Wavefunctions of Hydrogen Atom

$$\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r) \cdot Y_l^m(\theta,\phi)$$

$$\psi_{1,0,0} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} \boxed{e^{-r/a_o}} \qquad f(r)$$

$$\psi_{2,0,0} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2} \boxed{\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}} \qquad f(r)$$

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

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

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

1s and 2s Orbitals

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

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

Functions of only '*r*'

2p Orbitals

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

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

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

Functions of 'r', 'θ' and 'ϕ'

2p Orbitals

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

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

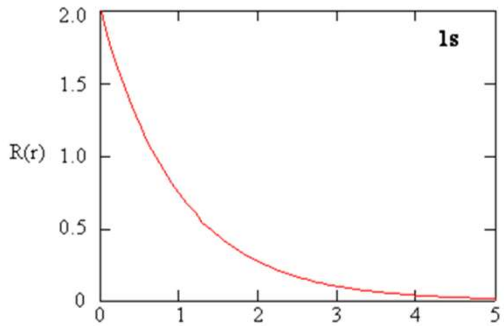
$$\psi_{2,1,-1} = \psi_{2p_{-1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\sin\theta\, e^{-i\phi}$$

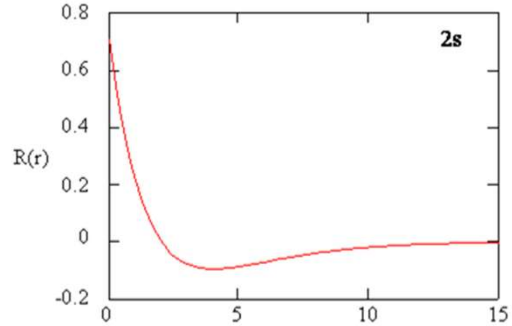
Linear combination

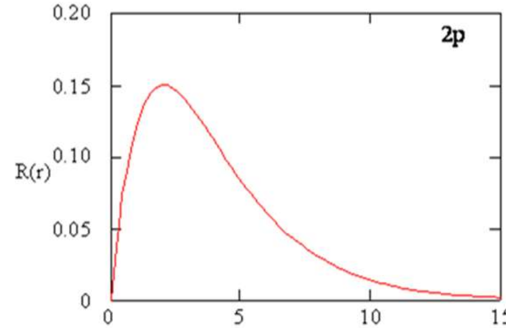
$$\psi_{2p_x} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\sin\theta\cos\phi = \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right)$$

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

Radial functions

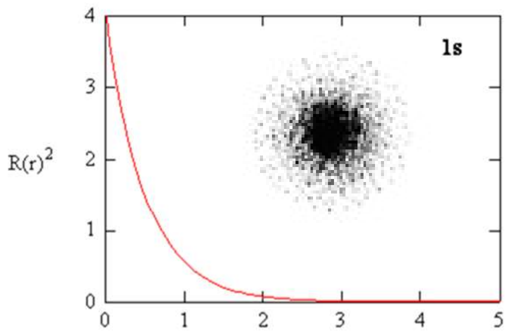


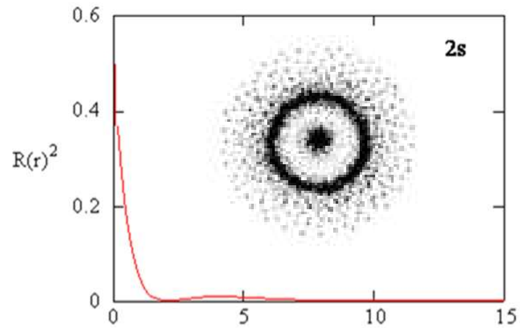


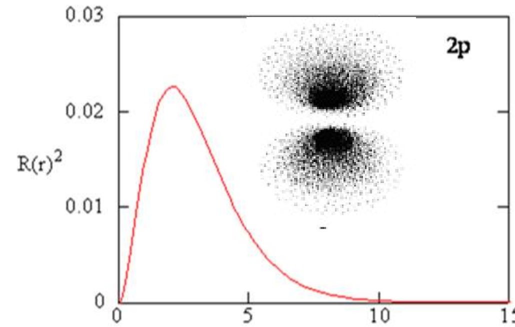


$$\rho = \frac{r}{a_o}$$

$$\psi_{1s}^{100} = N' e^{-\rho} \qquad \psi_{2s}^{200} = N''(2-\rho)e^{-\rho/2} \qquad \psi_{2p_z}^{210} = N'''\rho e^{-\rho/2}\cos\theta$$



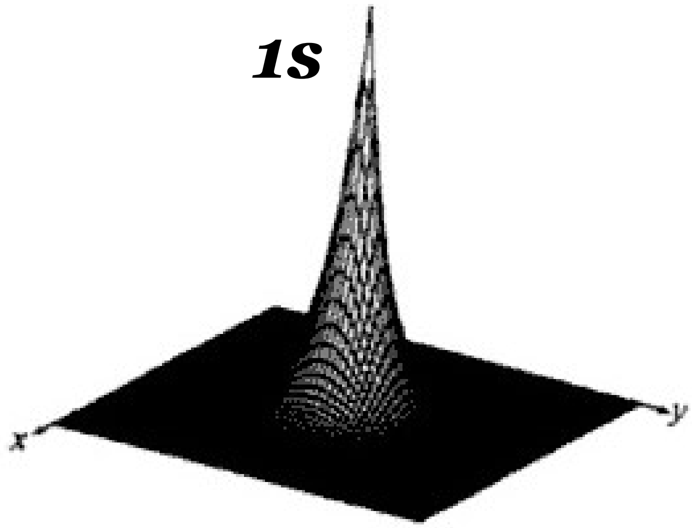




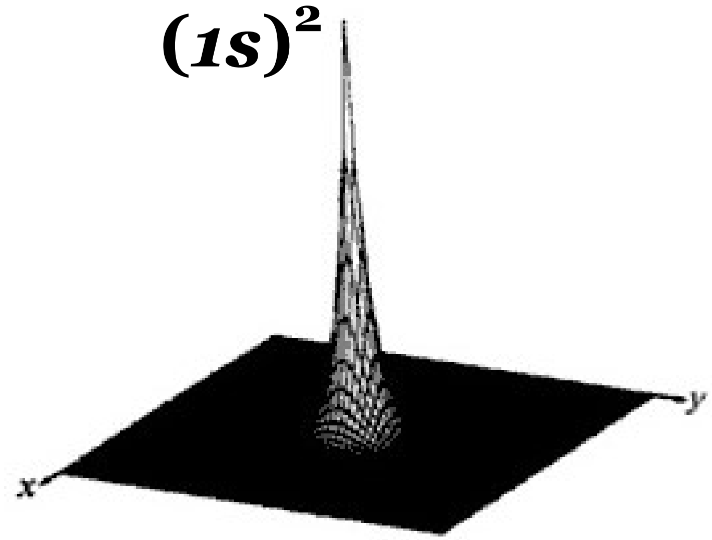
For s-Orbitals the maximum probability denisty of finding the electron is on the nucleus

For s-Orbitals the probability of finding the electron on the nucleus zero

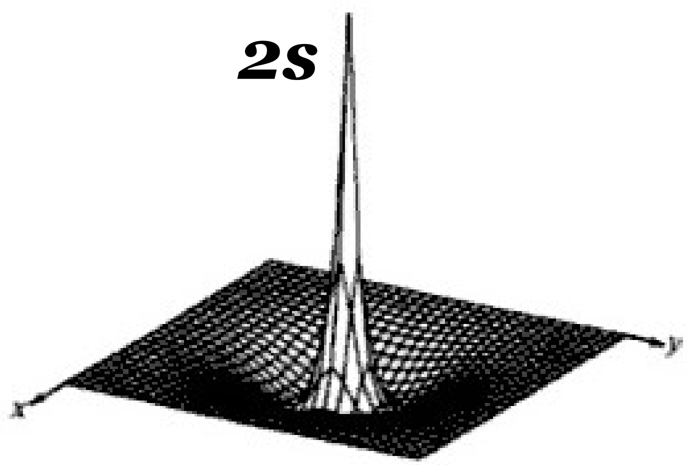
Surface plots



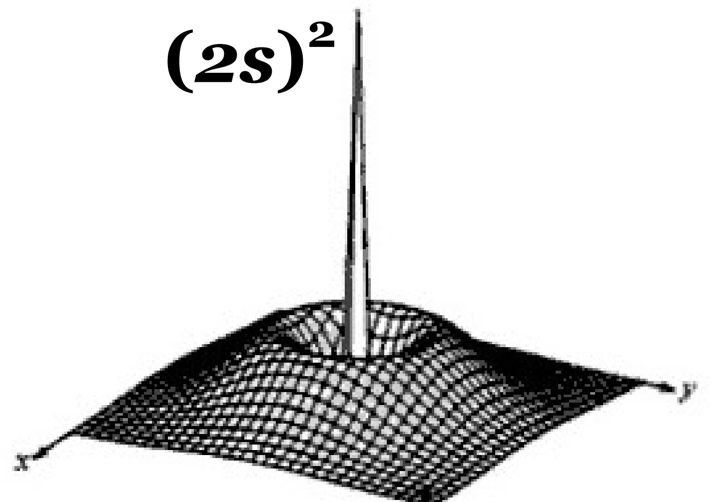
Surface plot of the 1s wavefunction (orbital) of the hydrogen atom. The height of any point on the surface above the *xy* plane (the nuclear plane) represents the magnitude of the Ψ_{1s} function at the at point (*x*,*y*) in the nuclear plane. The nucleus is located in the *xy* place immediately below the 'peak'



Surface plot of the $|\Psi_{1s}|^2$; the probability density associated with the 1s wavefunction of the hydrogen atom.

