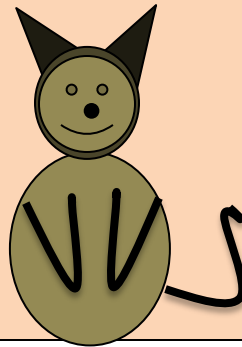# Chapter 6

Quantum Mechanics

Schrödinger Equation

Erwin Schrödinger proposed the theory of quantum mechanics which suggested that an electron (or any other particle) exhibiting wavelike properties should be described by a mathematical equation called a *wave function* (denoted by the Greek letter psi, ψ).

Specifically, he developed a mathematical formalism to describe the hydrogen atom as a wave. This equation (which involves differential calculus!) gives the probability of finding an electron at some point in a three-dimensional space at any given instant but offers no information about the path the electron follows (recall Heisenberg).

The region in space where there is a probability of finding an electron is known as an *orbital*, & in the Schrödinger equation, the *wave function* is used to calculate the probability of finding an electron in space.

1

QUANTUM MECHANICS
Erwin Schrodinger (1887 - 1961)

Schrodinger formulated the theory of wave mechanics: a description of the behavior of the tiny particles that make up matter in terms of waves. His wave equation describes the behavior of electrons in atoms.

$$H \Psi = E \Psi$$

Ψ **is the wave function/atomic orbital: a mathematical description of the motion of the electron's matter-wave in terms of position & time.**

**H is the Hamiltonian operator**
E is the energy of the atom

$$d^2 \Psi/dx^2 + d^2\Psi/dy^2 + d^2\Psi/dz^2 + (8\pi^2 m_e/h^2)[E-V_{(x,y,z)}] \Psi_{(x,y,z)}$$

Ψ^2 **is the probability of an electron being within a volume.**

3

QUANTUM CHEMISTRYQUANTUM CHEMISTRY

SCHRÖDINGER'S PHONE

UNTIL YOU LOOK, IT IS BOTH CRACKED AND NOT CRACKED

Probability and Radial Distribution Functions

- ψ^2 is the probability density.
  - The probability of finding an electron at a particular point in space
  - For **s** orbital maximum at the nucleus
  - Decreases as you move away from the nucleus
- The radial distribution function represents the total probability at a certain distance from the nucleus.
  - Maximum at most probable radius
- **Nodes** in the functions are where the probability drops to 0.

Nodes
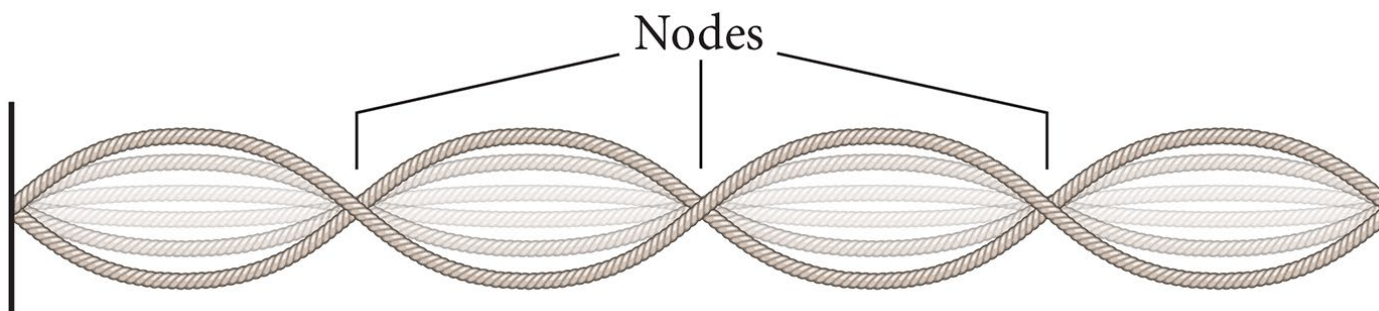
Radial Distribution Function

The radial distribution function represents the **total probability** of finding an electron within a thin spherical shell at a **distance r** from the nucleus.

The probability at a point decreases with increasing distance from the nucleus, but the volume of the spherical shell increases.

