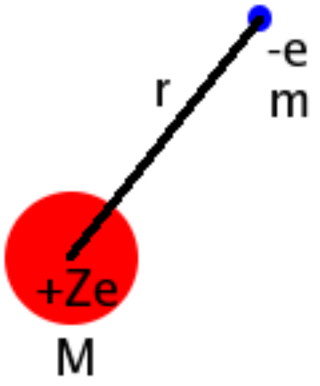
Quantum Mechanics and Atomic Orbitals

HYDROGEN ATOM

Hydrogen-like Atoms

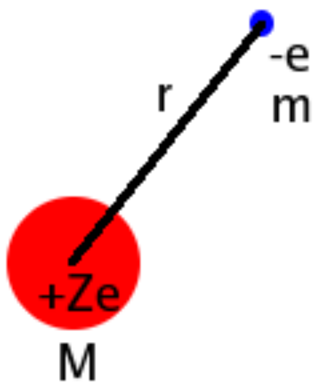
- Spherical symmetry
- Single electron
- Point charge +Ze in the center
- Coulomb interaction between nucleus and electron so the electron experiences a Coulomb potential:

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$$



Schrodinger Equation

$$\left[-\frac{h}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right]\Psi = E\Psi$$



Spherical symmetry:

Cartesian coordinate → spherical coordinate

$$\Psi(x,y,z)\rightarrow\Psi(r,\phi,\theta)$$

$$\boxed{\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\cdot Y_{lm}(\theta,\phi)}$$

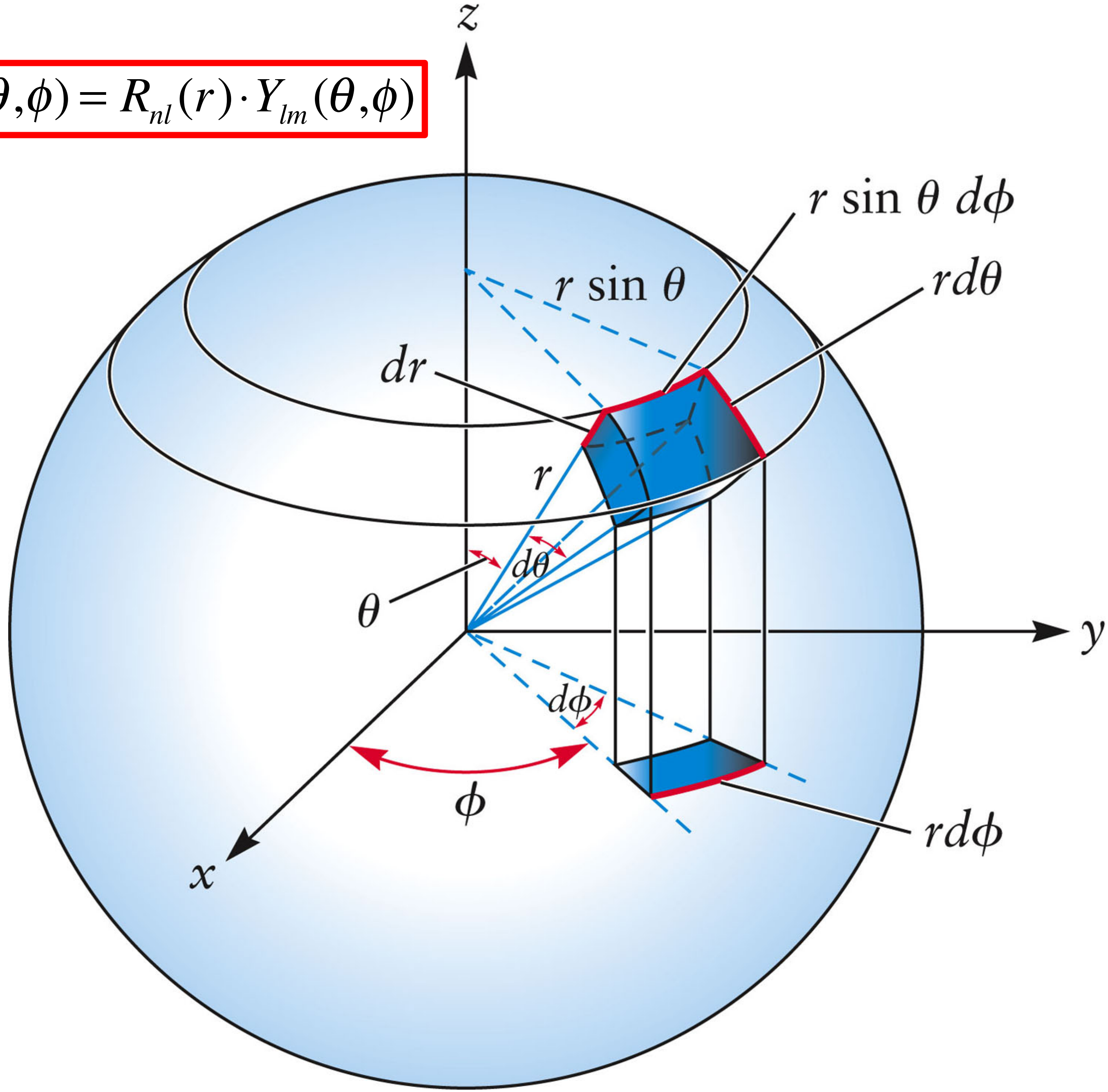


Fig. 5-3, p. 198

Solutions to the Schrodinger's Eq.

- Wavefunctions (three quantum numbers!):

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\cdot Y_{lm}(\theta,\phi)$$

  radial part + angular part

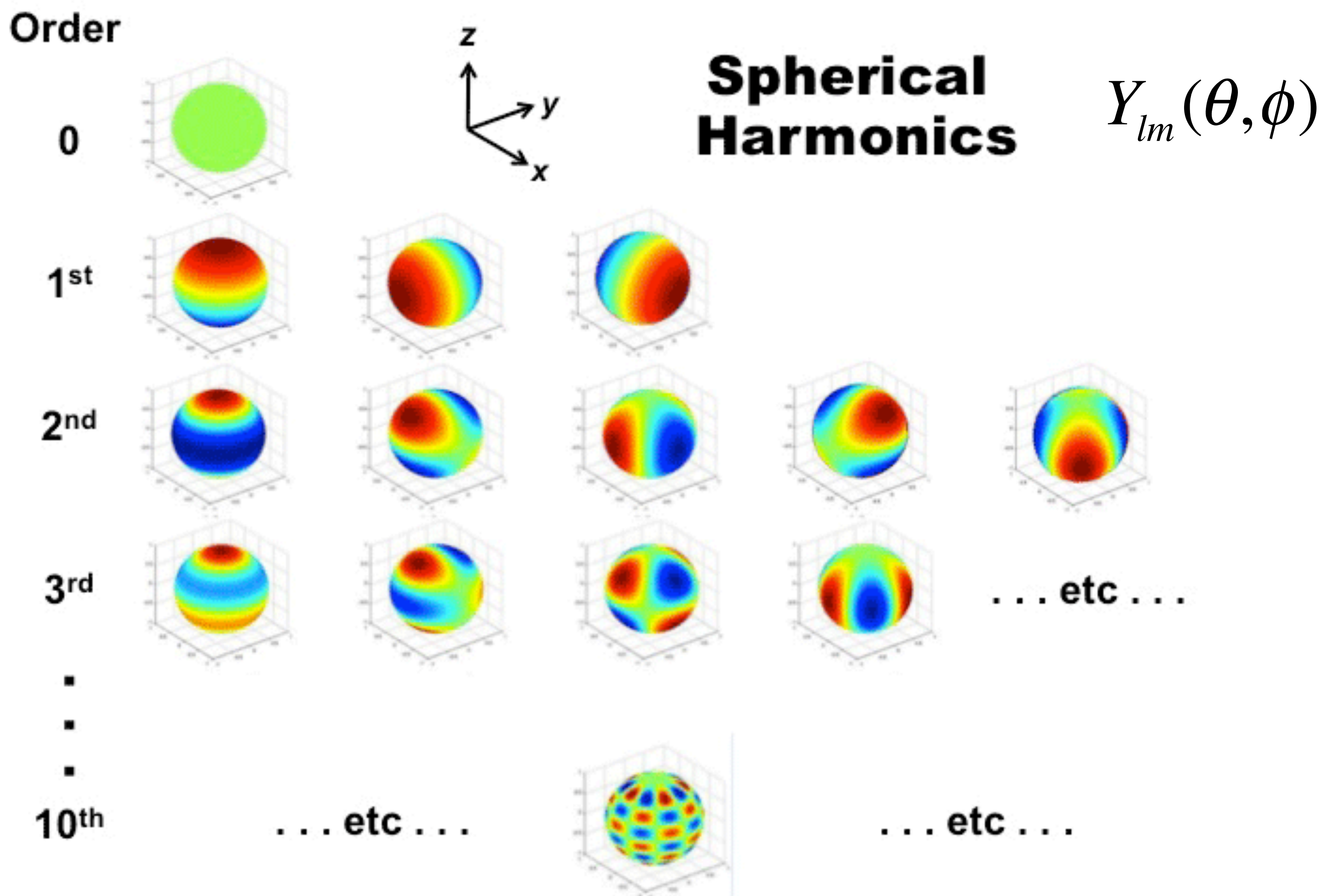
- Energy levels:

$$E_n = -\left(\frac{Z^2\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\right)\frac{1}{n^2} = -\left(\frac{Z^2\hbar^2}{2\mu a_\mu^2}\right)\frac{1}{n^2} = -\frac{\mu c^2 Z^2\alpha^2}{2n^2}.$$

$$E_n = -\frac{Z^2}{n^2}R,$$ R=13.6 eV (Rydberg constant)

- $Y_{lm}(\theta,\phi)$ are the angular wavefunction (rotational eigenstates) → spherical harmonics (vibrational modes on the surface of a sphere!)

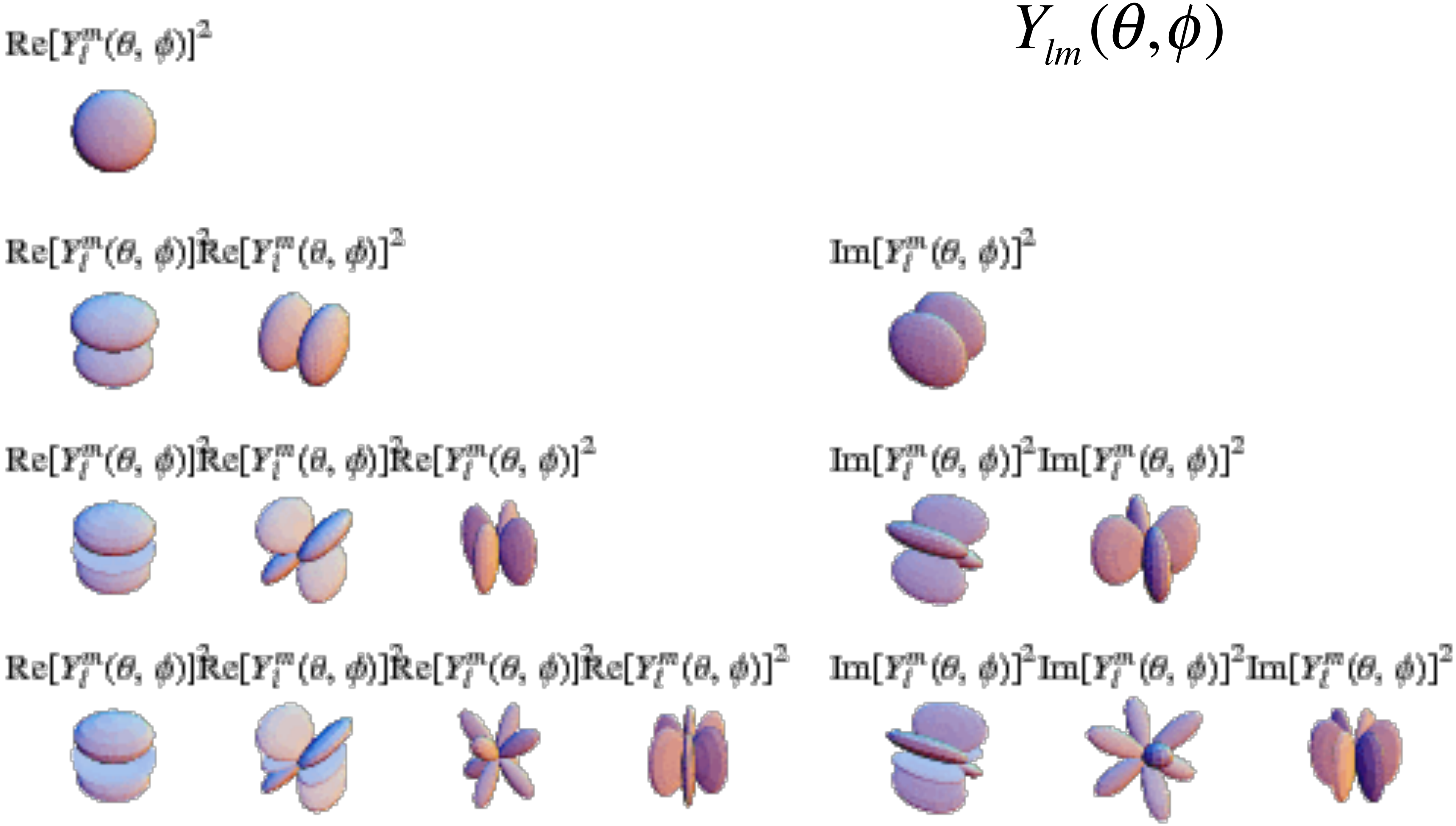
Spherical Harmonics on a Unit Sphere



http://mri-q.com/how-to-map-bo.html

Spherical Harmonics (Parametric Plots)

