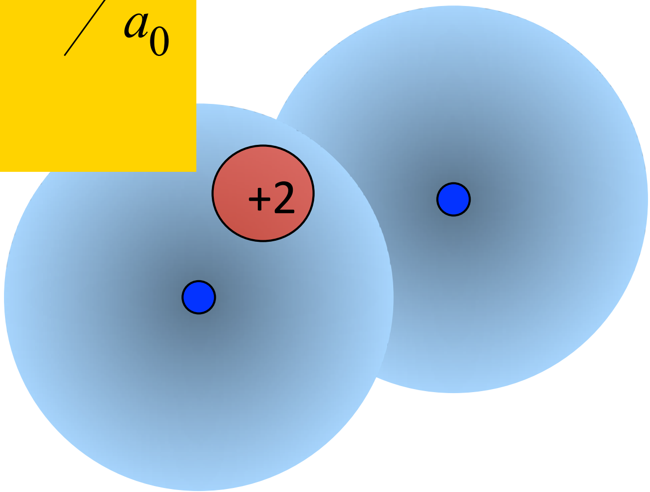
Assumption of no inter-electronic interaction is too drastic !
Electrons stay out of each other's way by undergoing "correlated" Motion to ensure electronic repulsion is minimum

$$\boxed{\frac{1}{r_{12}}\Psi_1(r_1)\Psi_2(r_2)} \Rightarrow not\ small,\ cannot\ be\ neglected!$$

Need to use other (numerical) approximate methods such as **Variational Method** or **Perturbation Theory** using Central Field Approximation (Not a part of CH107)

Electronic Shielding: Effective Nuclear Charge

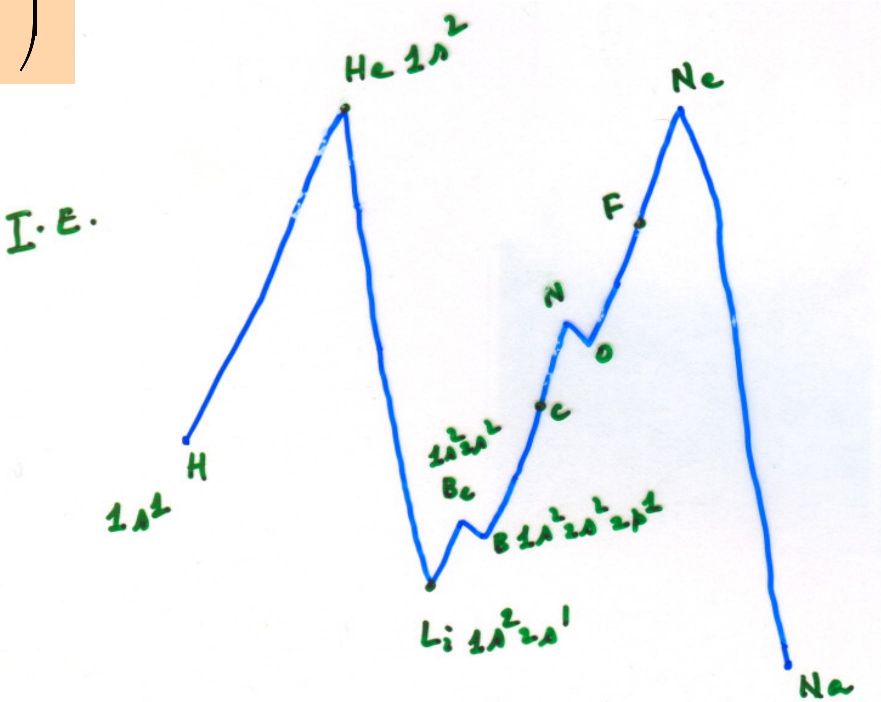
$$\Psi_{He} \approx 1s(1)1s(2) \approx \left(\frac{Z_{eff}}{a_0}\right)^{3/2} e^{-Z_{eff} r_1 / a_0} \cdot \left(\frac{Z_{eff}}{a_0}\right)^{3/2} e^{-Z_{eff} r_2 / a_0}$$



$$Z_{eff}^{i} = Z - \sigma^{i}, \ where \ \ i = s, p, d, f \ldots$$

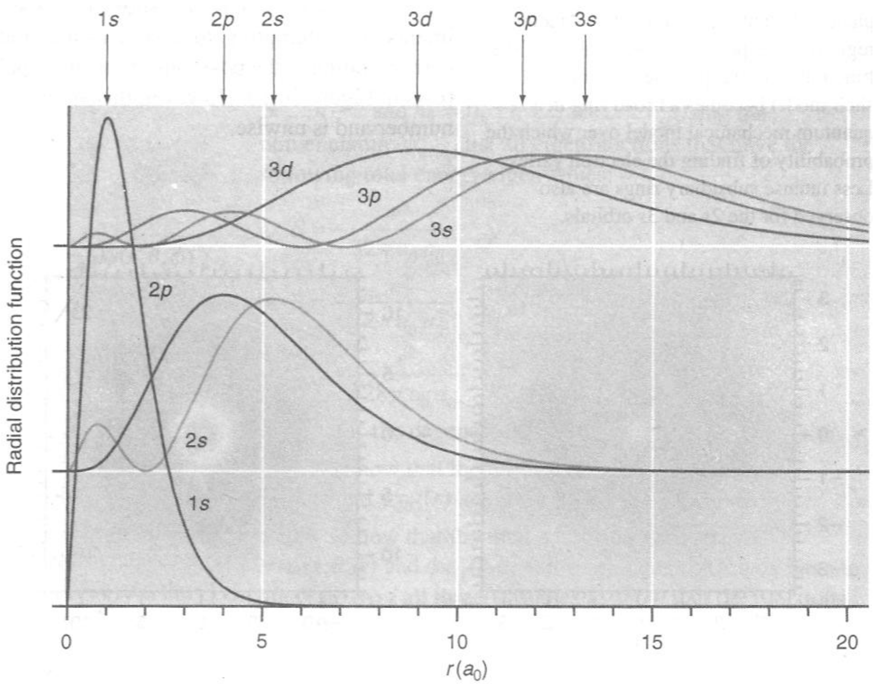
$$\langle IE_Z \rangle (avg, \ per \ e') = IE_H(-13.6eV) \times \left(\frac{Z_{eff}^{i}}{n_i}\right)^2$$