The net result is a plot that indicates the most probable distance of the electron in a 1s orbital of H is 52.9 pm.
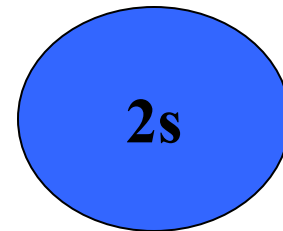
1s Radial Distribution Function

Maximum at 52.9 pm

1s

Total radial probability

0   200   400   600   800   1000

Distance from the nucleus, r (pm)
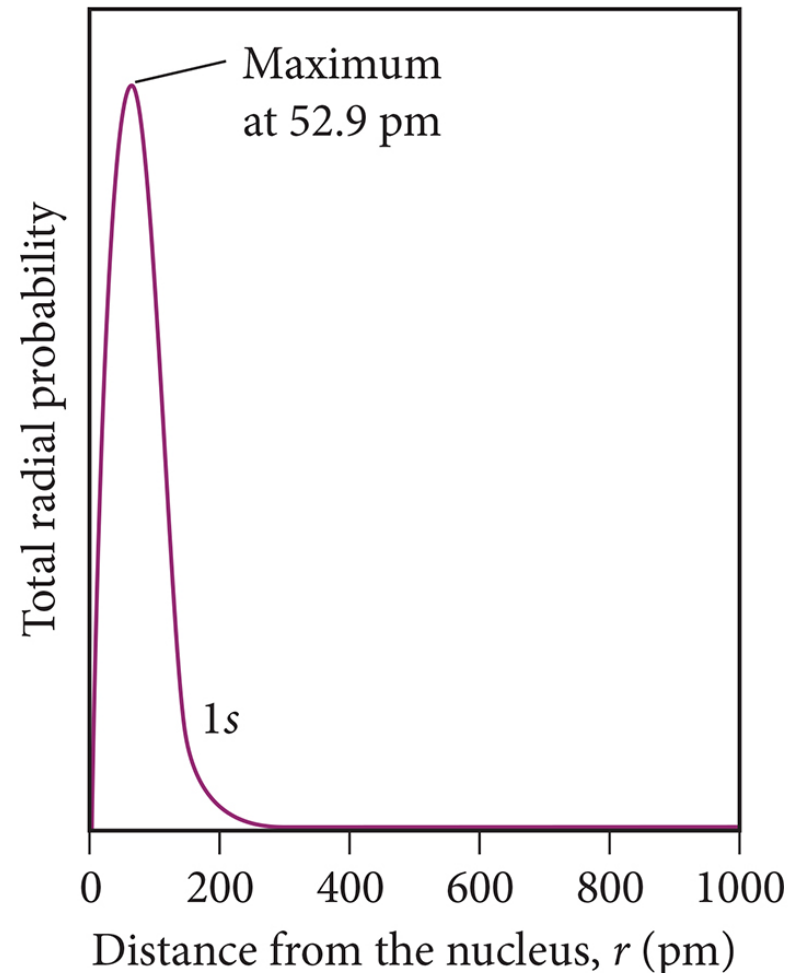
Quantum Mechanics

In **quantum mechanics,** the electrons occupy specific energy levels (as in Bohr's model) but they also exist within specific probability volumes called **orbitals** with specific orientations in space. The electrons within each orbital has a distinct spin.

n = **The principle quantum number**

Describes the possible energy levels and pictorially it describes the orbital size.
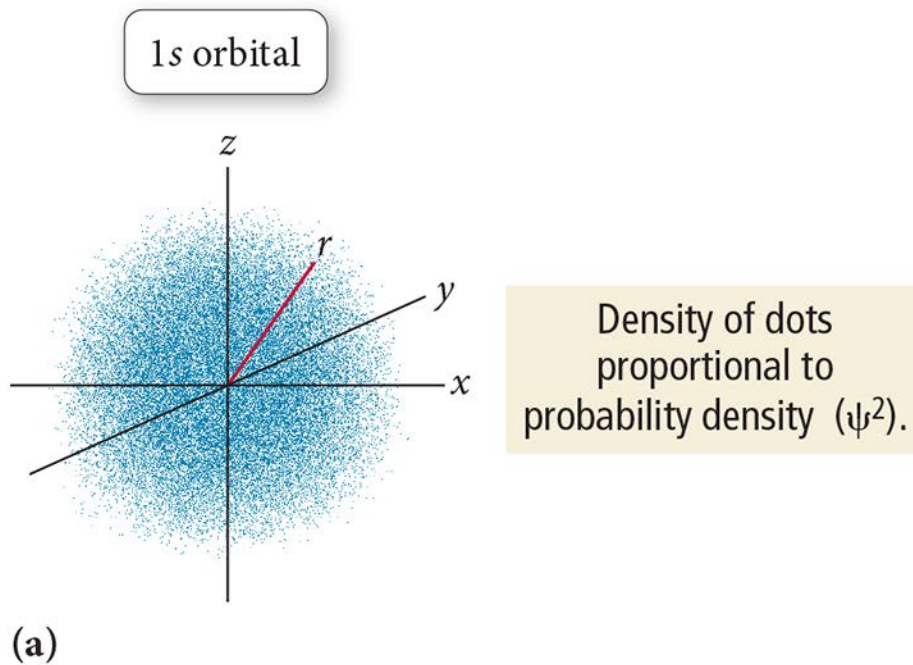
n = 1, 2, 3.... where an orbital with the value of 2 is larger than an orbital with the value of 1.

$$E_n = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n^2} \right)$$ for an electron in H

1s   **2s**

Probability Density for *s* Orbitals (*l* = 0)

The probability density function represents the total probability of finding an electron at a particular point in space.