$$Y_{lm}(\theta,\phi)$$

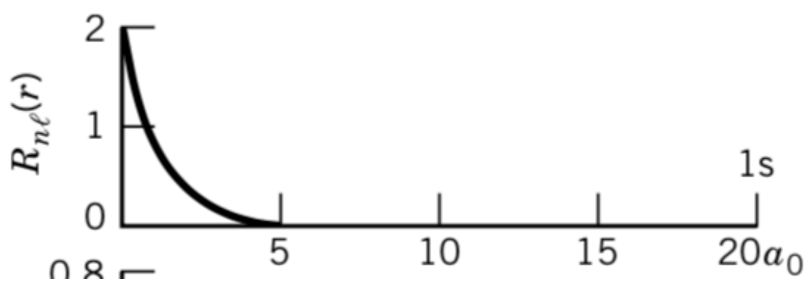


http://mathworld.wolfram.com/SphericalHarmonic.html

Nodal planes!!

Radial Part

- $R_{nl}(r)$: radial function
- $r^2 R_{nl}^2(r)$: radial probability density



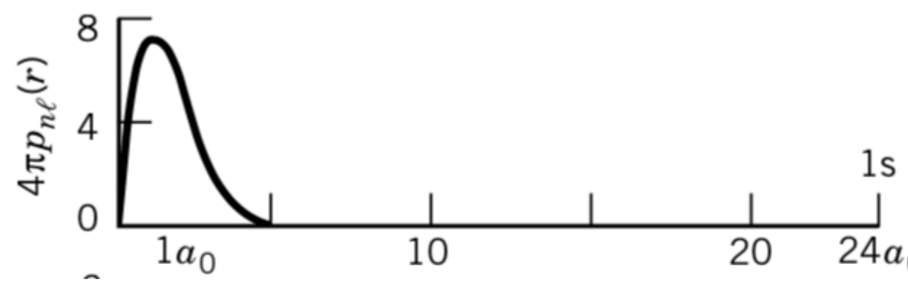
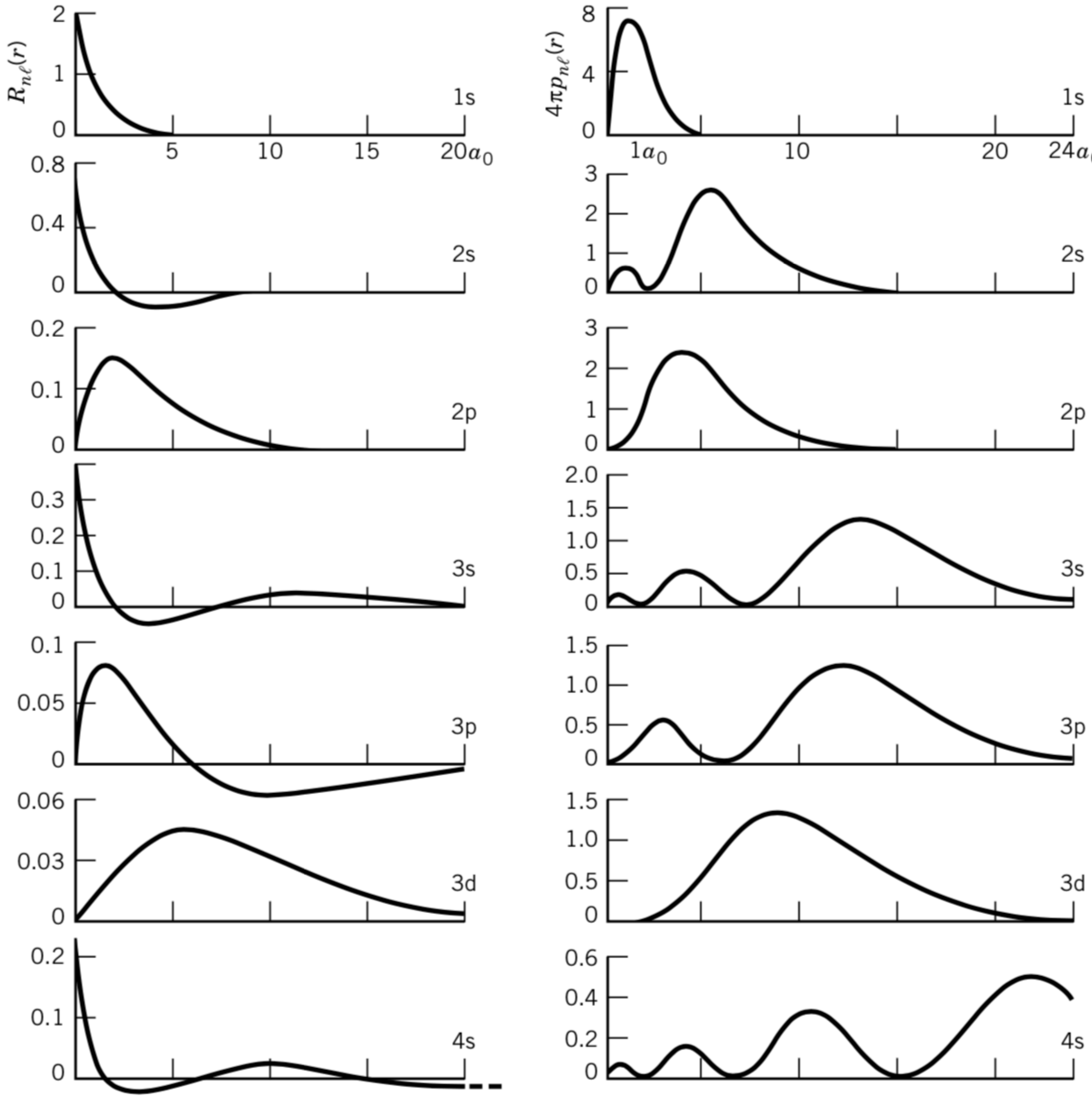


Table 10.1 Real Hydrogenlike Wavefunctions[a]

n	ℓ	m	*Wavefunction*
1	0	0	$\psi_{1s} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
2	0	0	$\psi_{2s} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (2-\sigma)\, e^{-\sigma/2}$
2	1	0	$\psi_{2p_z} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma\, e^{-\sigma/2} \cos\theta$
2	1	± 1	$\psi_{2p_x} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma\, e^{-\sigma/2} \sin\theta\cos\phi$
			$\psi_{2p_y} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma\, e^{-\sigma/2} \sin\theta\sin\phi$
3	0	0	$\psi_{3s} = \dfrac{1}{81\sqrt{3\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)\, e^{-\sigma/3}$
3	1	0	$\psi_{3p_z} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (6-\sigma)\sigma\, e^{-\sigma/3} \cos\theta$
3	1	± 1	$\psi_{3p_x} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (6-\sigma)\sigma\, e^{-\sigma/3} \sin\theta\cos\phi$
			$\psi_{3p_y} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (6-\sigma)\sigma\, e^{-\sigma/3} \sin\theta\sin\phi$
3	2	0	$\psi_{3d_{z^2}} = \dfrac{1}{81\sqrt{6\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2\, e^{-\sigma/3}(3\cos^2\theta - 1)$
3	2	± 1	$\psi_{3d_{xz}} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2\, e^{-\sigma/3} \sin\theta\cos\theta\cos\phi$
			$\psi_{3d_{yz}} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2\, e^{-\sigma/3} \sin\theta\cos\theta\sin\phi$
3	2	± 2	$\psi_{3d_{x^2-y^2}} = \dfrac{1}{81\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2\, e^{-\sigma/3} \sin^2\theta\cos 2\phi$
			$\psi_{3d_{xy}} = \dfrac{1}{81\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2\, e^{-\sigma/3} \sin^2\theta\sin 2\phi$

[a] $\sigma = \dfrac{Z}{a_0} r$.



$R_{n\ell}(r)$
$4\pi p_{n\ell}(r)$
1s
2s
2p
3s
3p
3d
4s
5
10
15
$20a_0$
$1a_0$
10
20
$24a_0$

Orbitals and Quantum Numbers

- Orbital → single-electron wavefunction
- Each orbital having a characteristic *shape* and *energy* is defined by a set of quantum numbers (n, l, and m_l)
  - Principal quantum number (n)
    defines the size and energy of the orbital
  - Angular momentum quantum number (l)
    magnitude of the angular momentum
    defines the shape of the orbital
  - Magnetic quantum number (m_l)
    projection of the angular momentum on the z-axis
    defines the orientation of the orbital

Principal Quantum Number (*n*)

- positive integral values from 1, 2, 3,...

- when *n* increases, the orbital become larger

- when *n* increases, the energy of the electron in the orbital is higher
  - for one-electron atom/ion

$$E_n = (-2.18\times 10^{-18} J)\left(\frac{Z^2}{n^2}\right)$$

Z : atomic number

n : principal quantum number $(1,2,3,\cdots)$

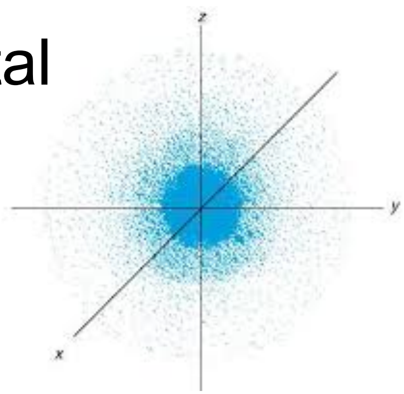
Angular Momentum Quantum Number (*l*)

- positive integral values from 0 to (n – 1) for each value of n
- Is related to the magnitude of electron angular moment
- Each *l* value is designated by a letter

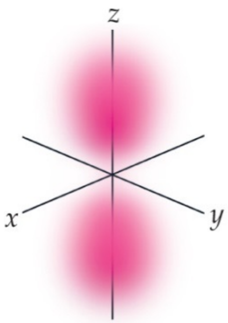
The Angular Momentum Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals