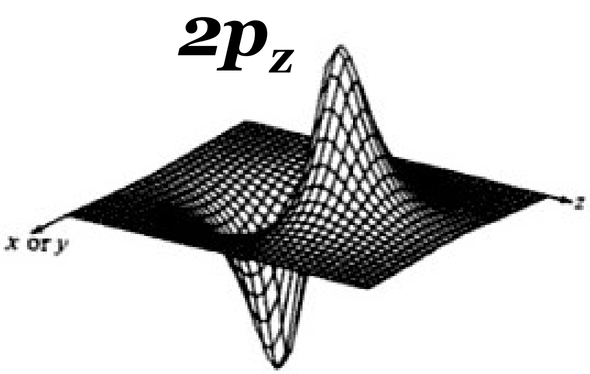


Surface plot of the Ψ_{2s} ; 2s wavefunction (orbital) of the hydrogen atom. The height of any point on the surface above the *xy* plane (the nuclear plane) represents the magnitude of the Ψ_{2s} function at the at point (*x*,*y*) in the nuclear plane. Note that there is a negative region (depression) about the nucleus; the negative region begins at $r=2a_0$ an goes asymptotically to zero at $r=\infty$.

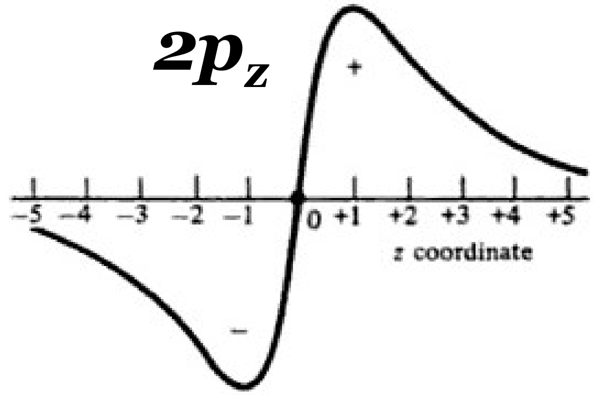


Surface plot of the $|\Psi_{2s}|^2$; the probability density associated with the 1s wavefunction of the hydrogen atom. Note that the negative region of the 2s plot on the left now appears as positive region.

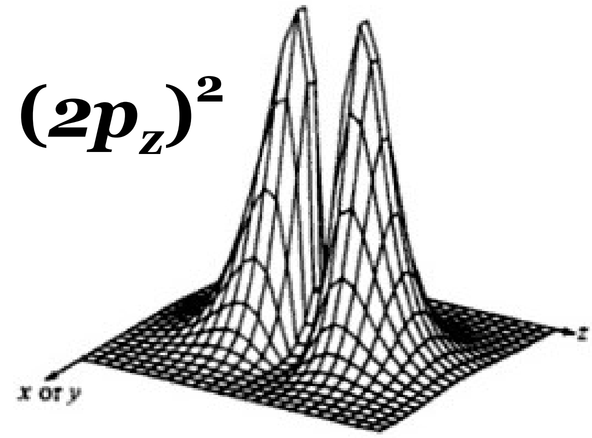
Surface plots



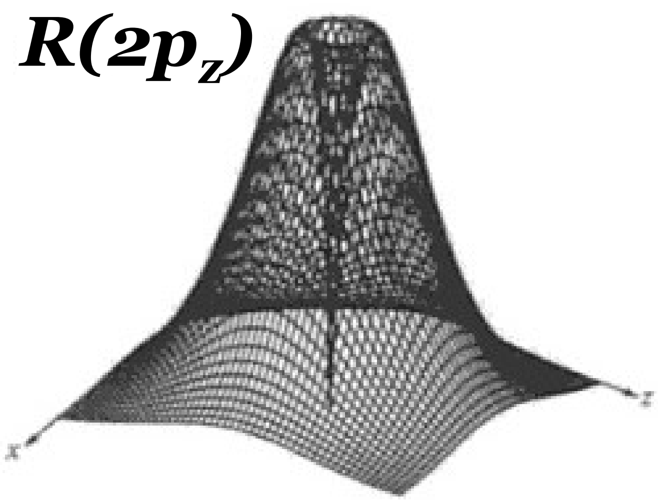
Surface plot of the *$2p_z$* wavefunction (orbital) in the *xz* (or *yz*) plane for the hydrogen atom. The 'pit' represents the negative lobe and the 'hill' the positive lobe of a 2p orbital.



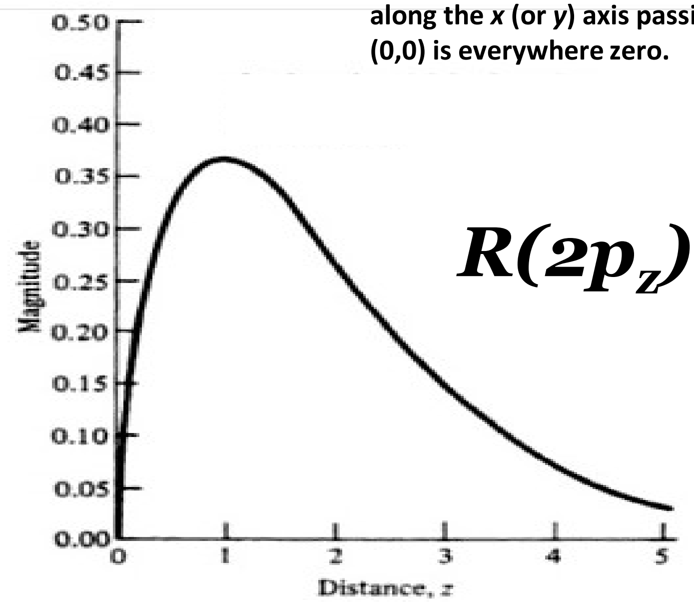
Profile of the $2p_z$ orbital along the z-azis.



Surface plot of the *$(2p_z)^2$*; the probability density associated with the *$2p_z$* wavefunction of the hydrogen atom. Each of the hills represents and 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.

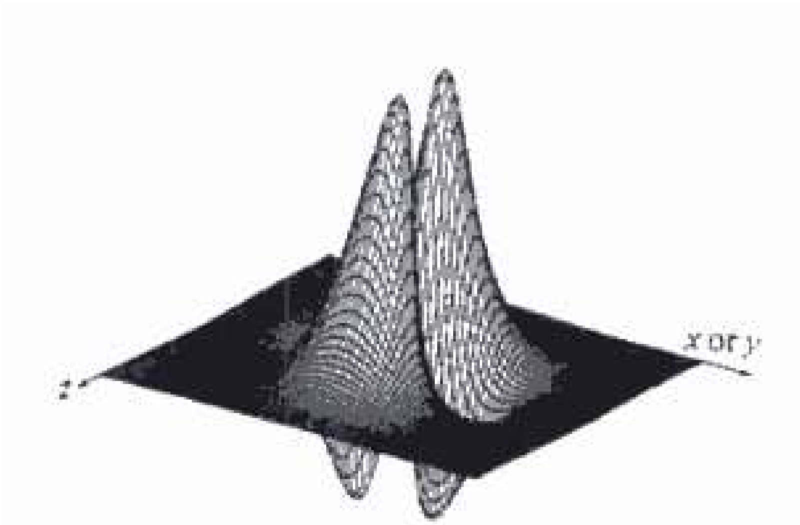


Surface plot of radial portion of a 2p wavefunction of the hydrogen atom. The gird lines have been left transparent so that the inner 'hollow' portion is visible.