1s orbital

Density of dots proportional to probability density (ψ^2).

Height of curve proportional to probability density (ψ^2).

(a)

(b)
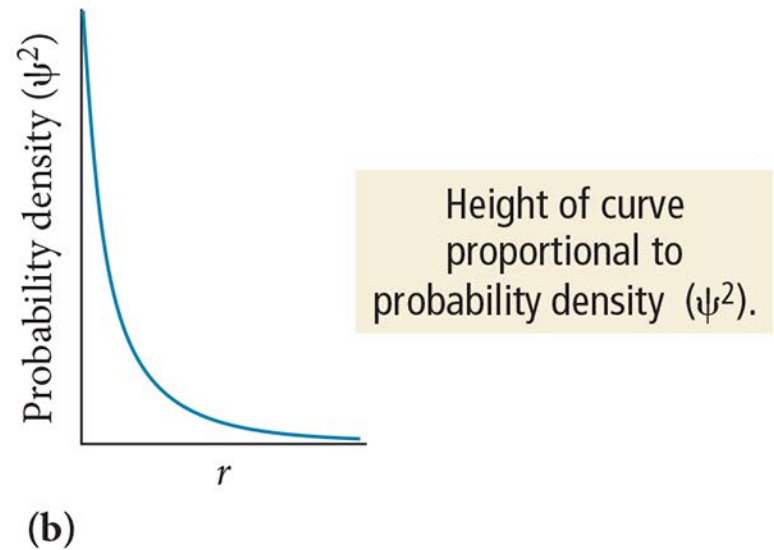
Probability Densities and Radial Distributions for 2*s* and 3*s* Orbitals

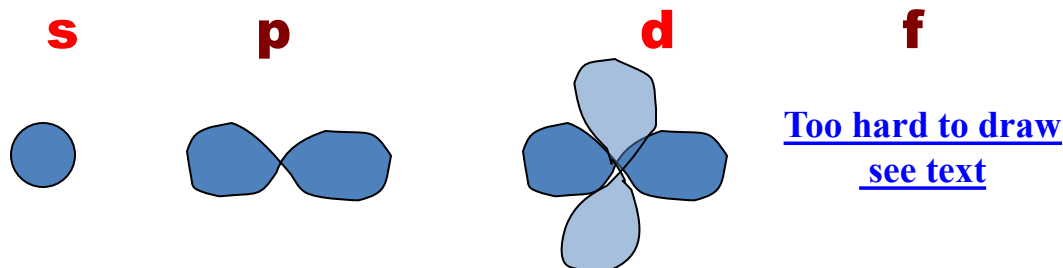The 2s and 3s Orbitals
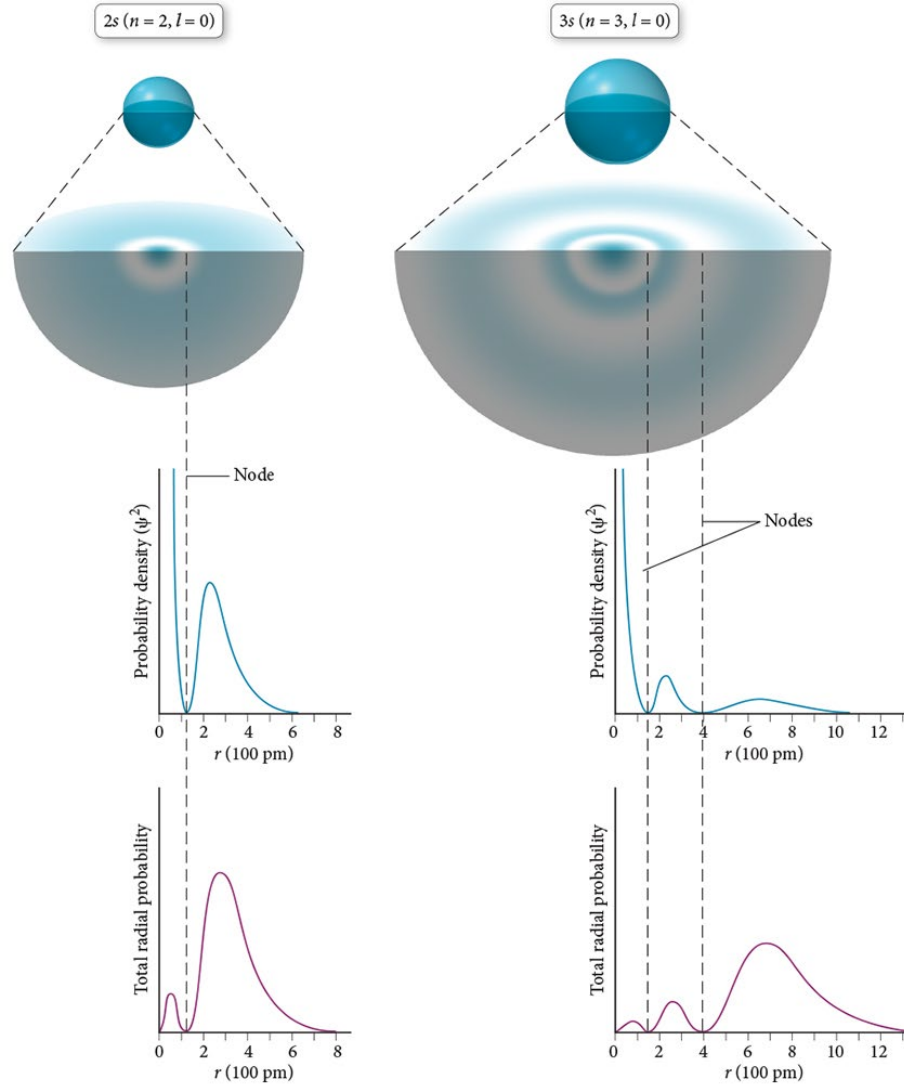
Quantum Mechanics 2