Value of ℓ	0	1	2	3	4
Letter Used	*s*	*p*	*d*	*f*	*g*

s orbital



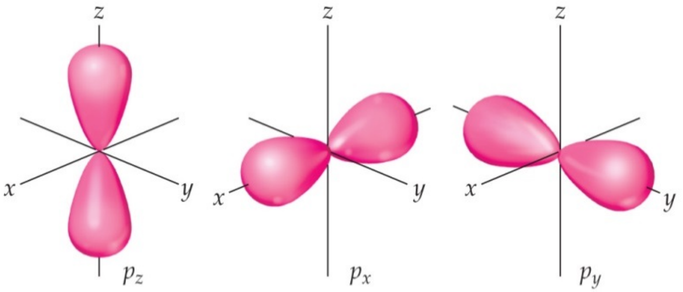
p orbital



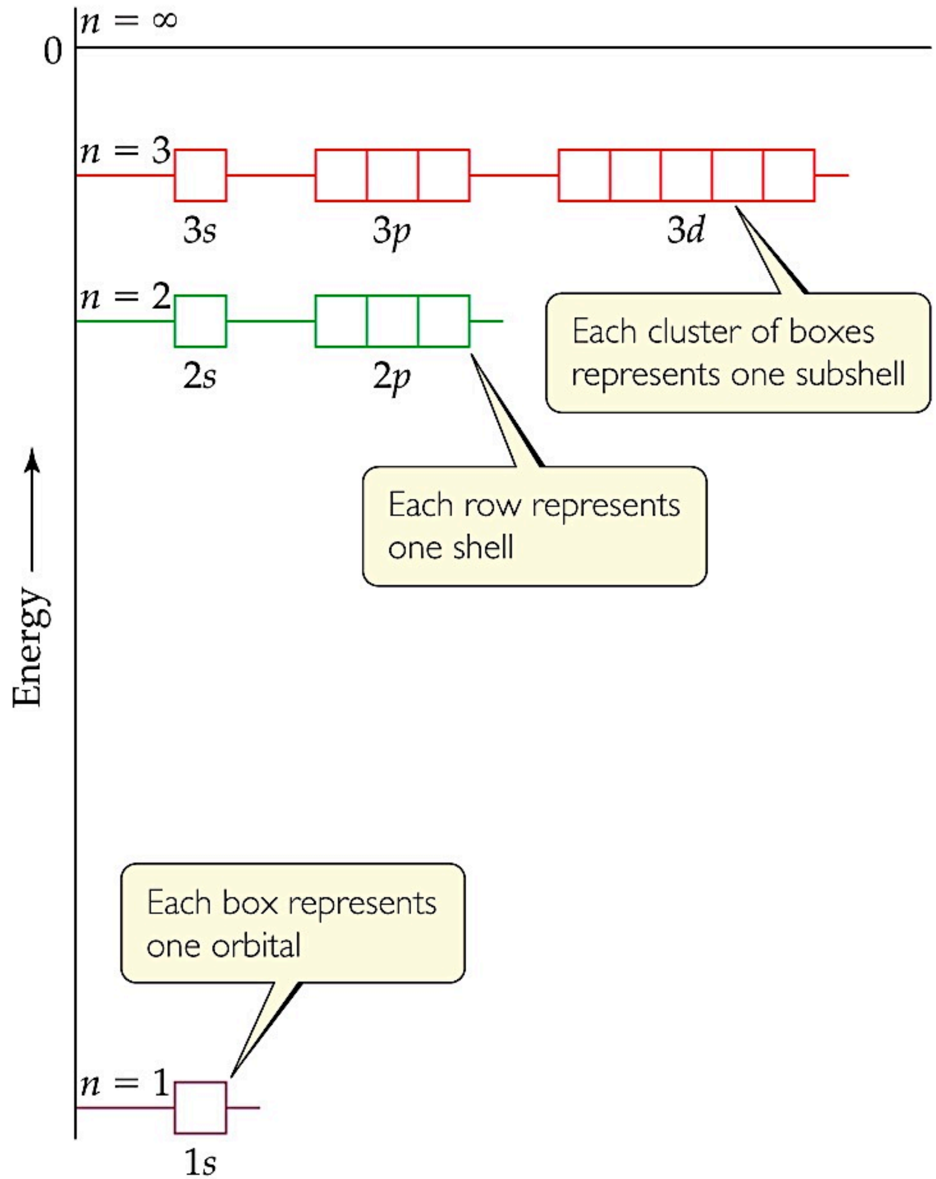
Magnetic Quantum Number (m_l)

- any integral value between –*l* and *l*, including zero
- defines the orientation of the orbital

Value of *l*	0	1	2
possible values of m_l	0	-1, 0, 1	-2, -1, 0, 1, 2



Energy Levels in Hydrogen Atom



- For a one-electron system, orbitals on the same electron shell have the same energy.
- That is, they are **degenerate**.

TABLE 5.1

Allowed Values of Quantum Numbers for One-Electron Atoms

n	1	2		3		
ℓ	0	0	1	0	1	2
m	0	0	$-1, 0, +1$	0	$-1, 0, +1$	$-2, -1, 0, +1, +2$
Number of degenerate states for each ℓ	1	1	3	1	3	5
Number of degenerate states for each n	1	4		9		

Degeneracy for each l: 2l+1

Degeneracy for each n: n^2

Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

TABLE 2.2 › Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

n	ℓ	Sublevel Designation	m_ℓ	Number of Orbitals
1	0	1*s*	0	1
2	0	2*s*	0	1
	1	2*p*	−1, 0, +1	3
3	0	3*s*	0	1
	1	3*p*	−1, 0, 1	3
	2	3*d*	−2, −1, 0, 1, 2	5
4	0	4*s*	0	1
	1	4*p*	−1, 0, 1	3
	2	4*d*	−2, −1, 0, 1, 2	5
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7

Schrödinger's Equation

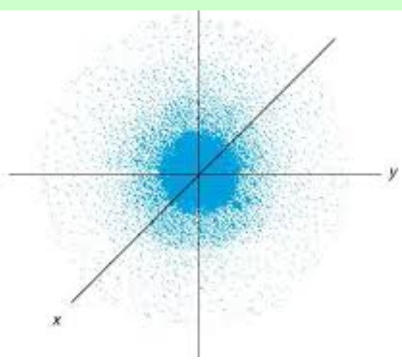
The general form of Schrödinger equation is

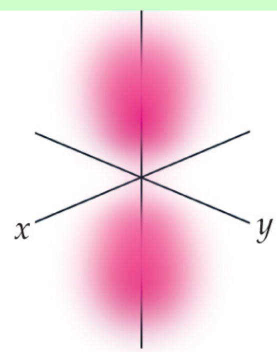
$$H\psi = E\psi$$

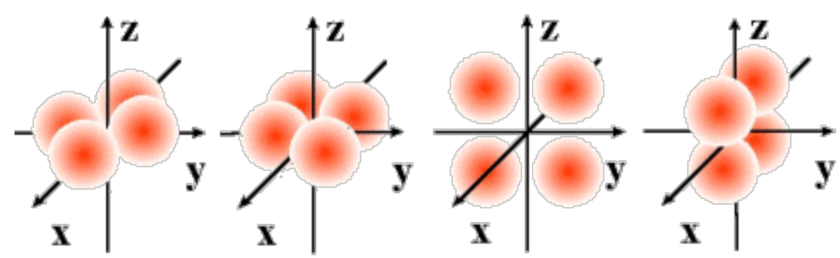
- H : total energy operator

Now we understand that different shapes of orbitals correspond to different rotational states:
No nodal plane → l=0, no rotation
1 nodal plane → l=1, first excited rotational state
2 nodal plane → l=2

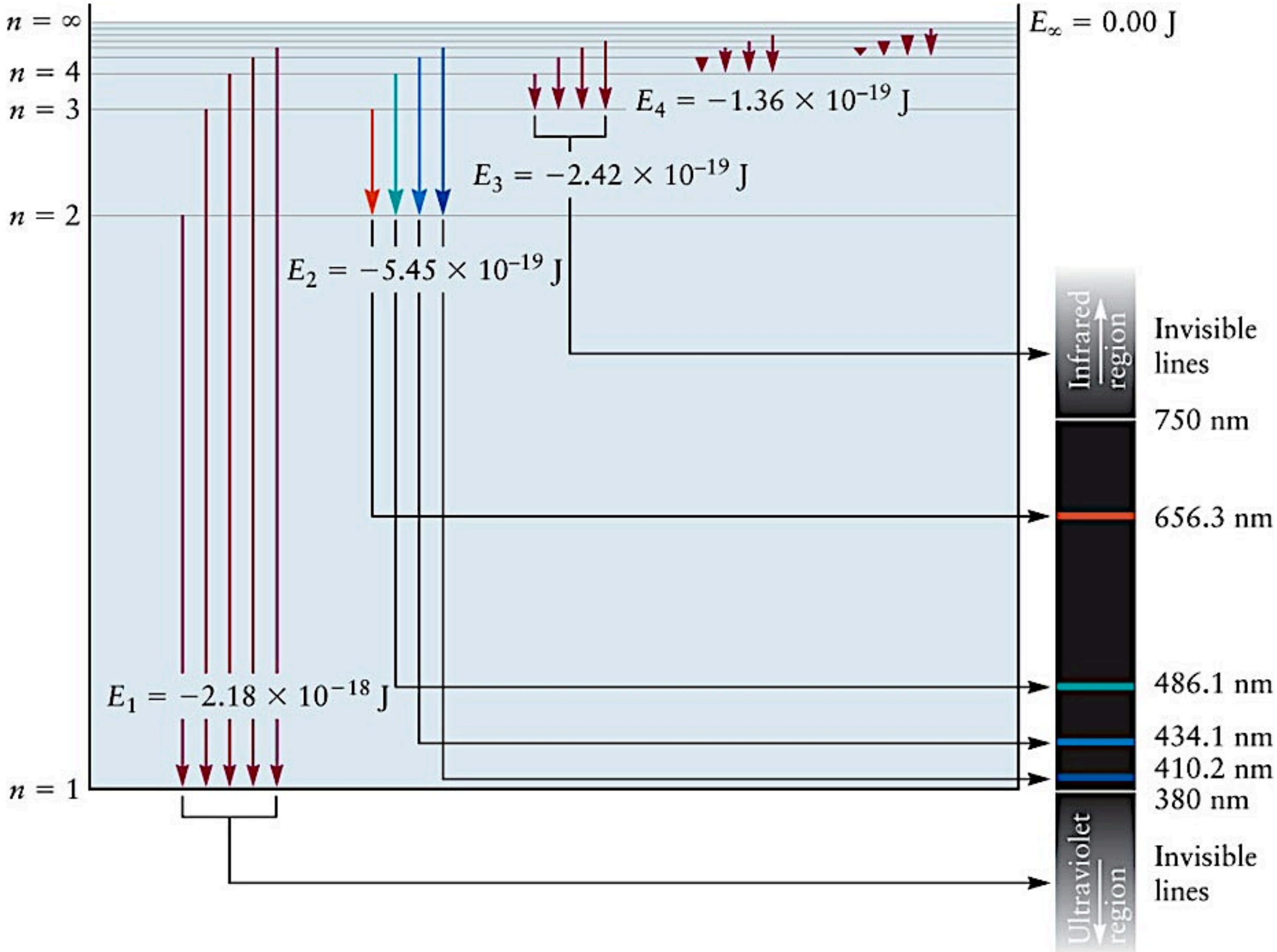
E
y







Energy Levels in Hydrogen Atom



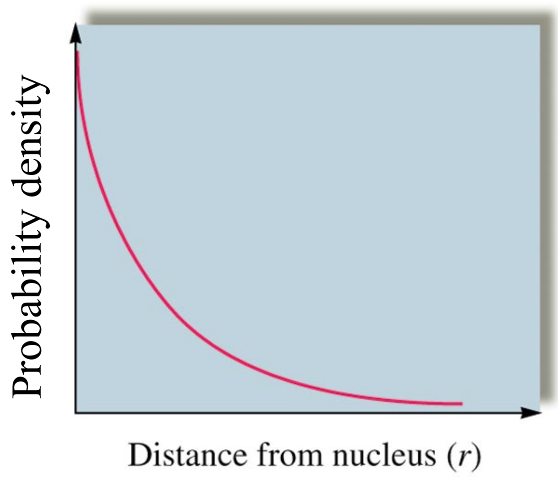
$H\psi = E\psi$

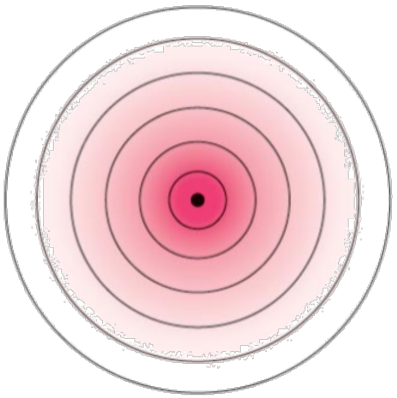
Excellent agreement with experiments

Probability Density

- The modulus squared of the wave function ($|\psi|^2$) represents the probability density of finding the electron at a particular point in space