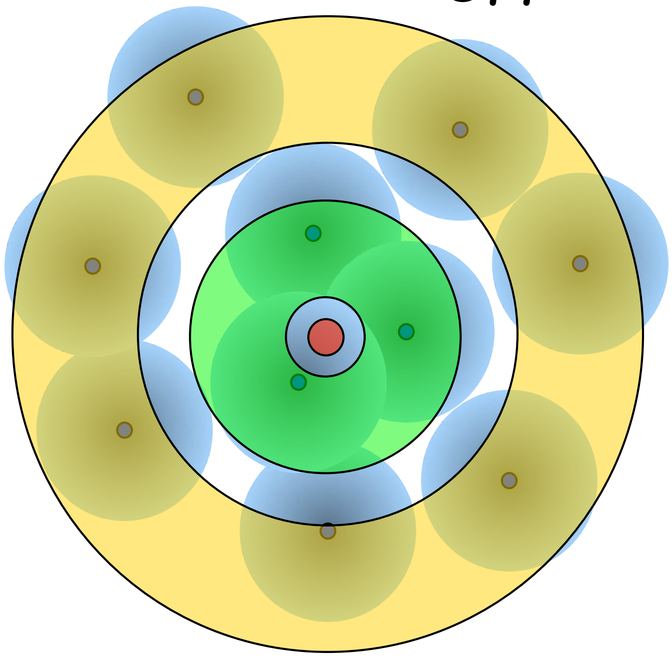
Effective nuclear charge is same for electrons in the same orbital, but greatly varies for electrons of different orbitals (s,p,d,f) and n. Z_{eff} determines several physical and chemical properties of multi-electron systems



Many-electrons: Consequences of Z_{eff}

- Why is 2p energy higher than 2S?
- How does Radial distributions change?
- How does Z_{eff} affect atomic properties?





Read up on electronic configuration of multi-electronic atoms: Hund's Rules & Aufbau Principle (most of you know!)

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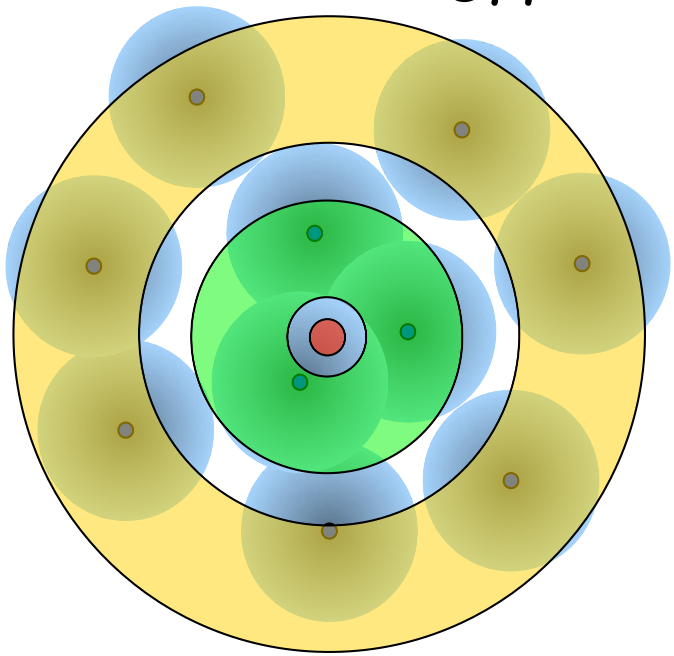

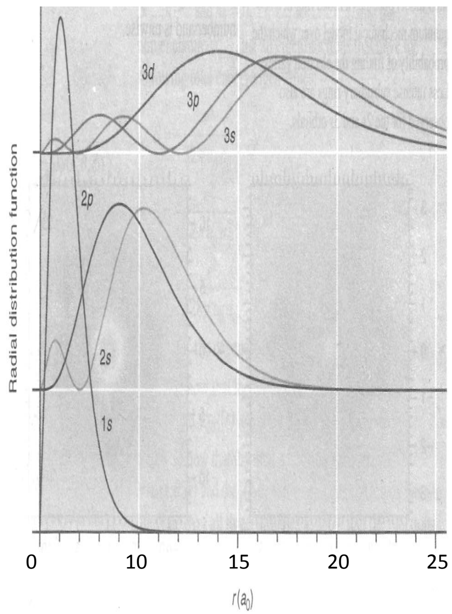

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