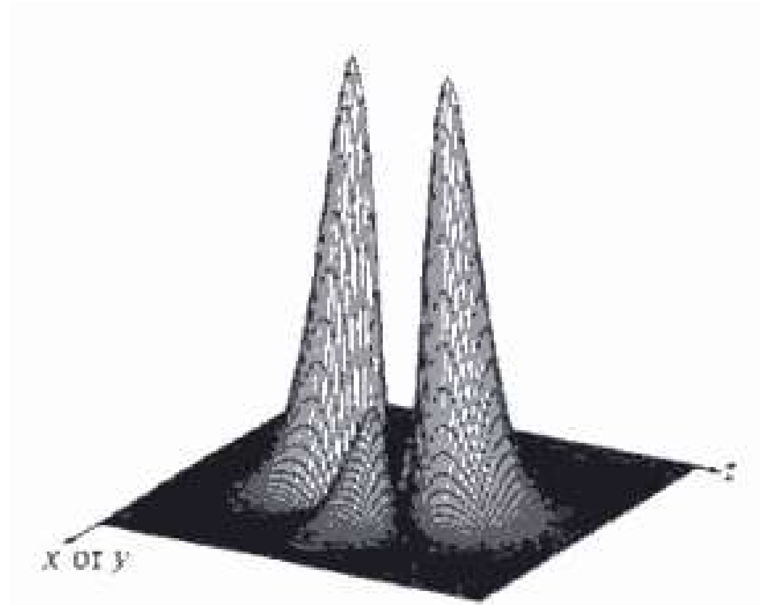


Profile of the radial portion of a 2p wavefunction of the hydrogen atom.

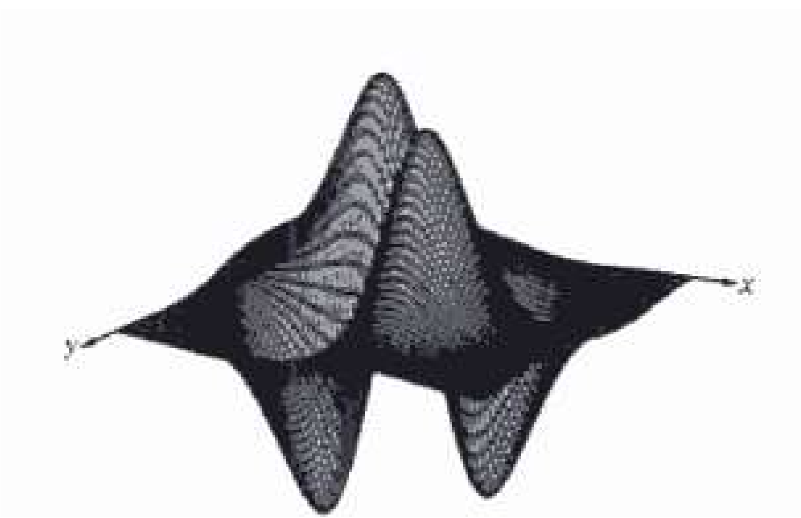
Surface plots



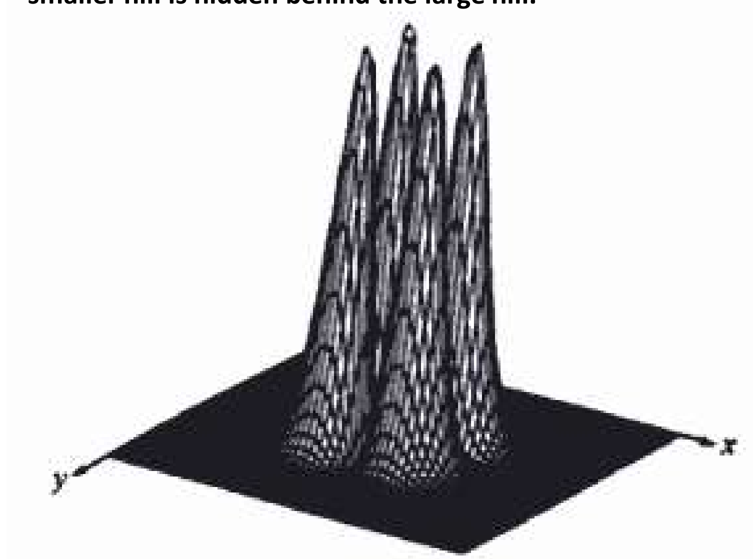
Surface plot of the $3d_{z2}$ wavefunction (orbital) in the *xz* (or *yz*) plane for the hydrogen atom. The large hills correspond to the positive lobes and the small pits correspond to the negative lobes.



Surface plot of the $(3d_{z2})^2$ the probability density associated with the $3d_{z2}$ orbital of the hydrogen atom. This figure is rotated with respect to the figure on the left so that the small hill will be clearly visible. Another smaller hill is hidden behind the large hill.



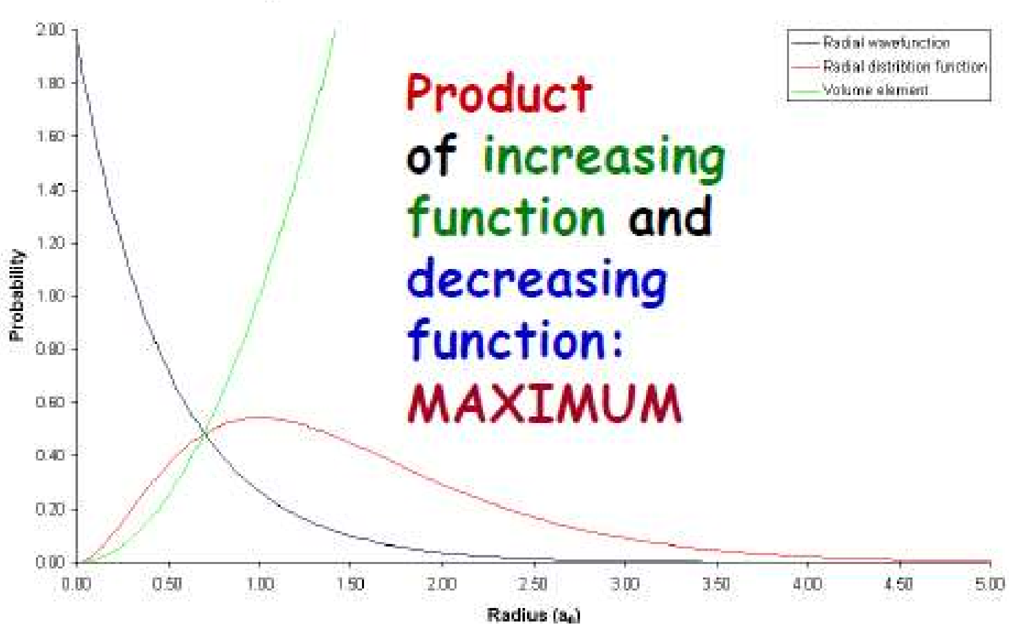
Surface plot of the $3d_{xy}$ wavefunction (orbital) in the *xz* plane for the hydrogen atom. The hills and the pits have same amplitude.

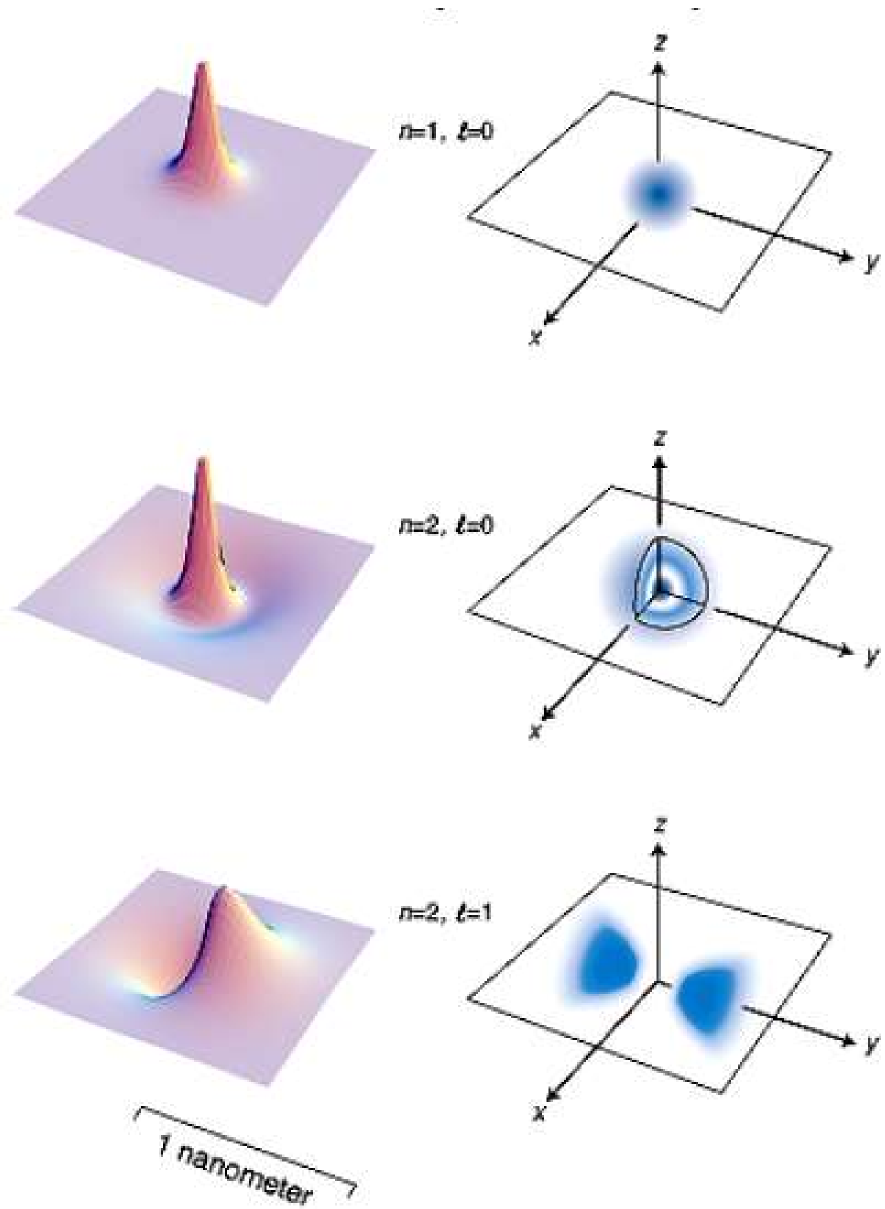


Surface plot of the $(3d_{xy})^2$ the probability density associated with the $3d_{xy}$ orbital of the hydrogen atom. Pits in the figure to the left appear has hills.