- The probability density of s orbitals at the nucleus is the highest but …

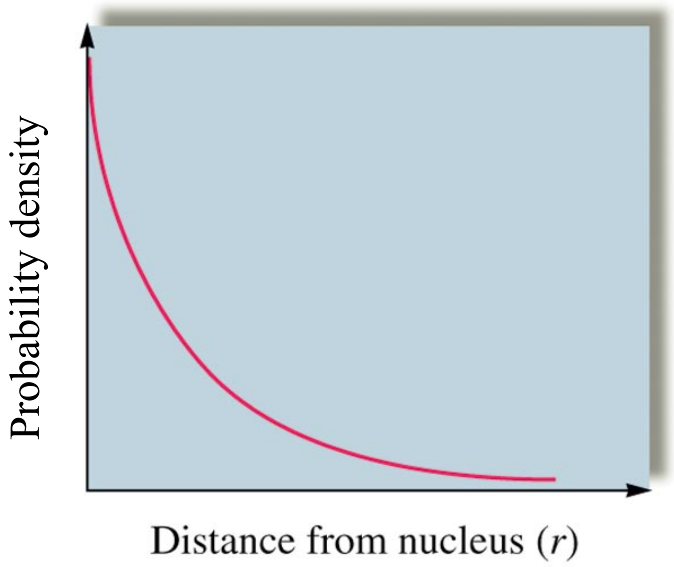


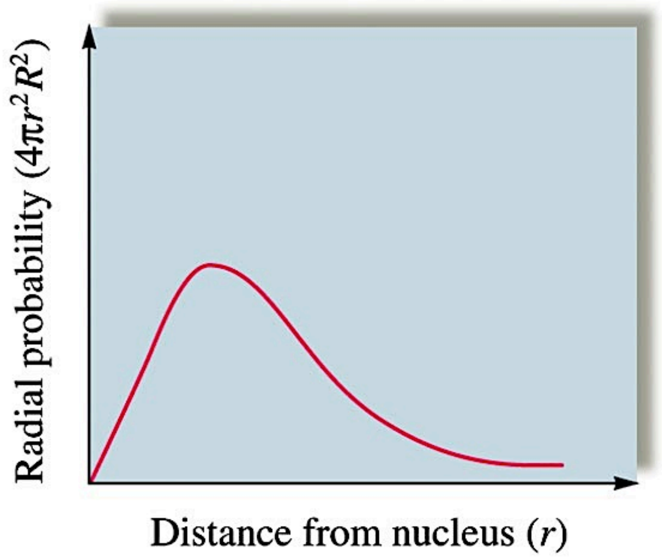


Probability = Probability density × Volume

Radial Probability Function

- Radial Probability Function
  $= 4\pi r^2\,|\psi(r)|^2$
  = sum of all $|\psi(r)|^2$ having the same given value of r





Probability of finding the electron
= area under the curve

Quantum Numbers

- Orbitals with the same value of n form a **shell**.
- Different orbital types within a shell are **subshells**.

TABLE 6.2 • Relationship among Values of n, l, and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16

How do we plot these 3-D objects?

Cut-plane

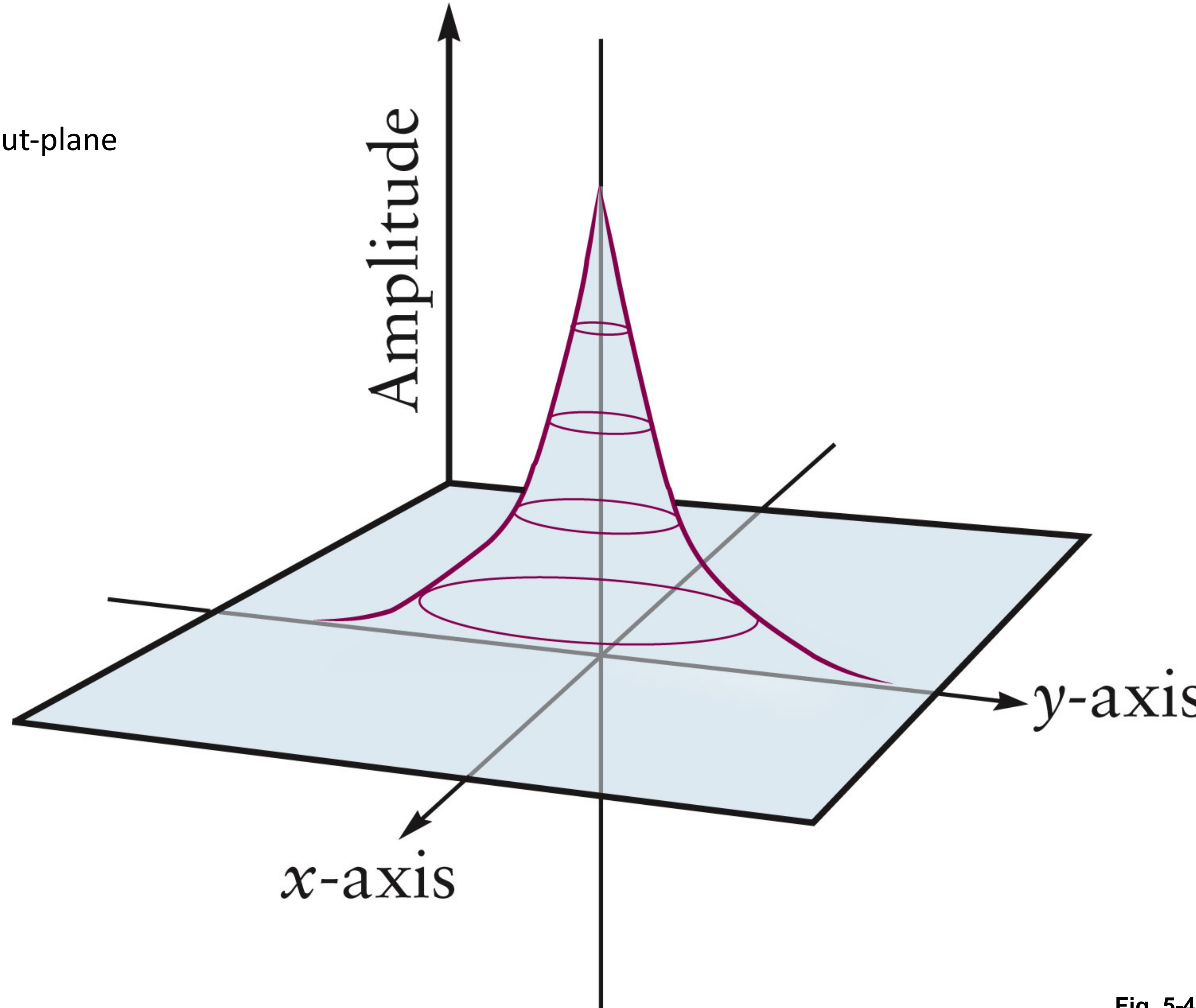
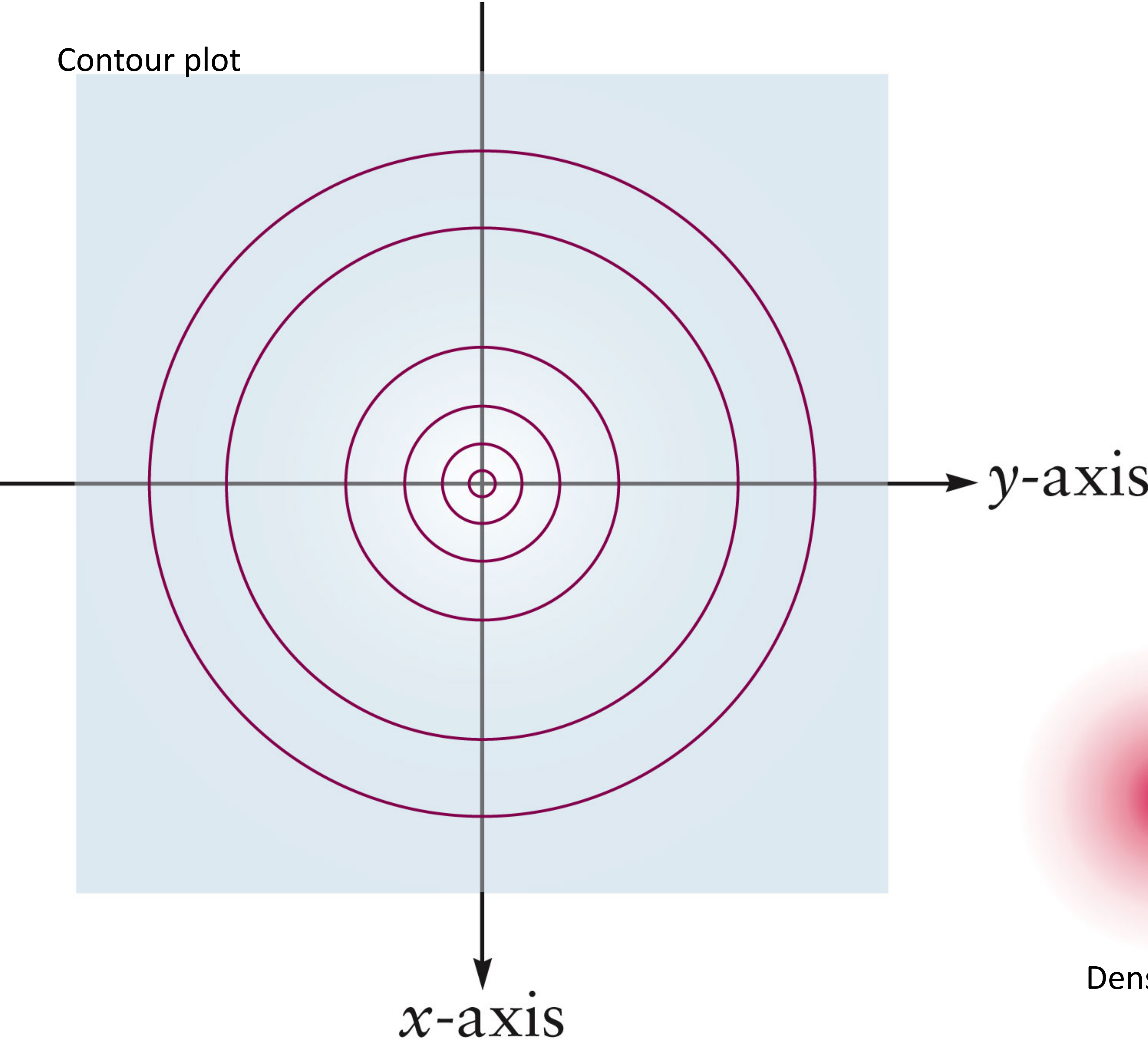