l = angular momentum quantum number

Describes the "shape" of the orbital and can have values from 0 to n - 1 for each n.

l = (n-1) to 0   (2 l + 1 subshells)

orbital designation :   s   p   d   f
(CLICK ON ORBITALS)

shape :

Too hard to draw
see text

m_l = magnetic quantum number

Related to the orientation of an orbital in space relative to the other orbitals with the same *l* quantum numbers. It can have values between *l* and - *l*.

m_s = spin quantum number

An electron has either $+\frac{1}{2}$ or $-\frac{1}{2}$ spin values; sometimes referred to as spin up and spin down.

s Orbitals
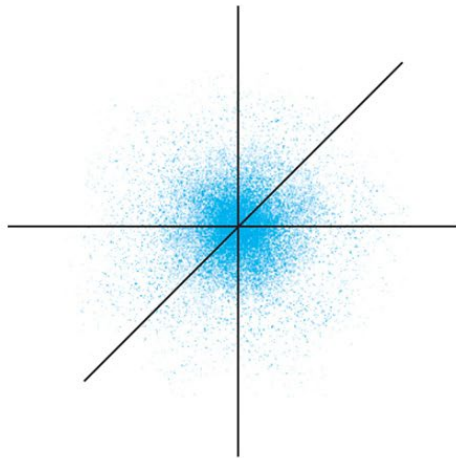

(a) An electron density model
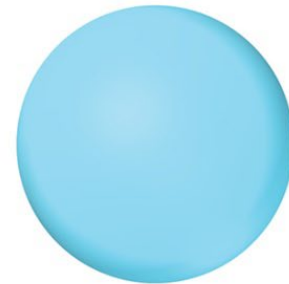
(b) Contour models

- The value of l for s orbitals is 0.
- They are spherical in shape.
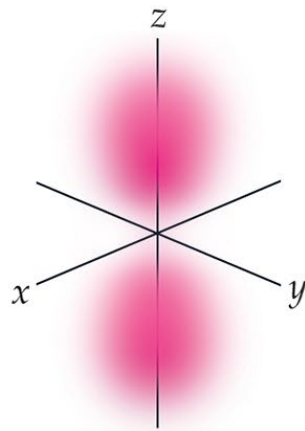- The radius of the sphere increases with the value of n.

s Orbitals

- For an *ns* orbital, the number of peaks is *n*.

- For an *ns* orbital, the number of nodes (where there is zero probability of finding an electron) is *n* − 1.