Radial and Radial Distribution Functions

Probability of finding the electron anywhere in a shell of thickness dr at radius r is $r^2 R_{nl}^2(r)dr$ (for s)
$r^2 \rightarrow$ increasing function
$r^2 R_{nl}^2(r)dr \rightarrow 0$ as $r^2 dr \rightarrow 0$





Radial Distribution Functions

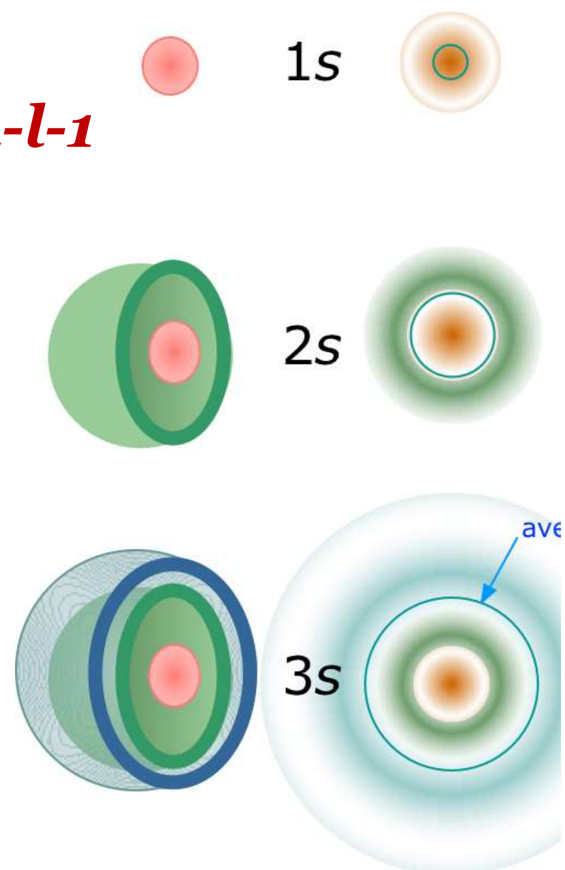
$$4\pi r^2 R_{nl}^2(r)$$

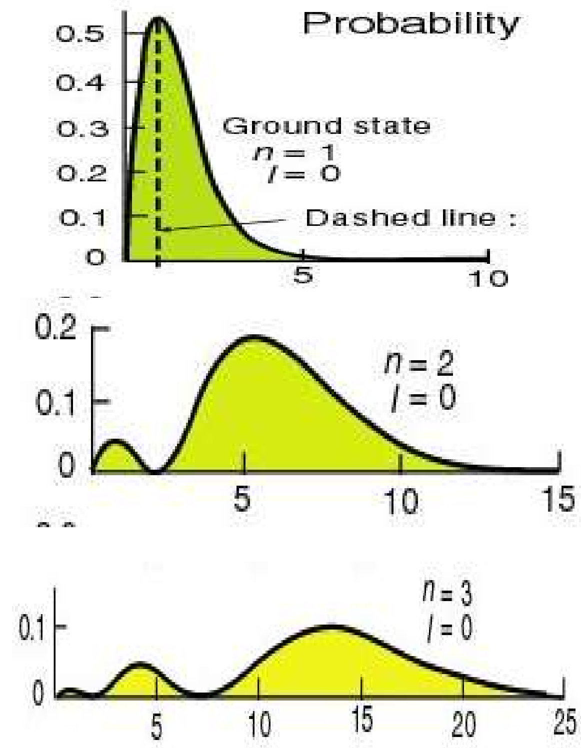
Number of radial nodes = *n-l-1*

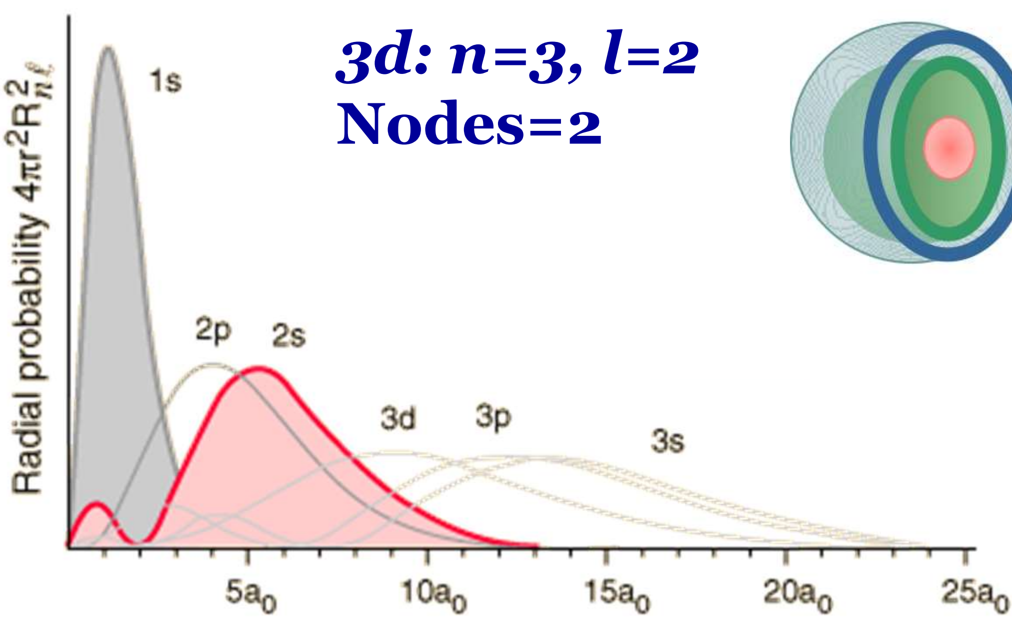
3s: n=3, l=0
Nodes=2

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

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







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

Shapes and Symmetries of the Orbitals

s-Orbitals

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o} \qquad \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$$

Function of only *r*; No angular dependence
⇒Spherical symmetric

n-l-1=0 ⟵	radial nodes	⟶ n-l-1=1
l=0 ⟵	angular nodes	⟶ l=0
n-l=0 ⟵	Total nodes	⟶ n-l=1

Shapes and Symmetries of the Orbitals

p-Orbitals

$$\psi_{210} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\cos\theta$$

Function of only r , θ (and ϕ)

$\Rightarrow$Not Spherical symmetric

$2p_z$ Orbital: No ϕ dependence

$\Rightarrow$Symmetric around z-axis

radial nodes *n-l-1=0*

angular nodes *l=1* *xy* nodal plane

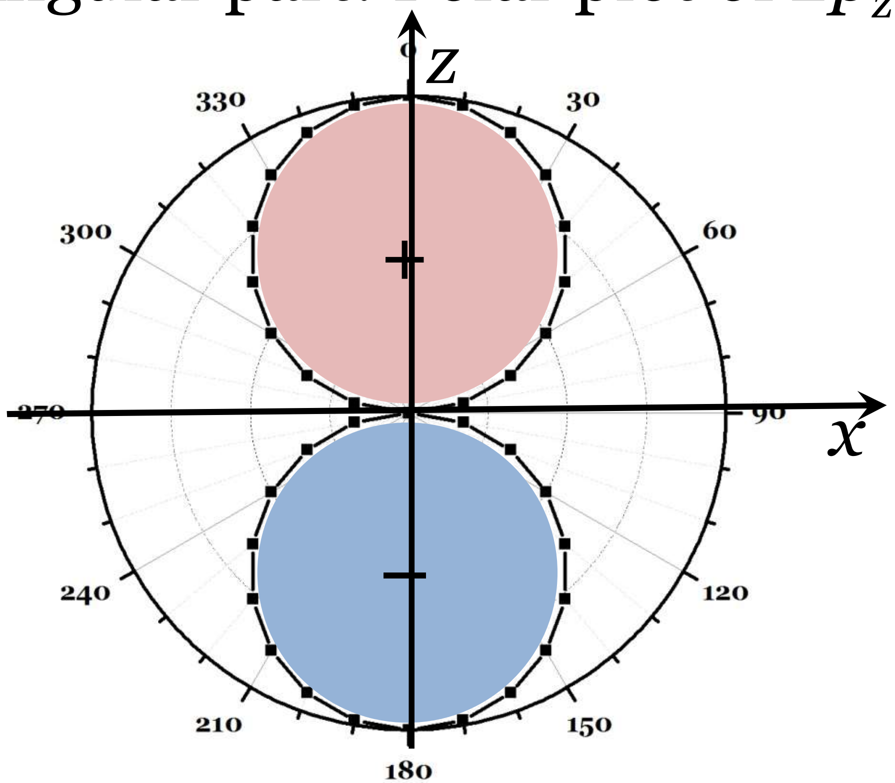
Total nodes *n-l=1* Zero amplitude at nucleus