Fig. 5-4a, p. 200



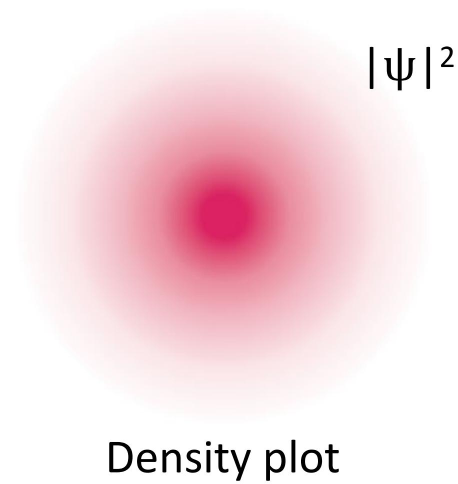
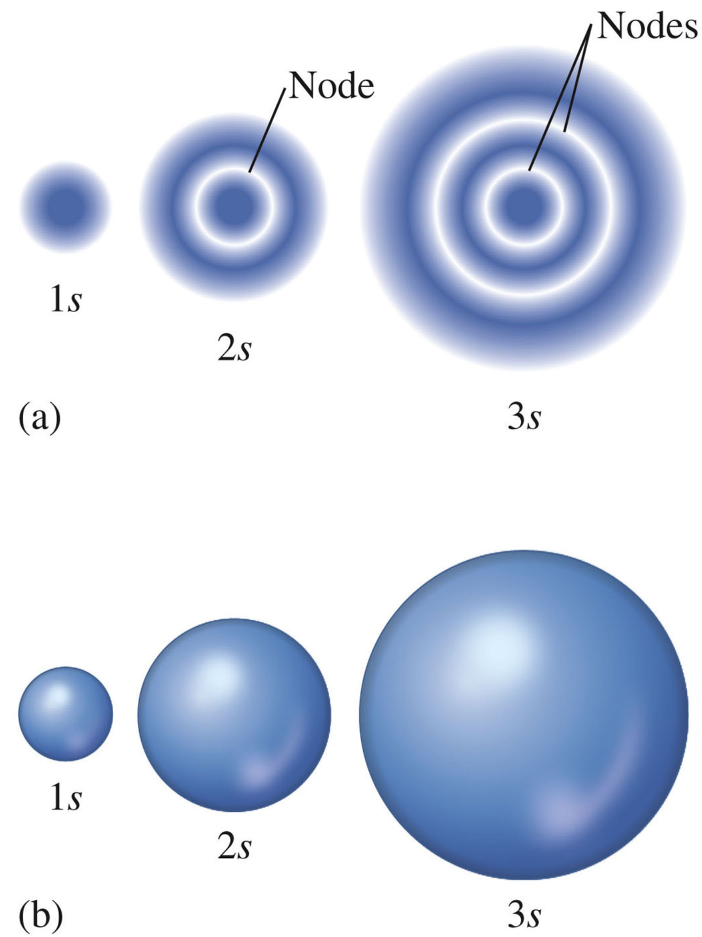


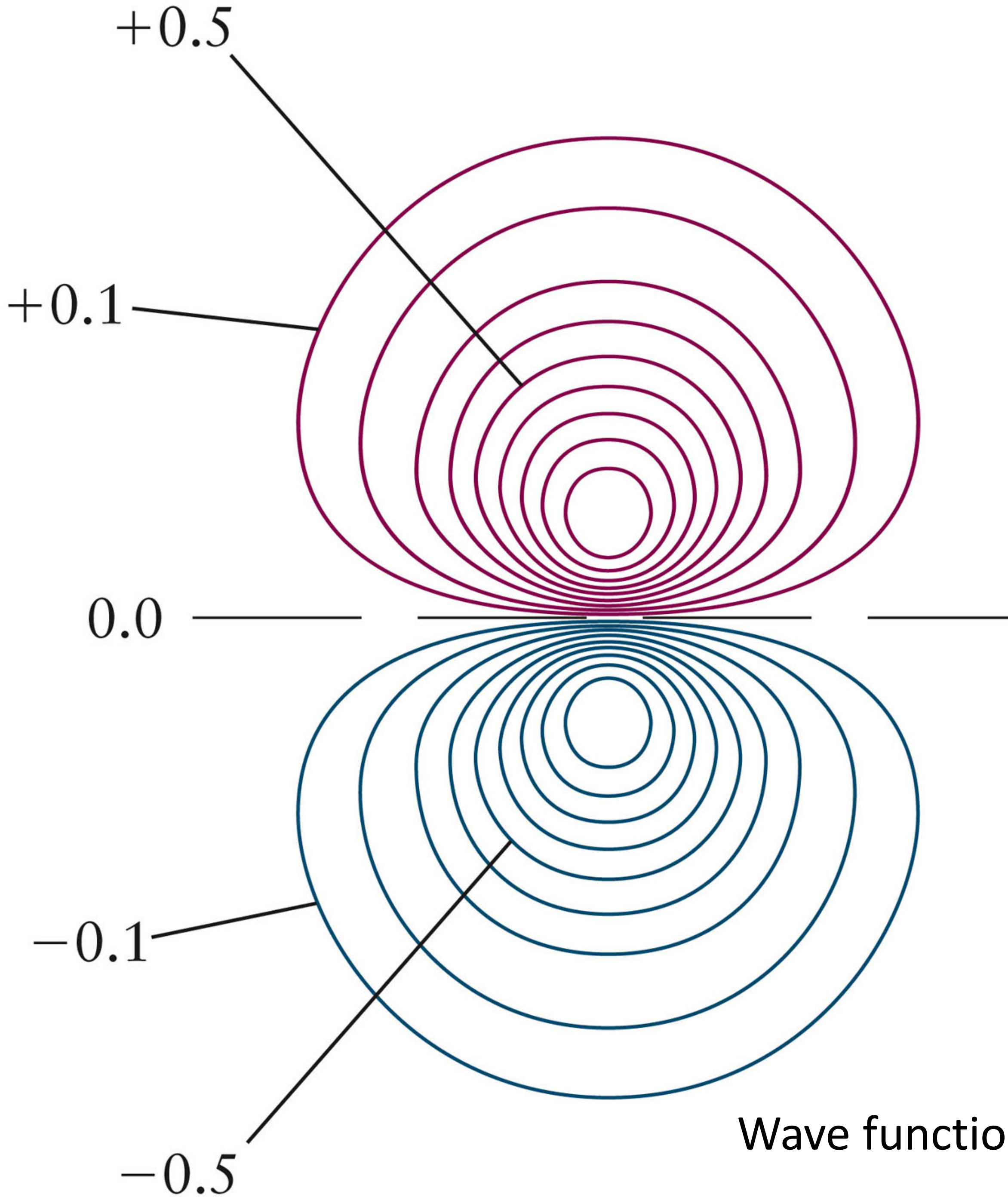
Fig. 5-4b, p. 200

Two Representations of the Hydrogen 1*s*, 2*s*, and 3*s* Orbitals



Isosurface or boundary surface

contours



Wave functions have signs!!

Fig. 5-11, p. 206

Isosurface at ±0.2 of the maximum value

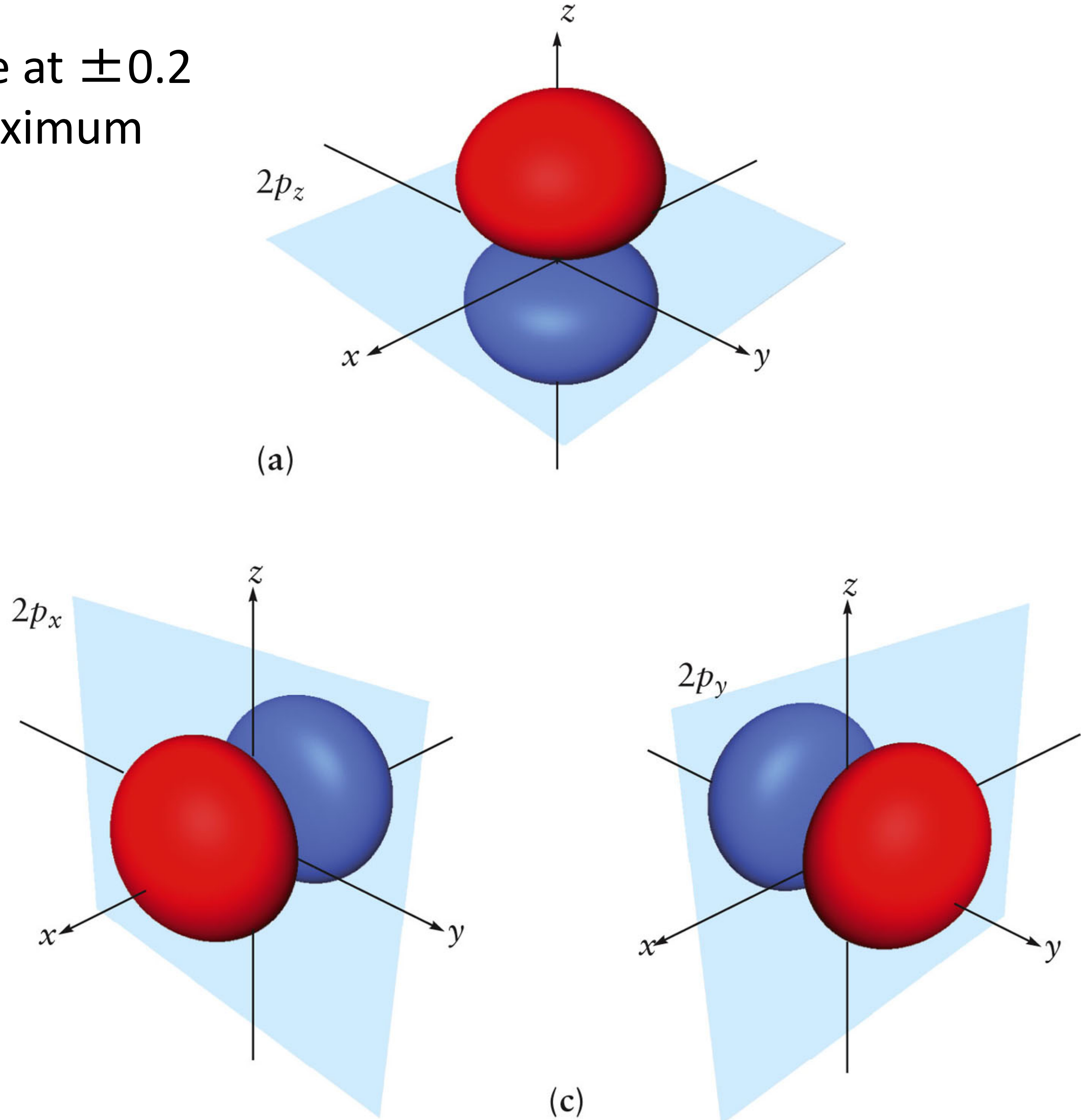
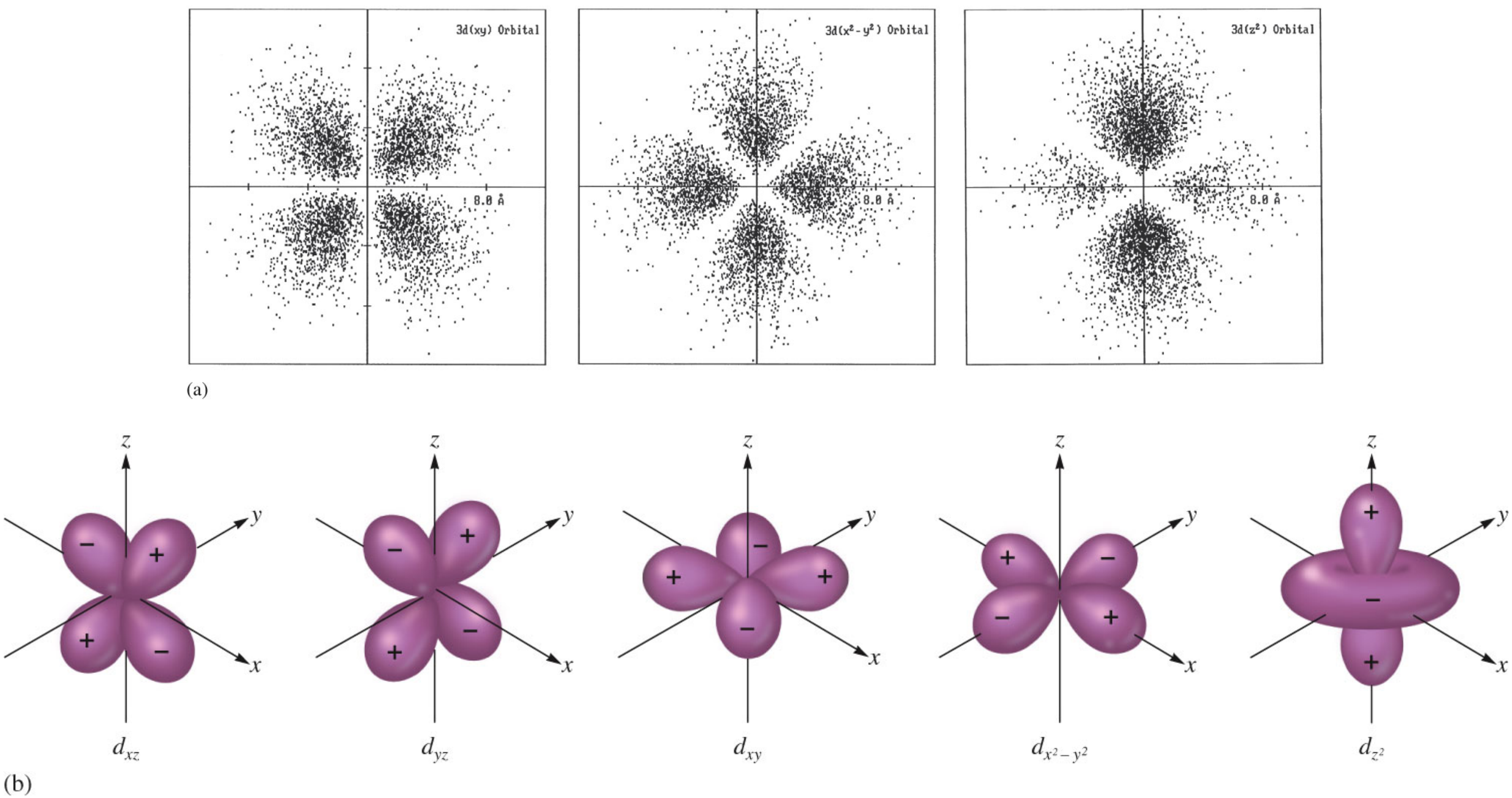