- As *n* increases, the electron density is more spread out and there is a greater probability of finding an electron further from the nucleus.
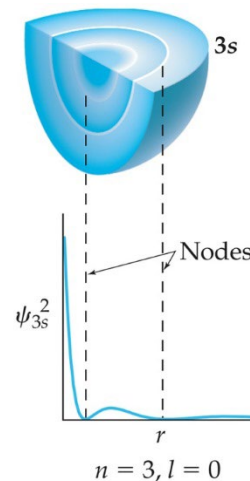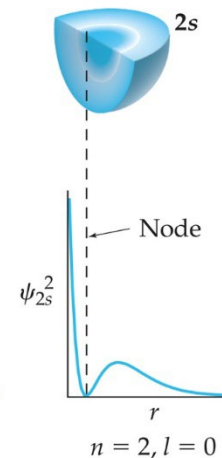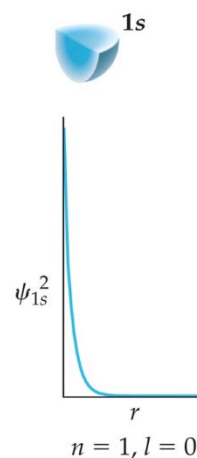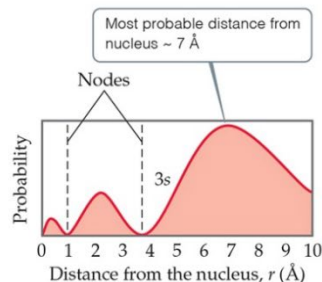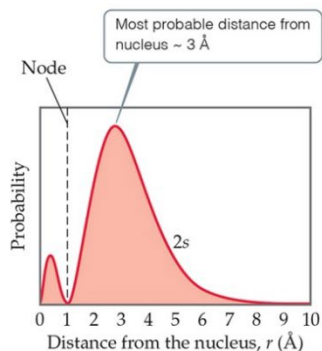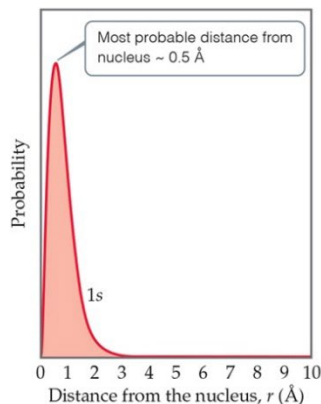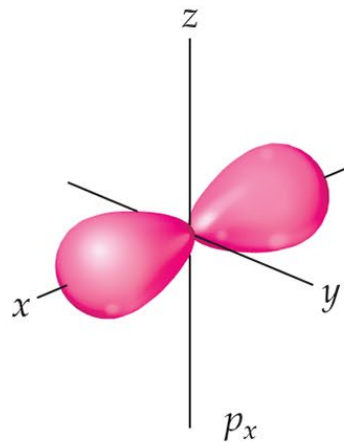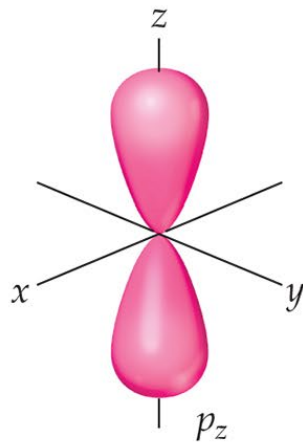
p Orbitals

- The value of *l* for *p* orbitals is 1.
- They have two lobes with a node between them.

p orbitals 2

p_x orbital

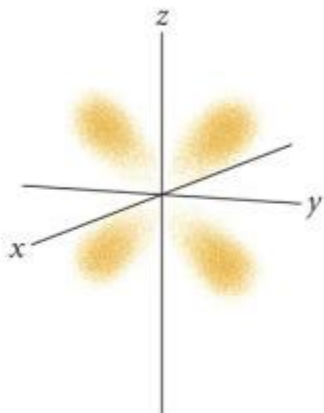p_y orbital

p_z orbital

Radial Distribution Function

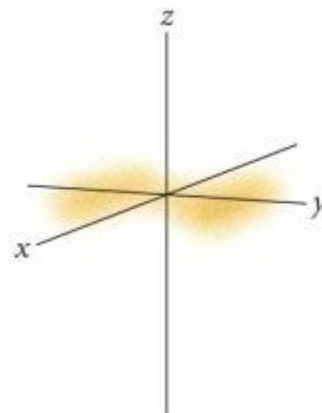Total radial probability
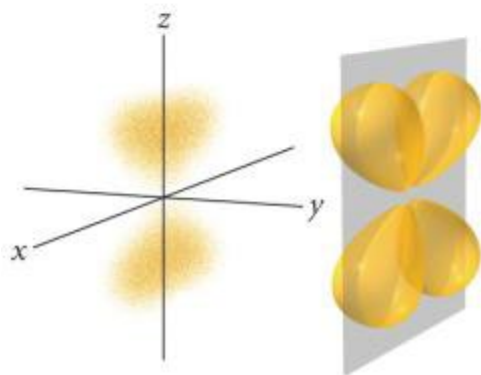
2p