Angular Distribution Functions

p-Orbitals

$$\psi_{210} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\cos\theta \qquad m = 0 \text{ case}$$

Angular part: Polar plot of $2p_z$ --- $\cos\theta$

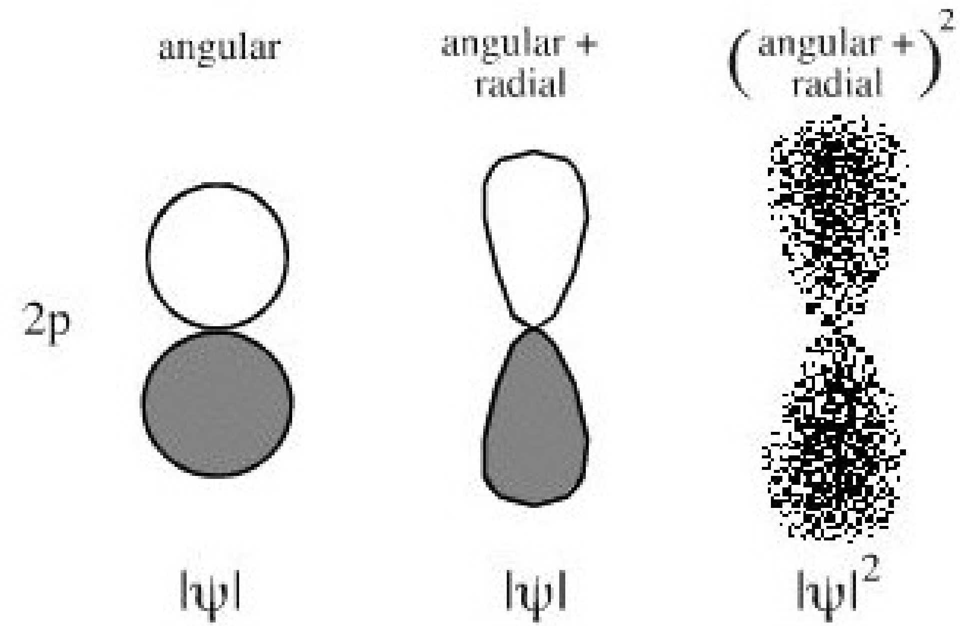


θ	cosθ
0	1.000
30	0.866
60	0.500
90	0.000
120	-0.500
150	-0.866
180	-1.000
210	-0.866
240	-0.500
270	0.000
300	0.500
330	0.866
360	1.000

$$\psi_{210} = \psi_{2p_z} = N\rho e^{-\rho/2}\cos\theta$$

p-Orbitals

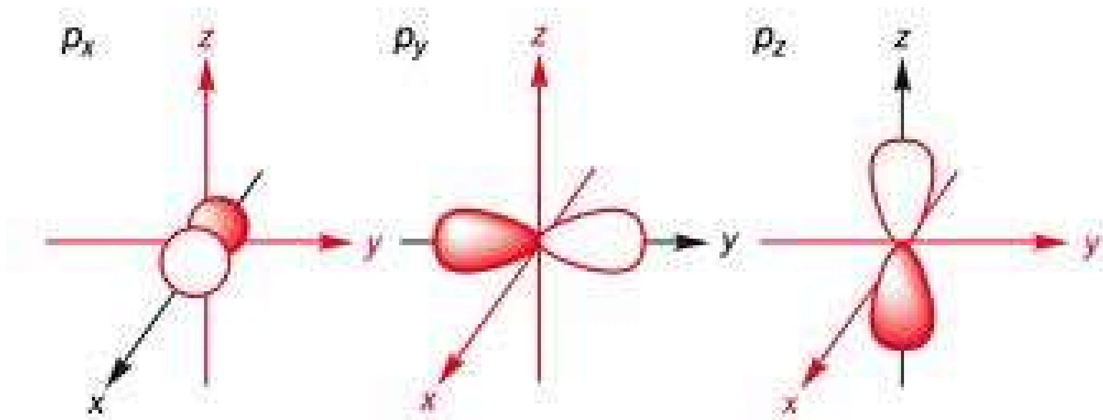
$$\psi_{210} = \psi_{2p_z} = N\rho e^{-\rho/2}\cos\theta$$



$$\psi_{2p_z} = N\rho e^{-\rho/2}\cos\theta$$

$$\psi_{2p_x} = N\rho e^{-\rho/2}\sin\theta\cos\phi$$

$$\psi_{2p_x} = N\rho e^{-\rho/2}\sin\theta\sin\phi$$



Color/shading are related to sign of the wavefunction

d-Orbitals

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

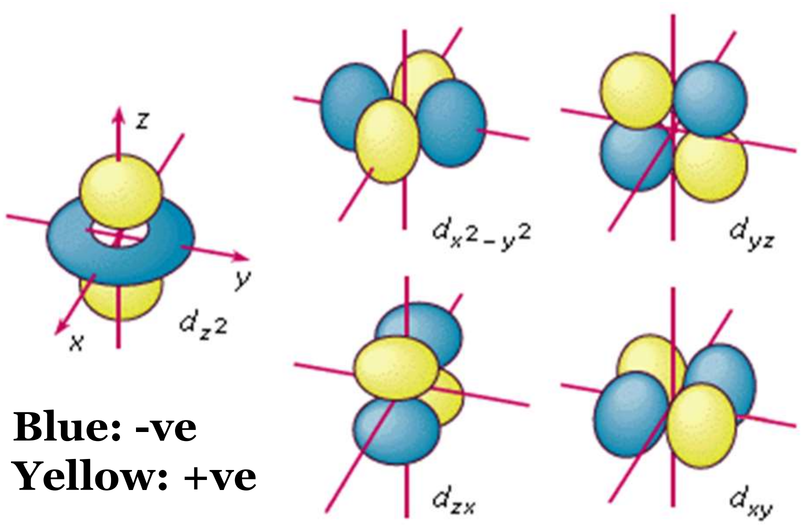
$$\psi_{3d_{xz}} = N_2\rho^2(\sin\theta\cos\theta\cos\phi)e^{-\rho/3}$$