Fig. 5-12, p. 206

The Boundary Surfaces of All of the 3*d* Orbitals



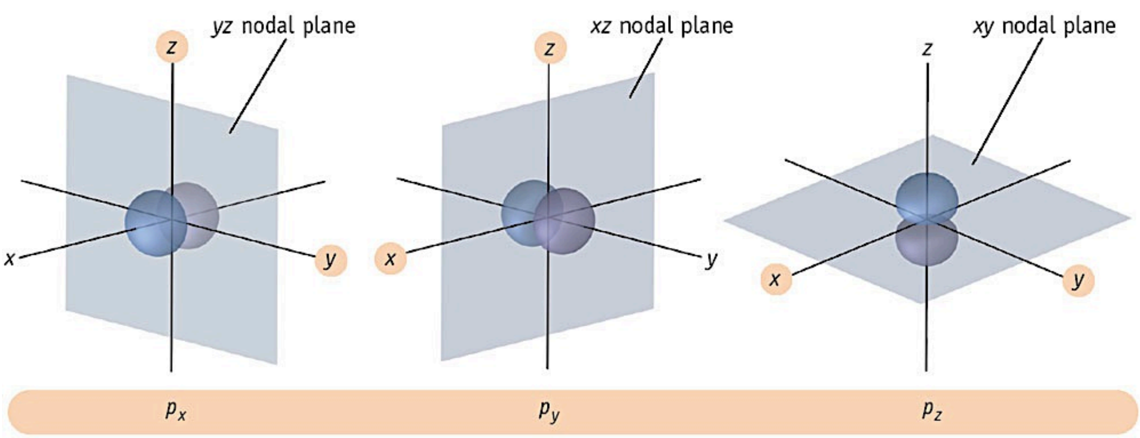
Nodes

The probability of finding an electron is **ZERO**.

$$|\psi(r)|^2 = 0$$

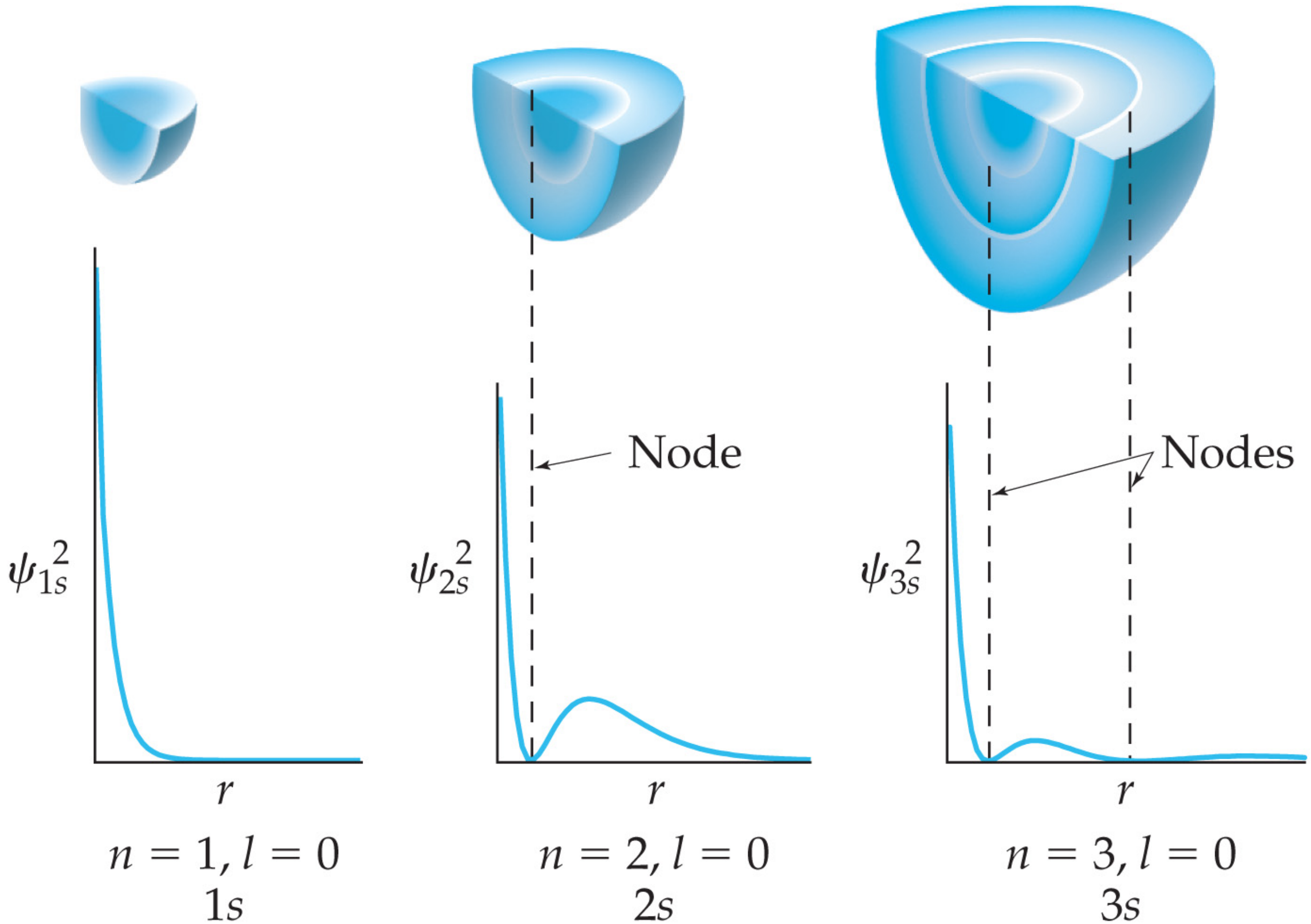
- Number of nodes = $n - 1$ (angular and spherical)
- # of Angular nodes = angular momentum quantum #

s	0
p	1
d	2
f	3



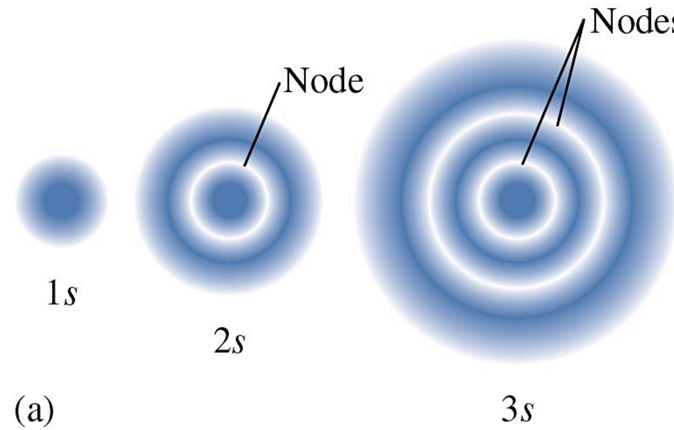
The *s* orbitals

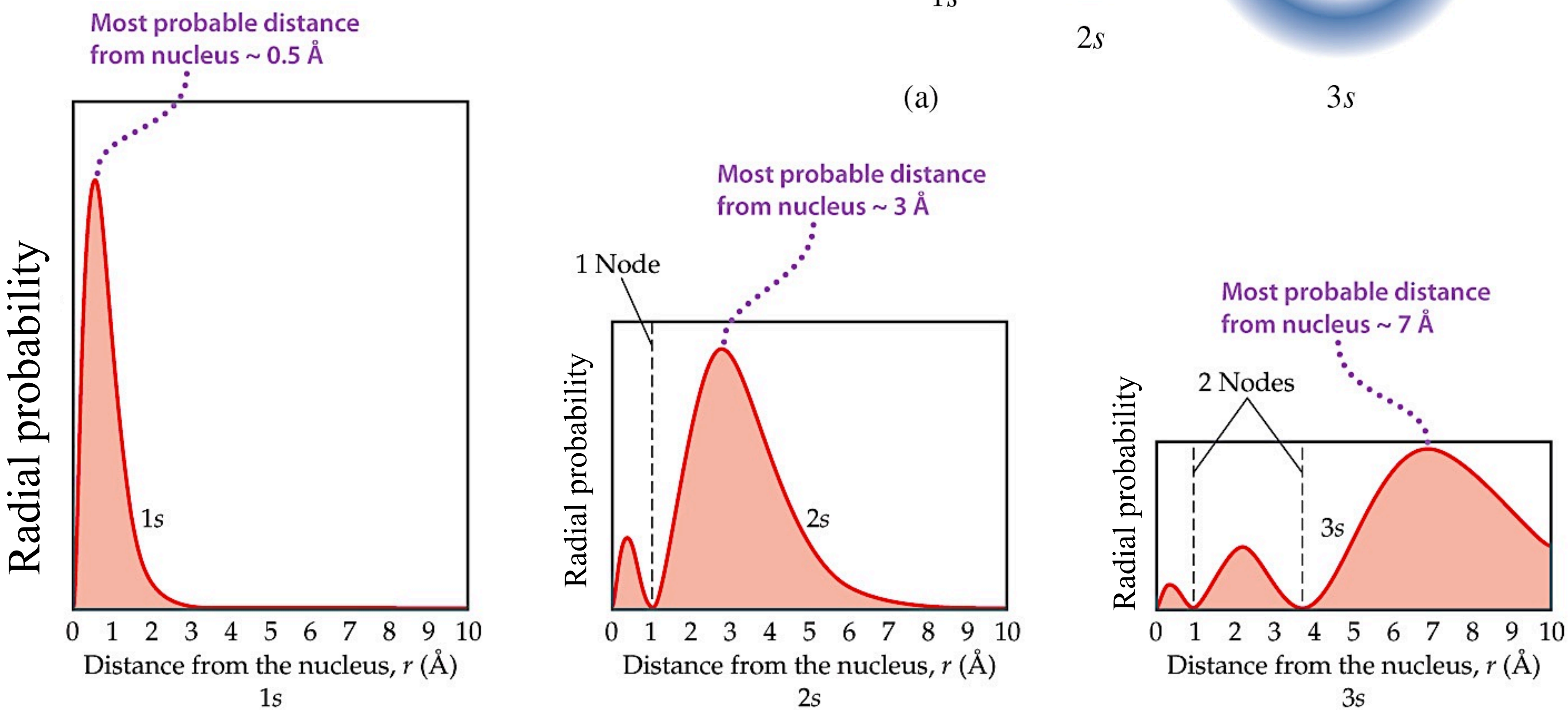
- $l = 0$.
- spherical shape
- Increases in size as *n* increases.
- a single orbital found in each *s* sublevel.
- Spherical nodes.