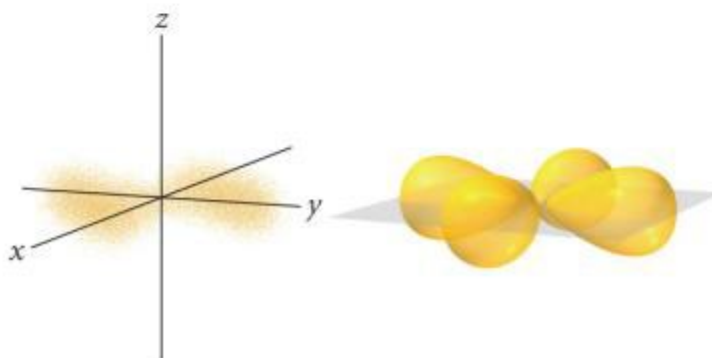r (along lobe), 100 ppm
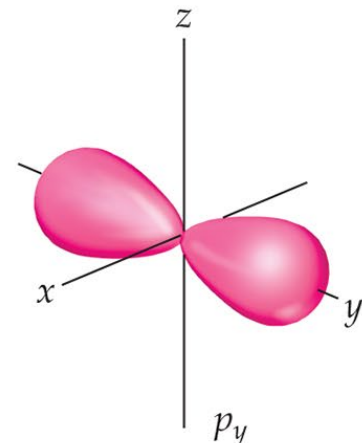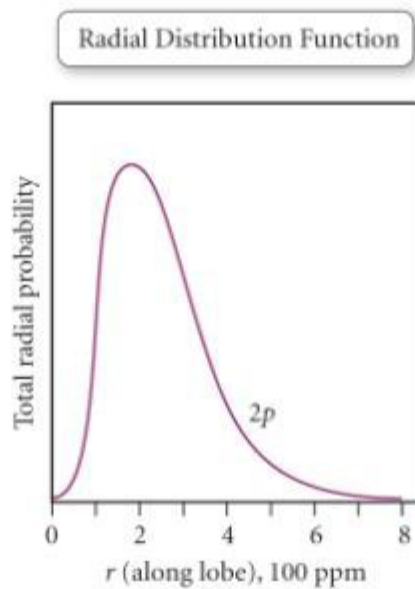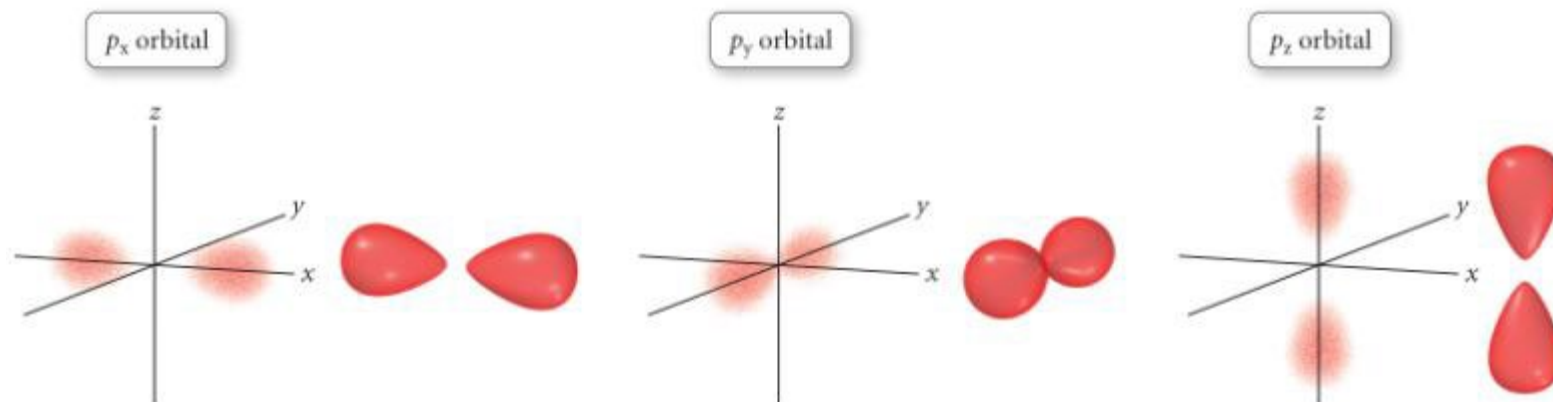
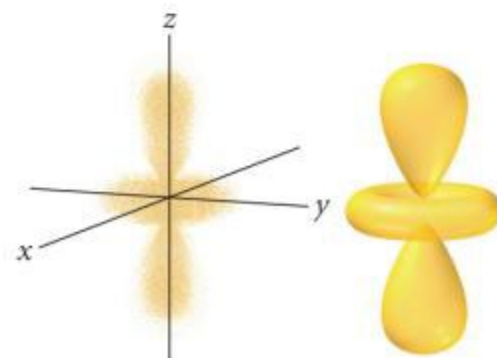# *d* orbitals
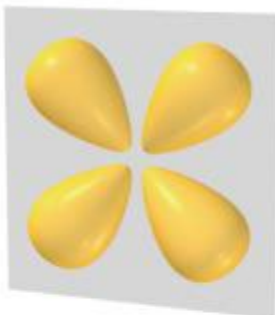
d_{yz} orbital