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

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

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

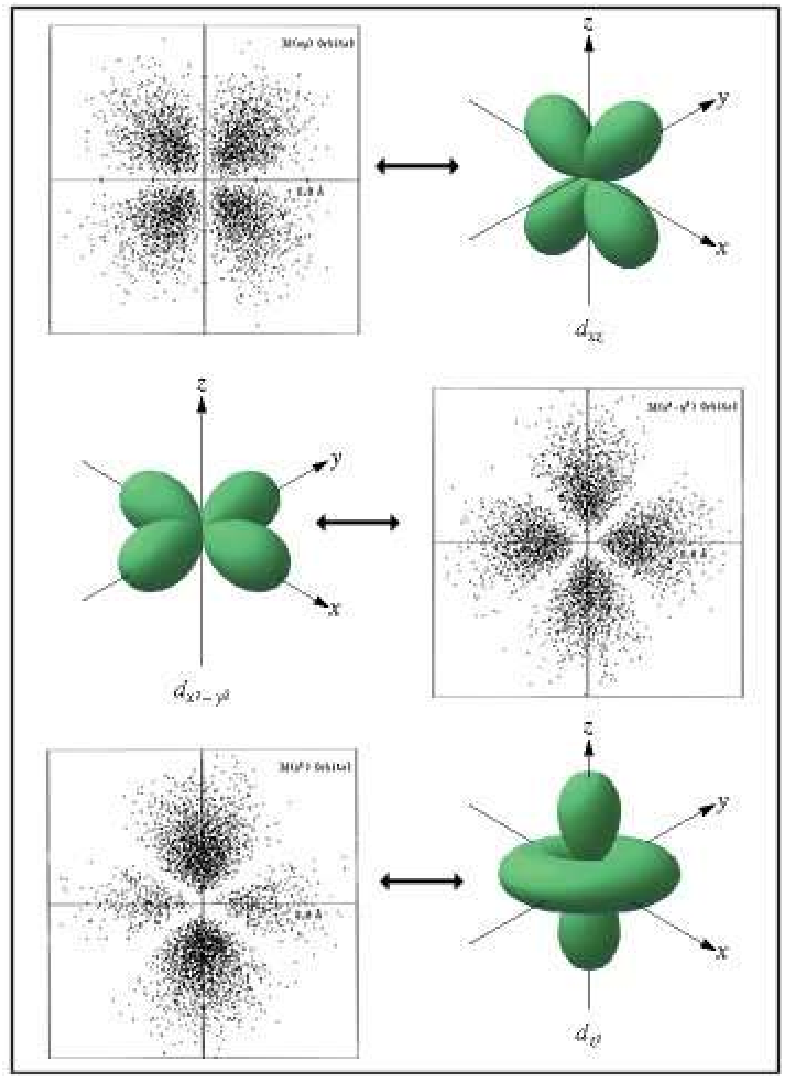
Angular part



Blue: -ve
Yellow: +ve

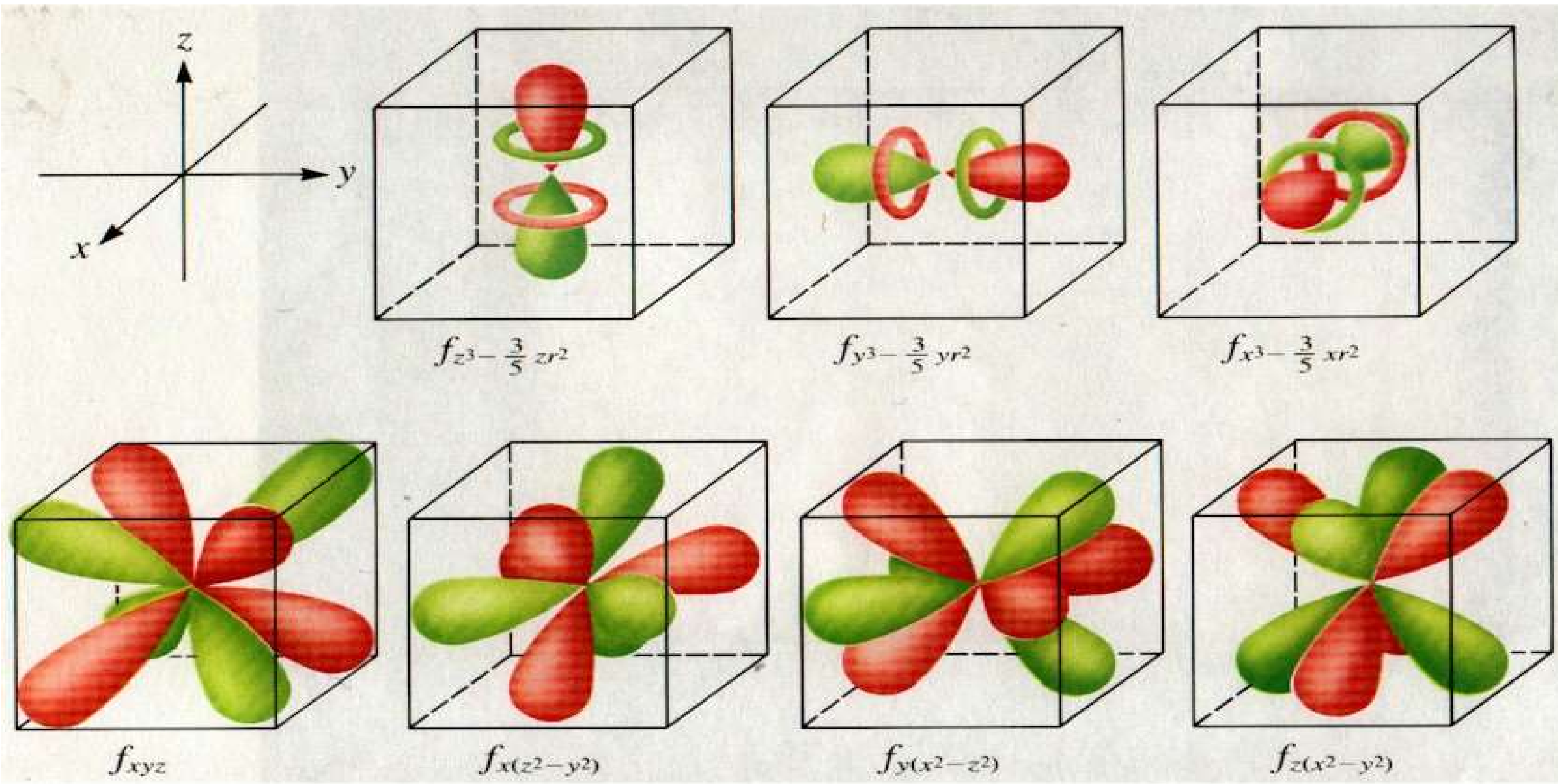
n=3; l=2; m=0,±1, ±2

Angular + Radial



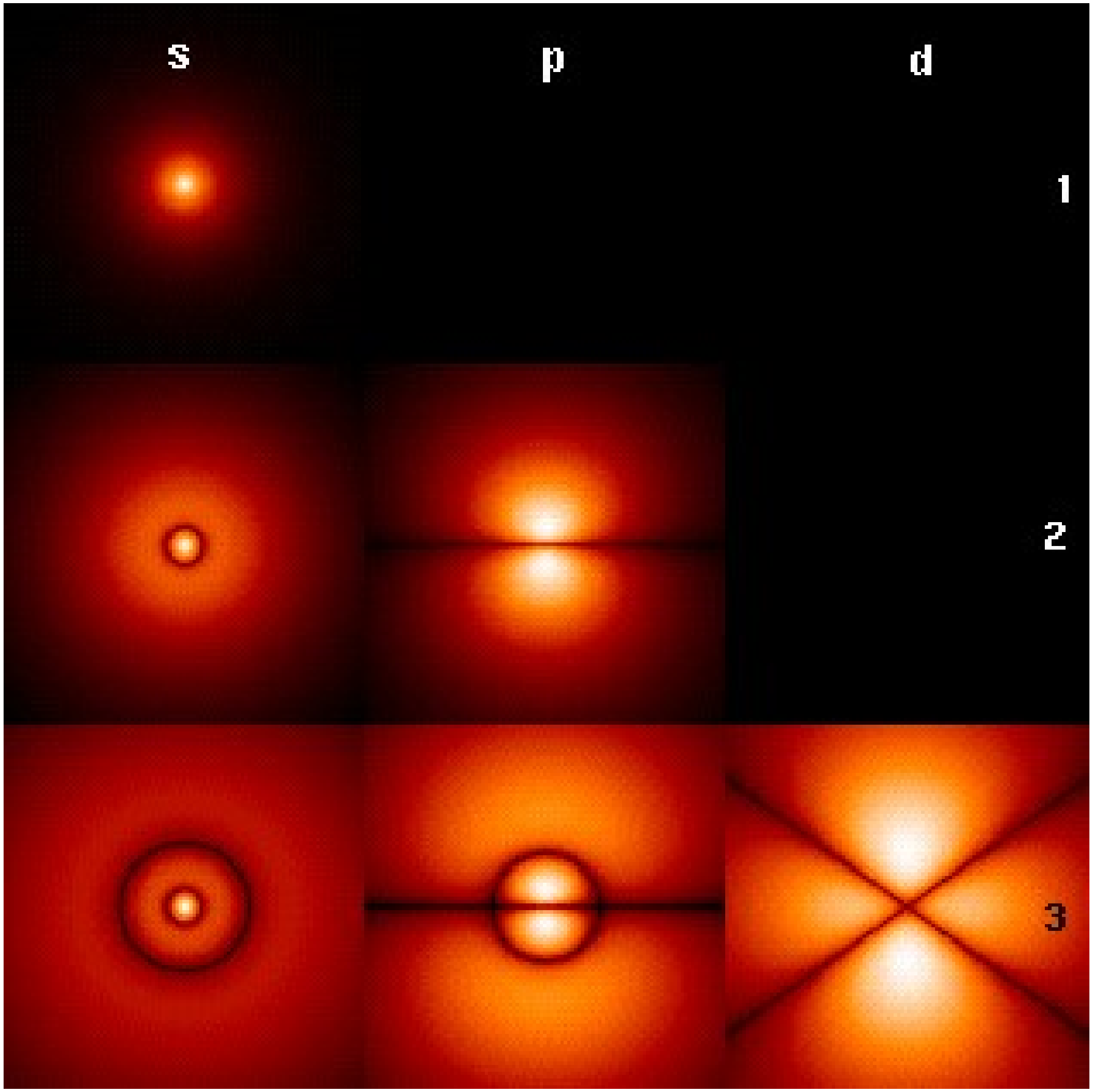
f-Orbitals

$n=4;\ l=3;\ m=0, \pm 1, \pm 2, \pm 3$

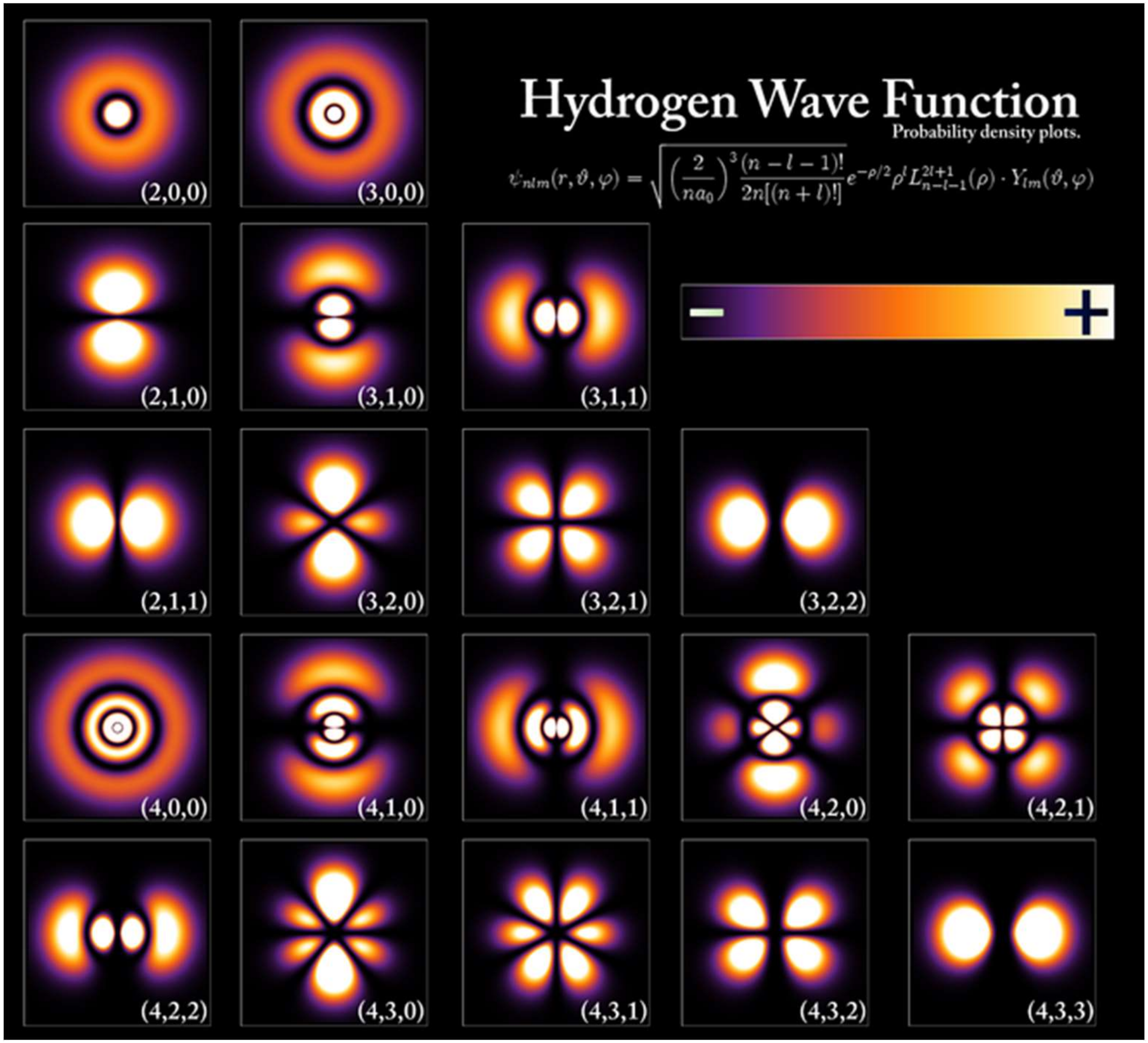


Green: -ve
Red: +ve

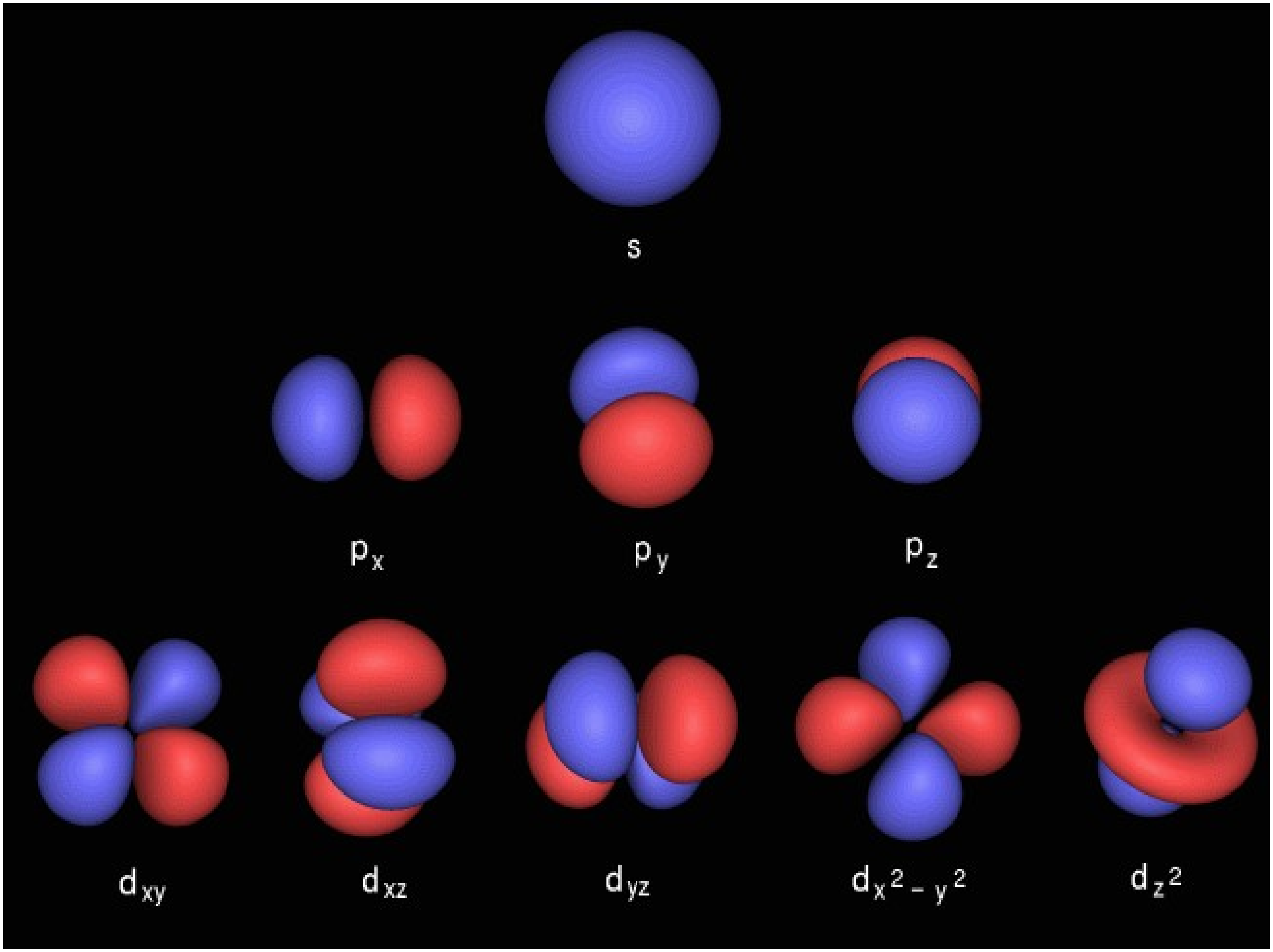
Cross-sections of Orbitals



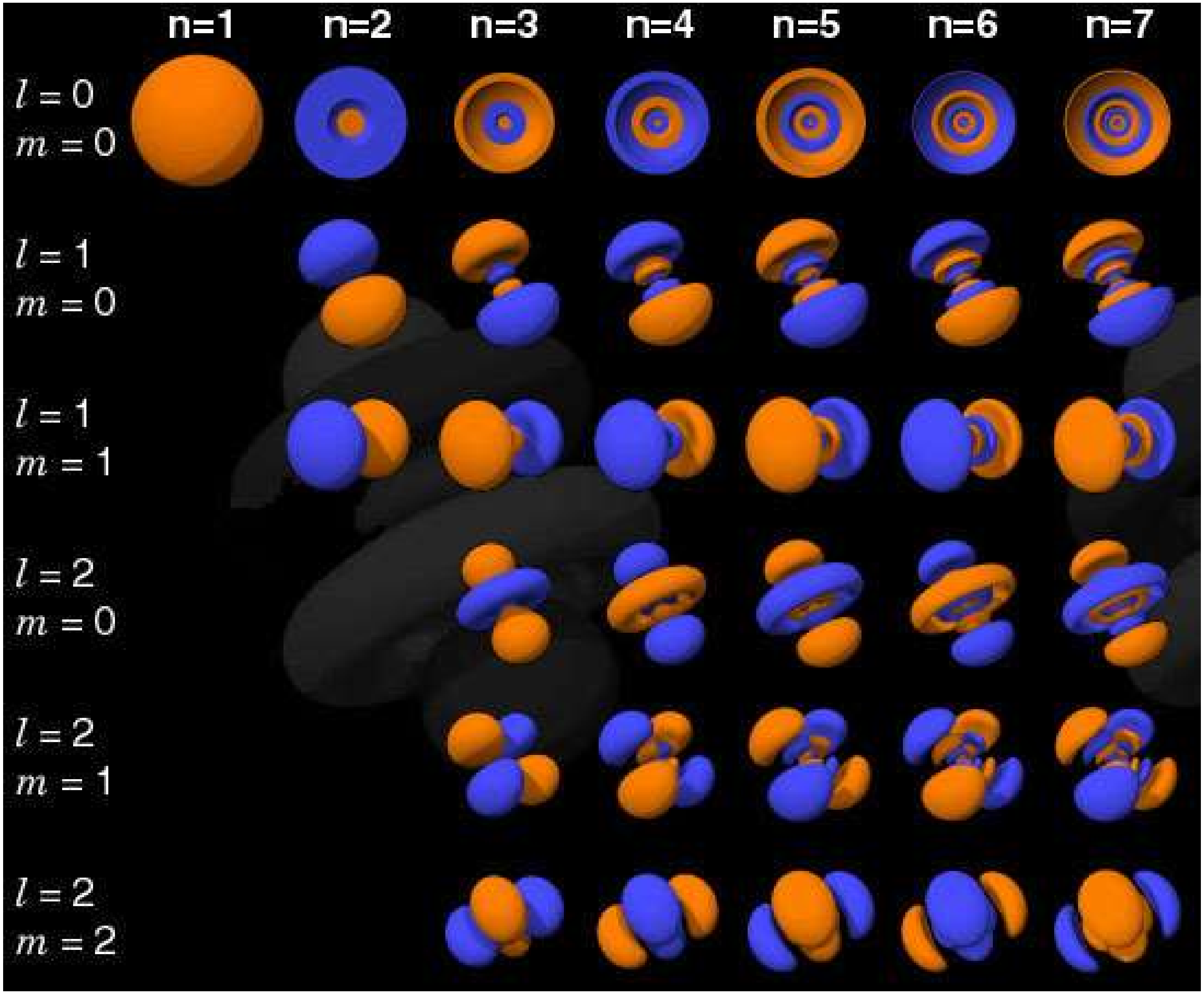
Hydrogen Wavefunctions



Orbitals: External Structure



Orbitals: Internal Stucture



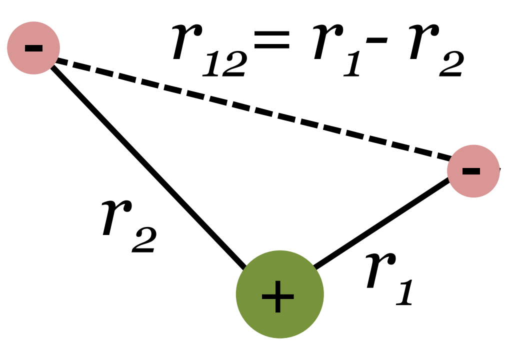
Hydrogen atom & Orbitals

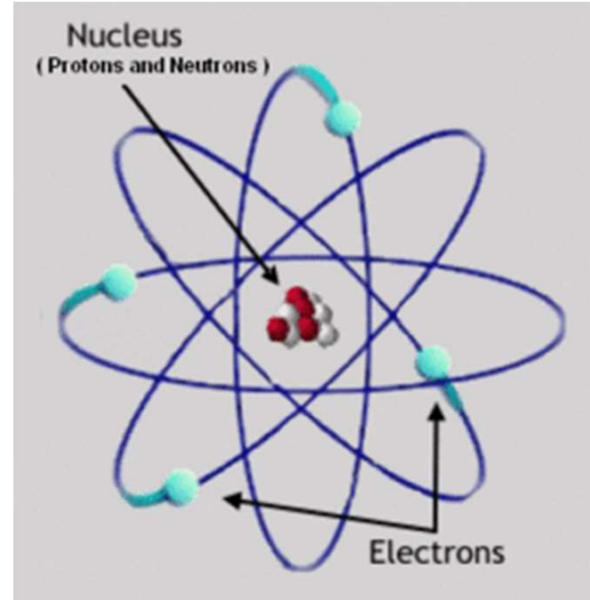
Hydrogen atom has only one electron, so why bother about all these orbitals?

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

Many Electron Atoms

Helium is the simplest many electron atom





KE of Nucleus

KE of Electron2

Attraction between nucleus and Electron1

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\left(\frac{Z_N e^2}{r_1} + \frac{Z_N e^2}{r_2} - \frac{e^2}{r_{12}}\right)$$

KE of Electron1

Attraction between nucleus and Electron1

Repulsion between Electron1 and Electron2

Helium Atom

$$\widehat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\left(\frac{Z_N e^2}{r_1} + \frac{Z_N e^2}{r_2} - \frac{e^2}{r_{12}}\right)$$

$$\widehat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2} + \frac{Qe^2}{r_{12}}; Q = \frac{1}{4\pi\varepsilon_0}$$

$$\widehat{H}_N = -\frac{\hbar^2}{2m_N}\nabla_N^2 \qquad \widehat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2} + \frac{Qe^2}{r_{12}}$$