The *s* orbitals

$$|\psi_{ns}|^2 \times 4\pi r^2$$



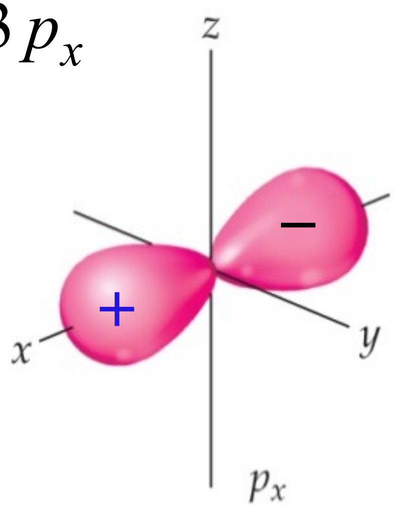


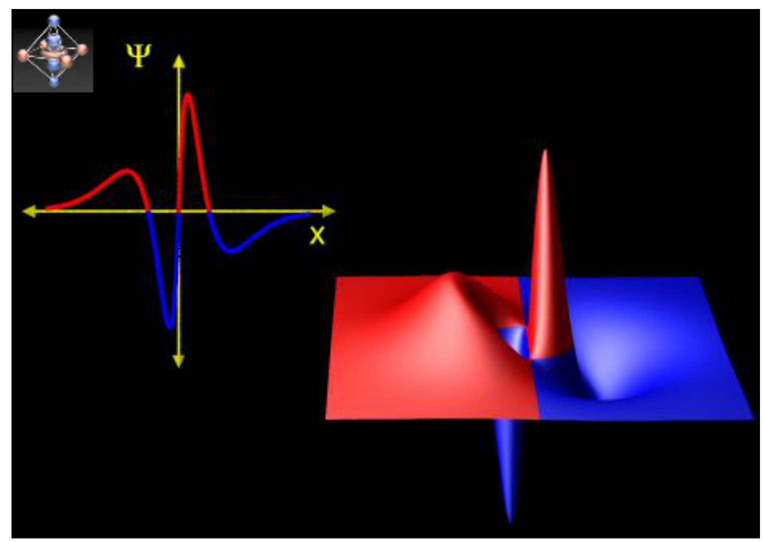
The *p* orbitals

- $l = 1$
- two-lobed shape.
- Increases in size as the value of *n* increases.
- Has three degenerate orbitals: p_x, p_y, and p_z.