d_{xy} orbital
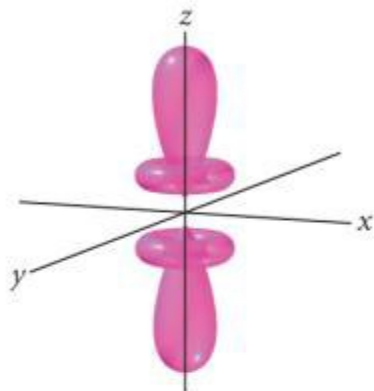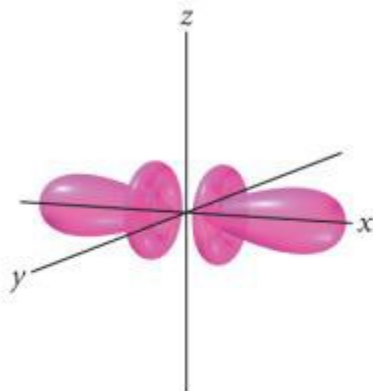
d_{xz} orbital

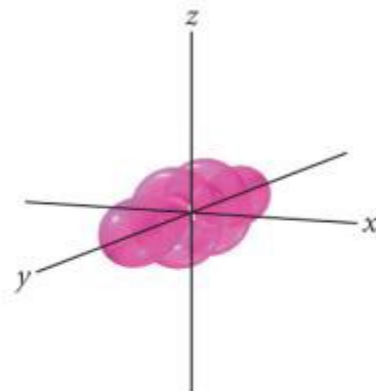$d_{x^2-y^2}$ orbital

d_{z^2} orbital
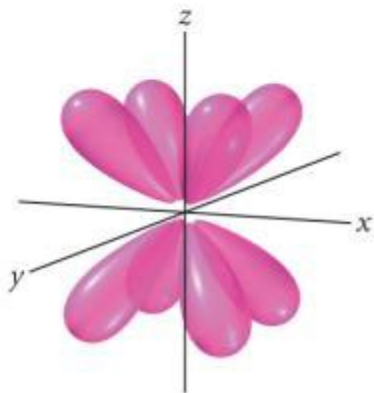
f orbitals

$f_{z^3 - \frac{3}{5}zr^2}$ orbital

$f_{x^3 - \frac{3}{5}xr^2}$ orbital

$f_{y^3 - \frac{3}{5}yr^2}$ orbital

f_{xyz} orbital

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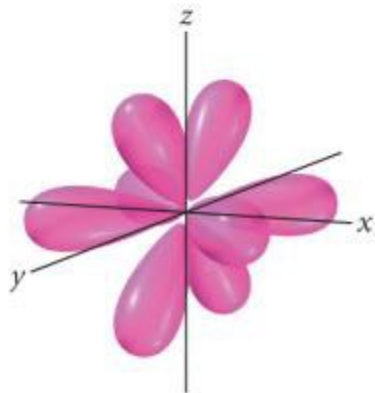
$f_{x(z^2 - y^2)}$ orbital

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

16
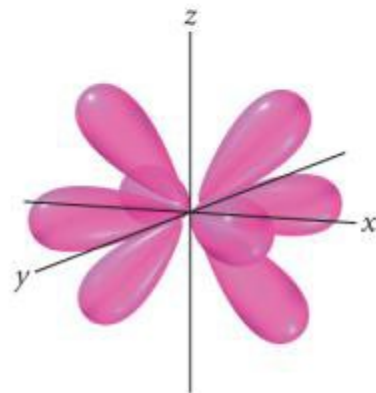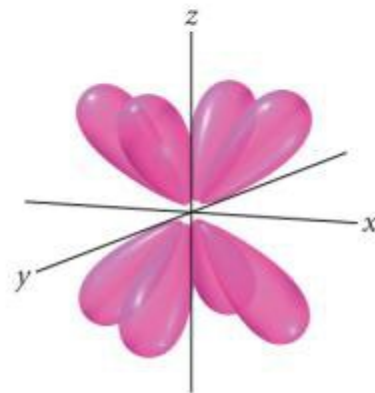
Why are Atoms Spherical?