$$\widehat{H}_N \chi_N = E_n \chi_N \qquad \widehat{H}_e \psi_e = E_e \psi_e$$

Helium Atom

$$\widehat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2} + \frac{Qe^2}{r_{12}}$$

$$\widehat{H}_e = \widehat{H}_1 + \widehat{H}_2 + \frac{Qe^2}{r_{12}}$$

$$\widehat{H}_1 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{QZ_N e^2}{r_1} \quad \text{and} \quad \widehat{H}_2 = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{QZ_N e^2}{r_2}$$

The Hamiltonians $\boldsymbol{\hat{H}_1}$ and $\boldsymbol{\hat{H}_1}$ are one electron Hamiltonians similar to that of hydrogen atom

$$\widehat{H}_e\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \widehat{H}_1\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \widehat{H}_2\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

Orbital Approximation

$$\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\psi_e(1,2,3,\ldots n) \approx \phi(1)\cdot\phi(2)\cdot\phi(3)\cdot\cdots\cdot\phi(n)$$

Orbital is a one electron wavefunction

The total electronic wavefunction of n number of electrons can be written as a product of n one electron wavefunctions

Helium Atom: Orbital Approximation

$$\hat{H}_e \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \hat{H}_1 \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \hat{H}_2 \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}} \psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

$$\psi_e(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\hat{H}_e \psi_e = \hat{H}_1 \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \hat{H}_2 \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}} \psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