m_l = -1, 0, 1

ψ_{3p_x}

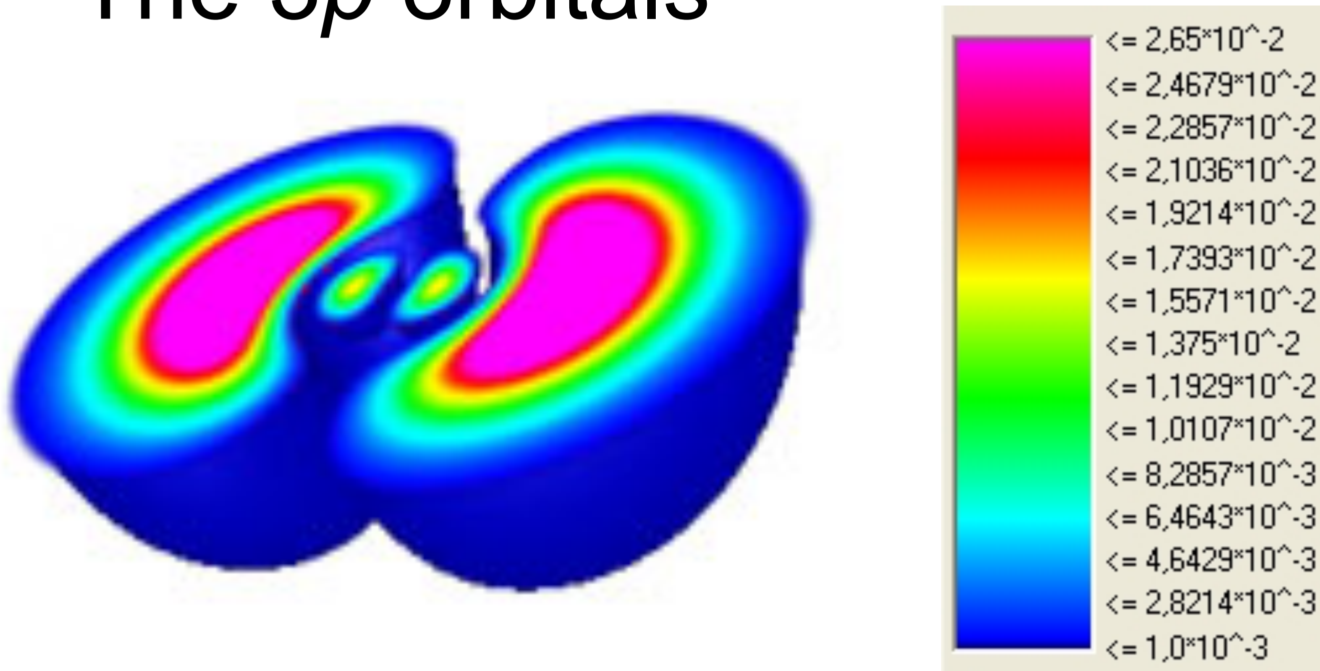


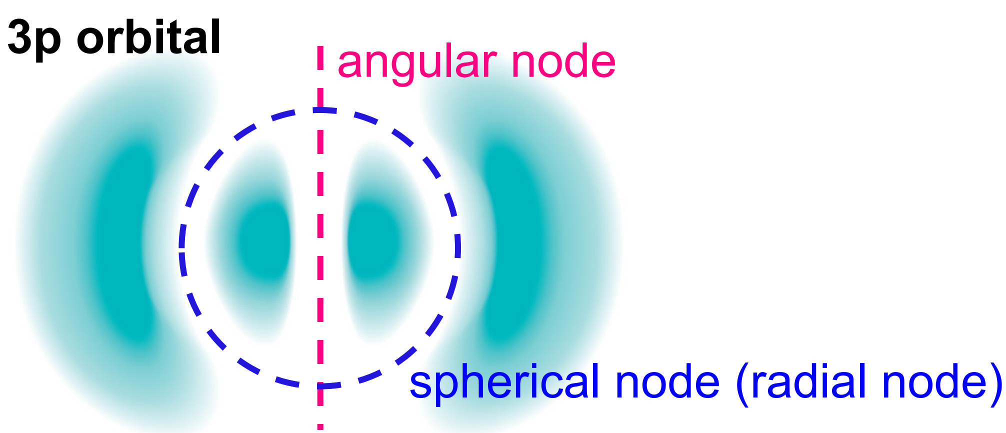


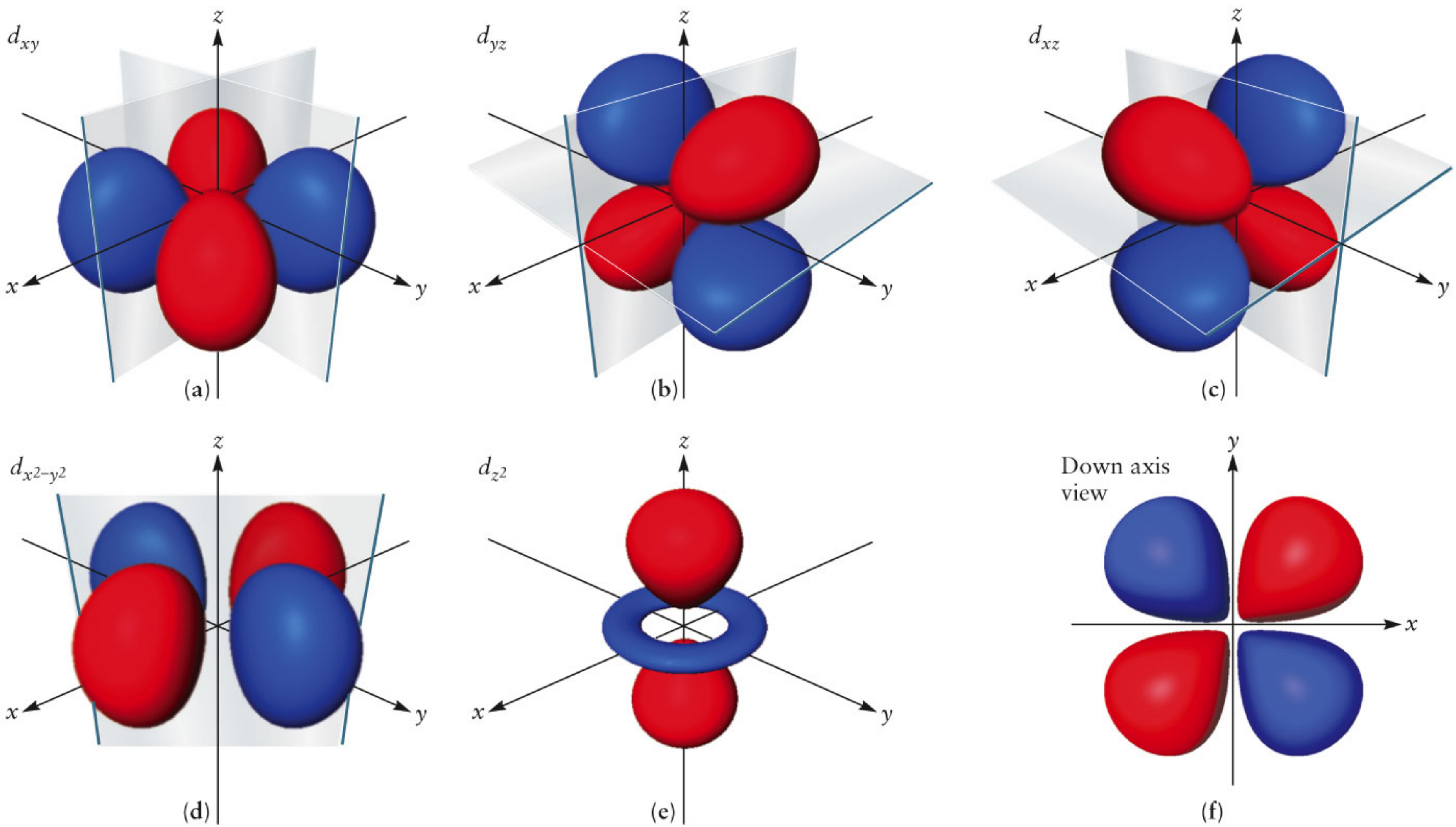
http://winter.group.shef.ac.uk/orbitron

The 3*p* orbitals

$$\left|\psi_{3p_x}\right|^2$$



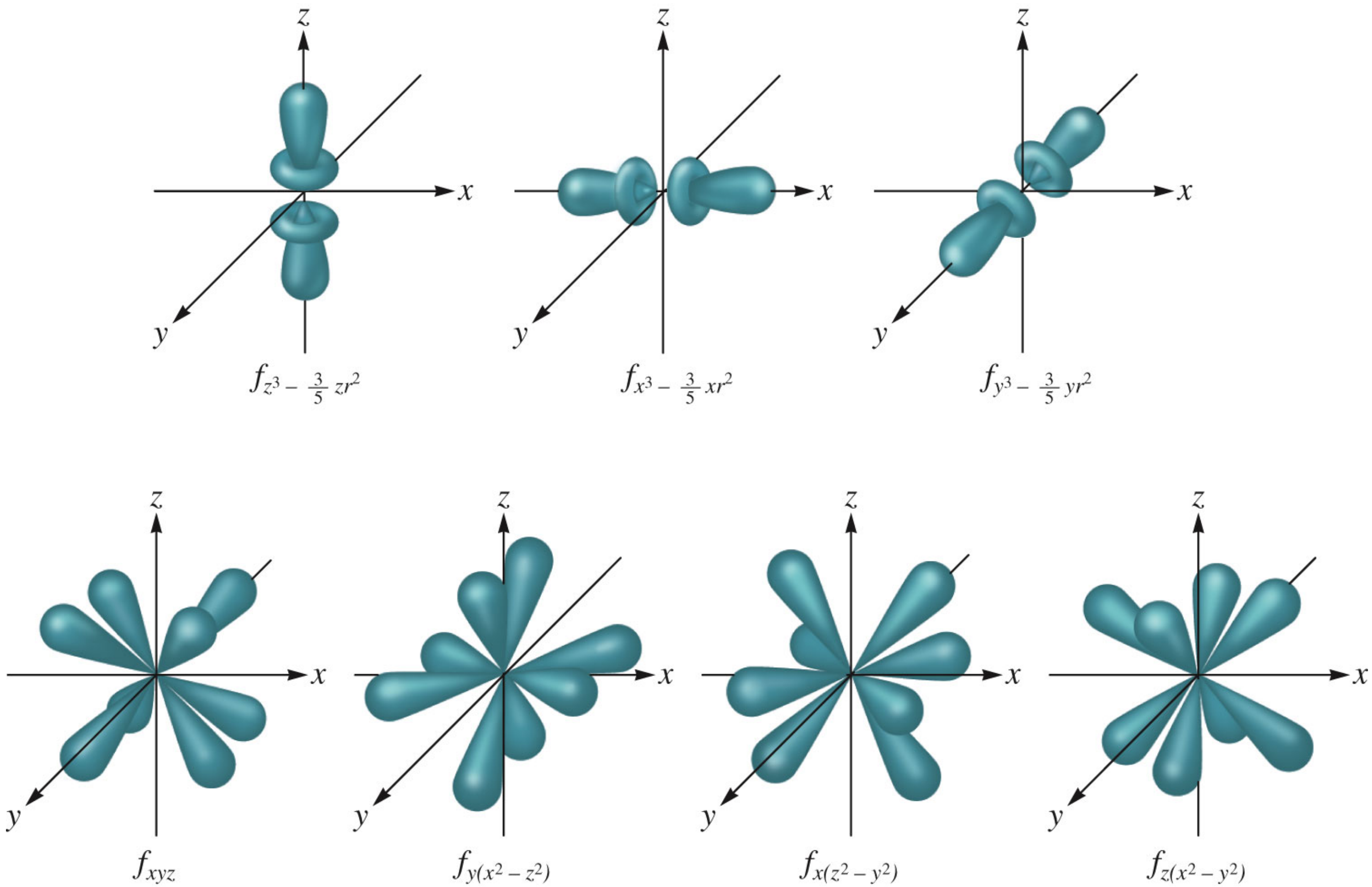


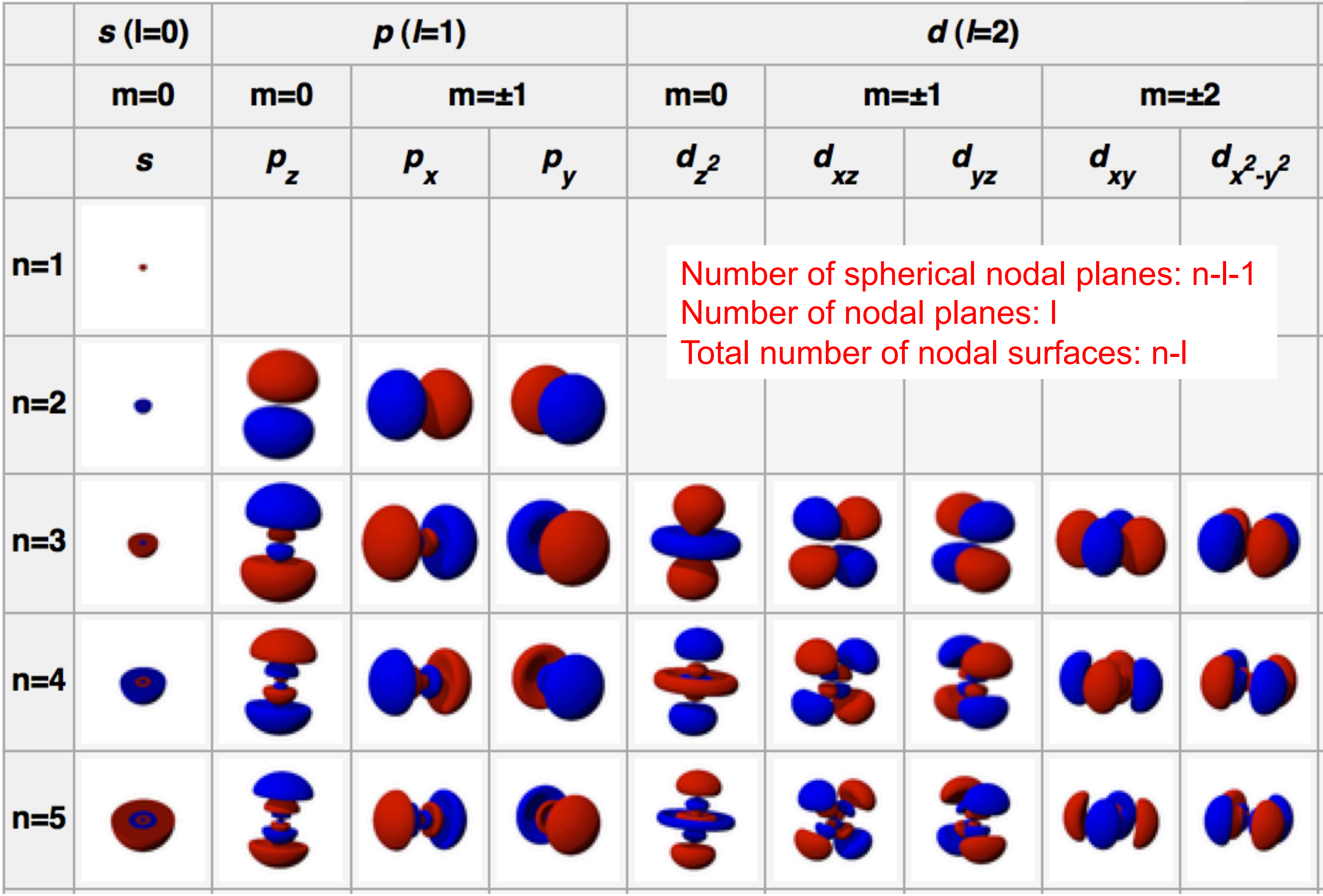


d_{xy} → $f(x,y) = x \times y$ → function equals to zero when wither x=0 or y=0 → x=0: yz plane, y=0: xz plane → determines nodal planes

Fig. 5-13, p. 207

Representation of the 4*f* Orbitals in Terms of Their Boundary Surfaces

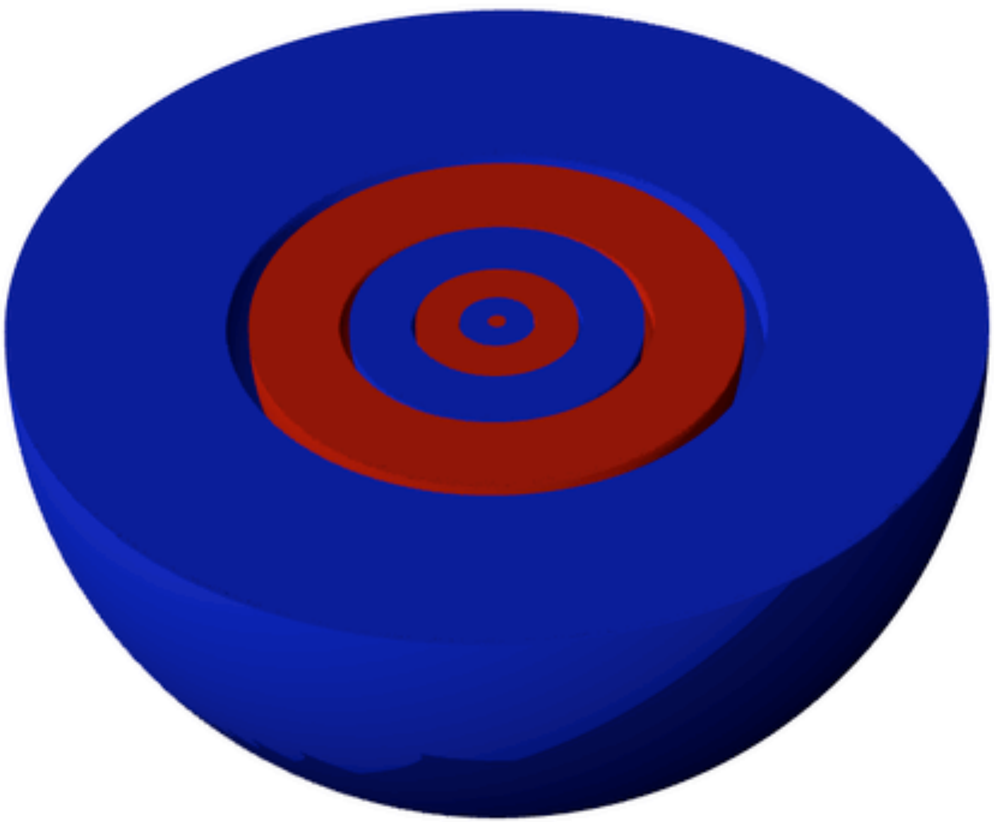




Number of spherical nodal planes: n-l-1
Number of nodal planes: l
Total number of nodal surfaces: n-l

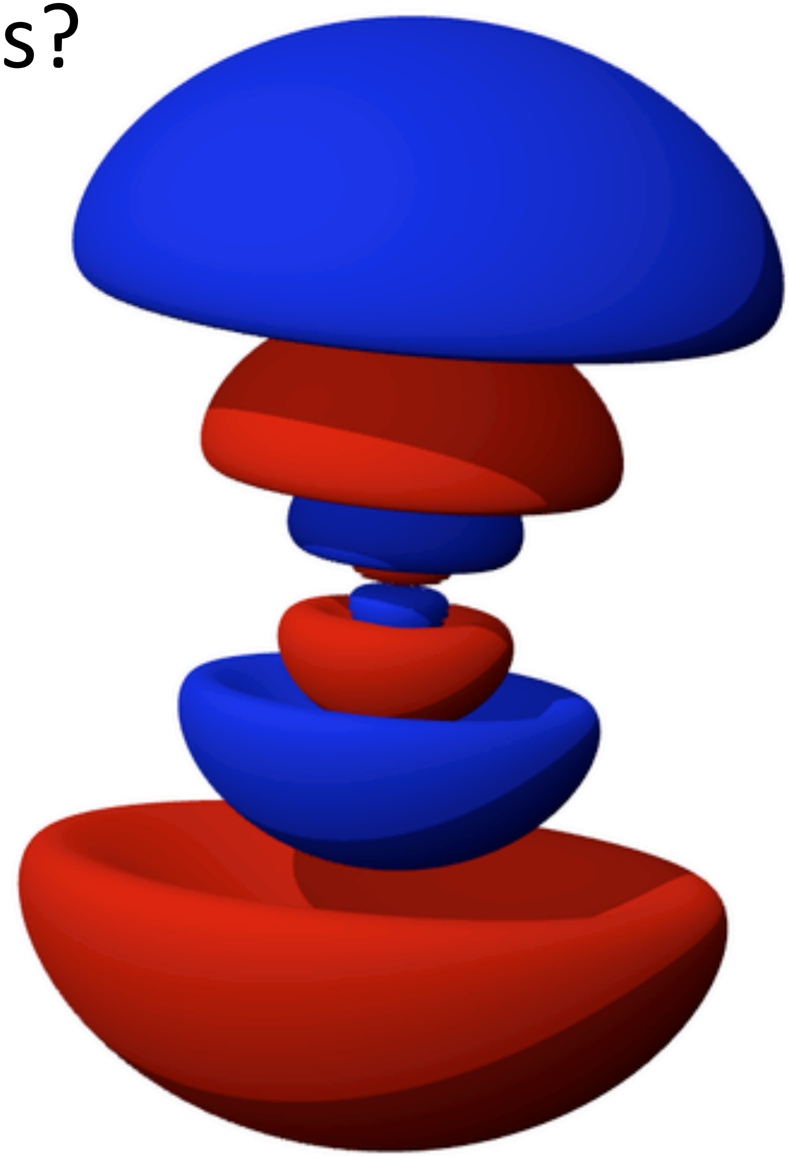
http://en.wikipedia.org/wiki/Atomic_orbital

Which orbital is this?



6s

Which orbital is this?



5p

Significance of Atomic Orbitals (AOs)

- Describe stationary states of an electron moving around a point charge → orbital = single-electron wavefunction
- Yield the distribution of electron in space by their squares → but wave functions have signs that determine the interferences
- Provide good basis to understand many-electron atoms → periodic table!
- Give good approximations to describe motions of electrons in molecules → molecular orbitals are linear combinations of AOs