Helium Atom: Orbital Approximation

$$\widehat{H}_e\psi_e = \widehat{H}_1\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \widehat{H}_2\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\widehat{H}_e\psi_e = \varepsilon_1\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \varepsilon_2\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2) + \frac{Qe^2}{r_{12}}\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)$$

$$\widehat{H}_e\psi_e = \left(\varepsilon_1 + \varepsilon_2 + \frac{Qe^2}{r_{12}}\right)\left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)\right]$$

$$\varepsilon_1 = \varepsilon_2 = -\frac{Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} = \frac{-13.6Z^2}{n^2}eV$$

Helium Atom: Orbital Approximation

$$\widehat{H}_e\psi_e = \left(\varepsilon_1 + \varepsilon_2 + \frac{Qe^2}{r_{12}}\right)\left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)\right]$$

If we ignore the term $\dfrac{Qe^2}{r_{12}}$

$$\widehat{H}_e\psi_e = (\varepsilon_1 + \varepsilon_2)\left[\psi_{1e}(r_1,\theta_1,\phi_1)\psi_{2e}(r_2,\theta_2,\phi_2)\right]$$

$$\mathrm{E}_{\mathrm{He}} = \varepsilon_1 + \varepsilon_2 = -108.8eV$$

$$\psi_e = \left(\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o}\right)\cdot\left(\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o}\right) = \psi_{1s}(1)\cdot\psi_{1s}(2)$$

Helium Atom: Orbital Approximation

$$E_{He} = \varepsilon_1 + \varepsilon_2 = -(54.4 + 54.4)eV = -108.8eV$$

$$E_{He} = -(24.59 + 54.4)eV = -78.99eV \text{ (Experimental)}$$

Ignoring $\frac{Qe^2}{r_{12}}$ is not justified! Need better approximation