Quantum Mechanics and the Periodic Table

1. Principle Quantum Number (n): specifies the energy level of an electron and labels the shell of an atom. Represented by the period number.

2. Angular Momentum Quantum Number (l): specifies the subshell of a given shell in an atom and determines the shape of the orbitals in the subshell.

Period

1
2
3
4
5
6
7

s

S

D

d

p

P

F

f
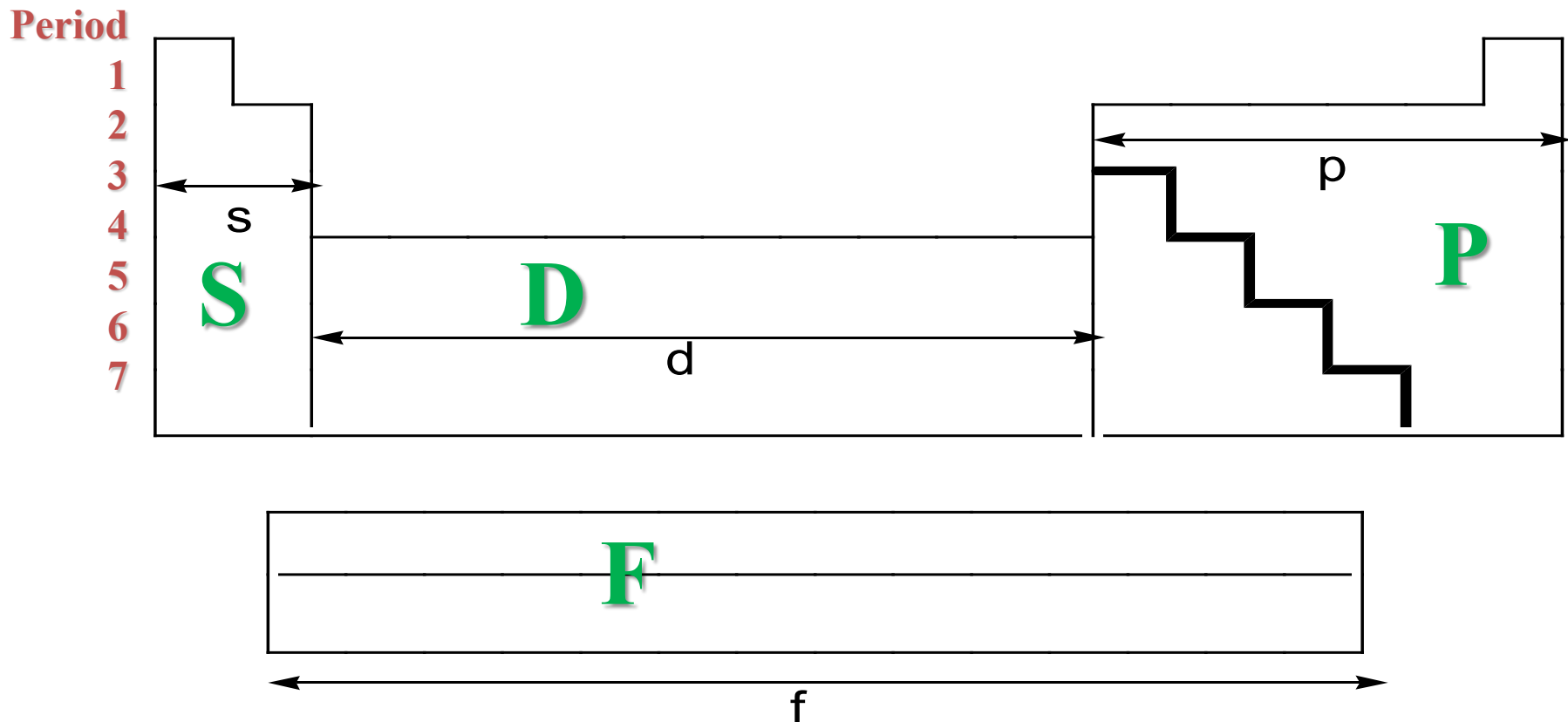
Energy Shells and Subshells

$n = \#$

$\ell = n\text{-}1, 0$

$m_\ell = + \ell \text{ to } -\ell$

$n = 1$

$\ell = 1\text{-}1, 0 \text{ or } 0$
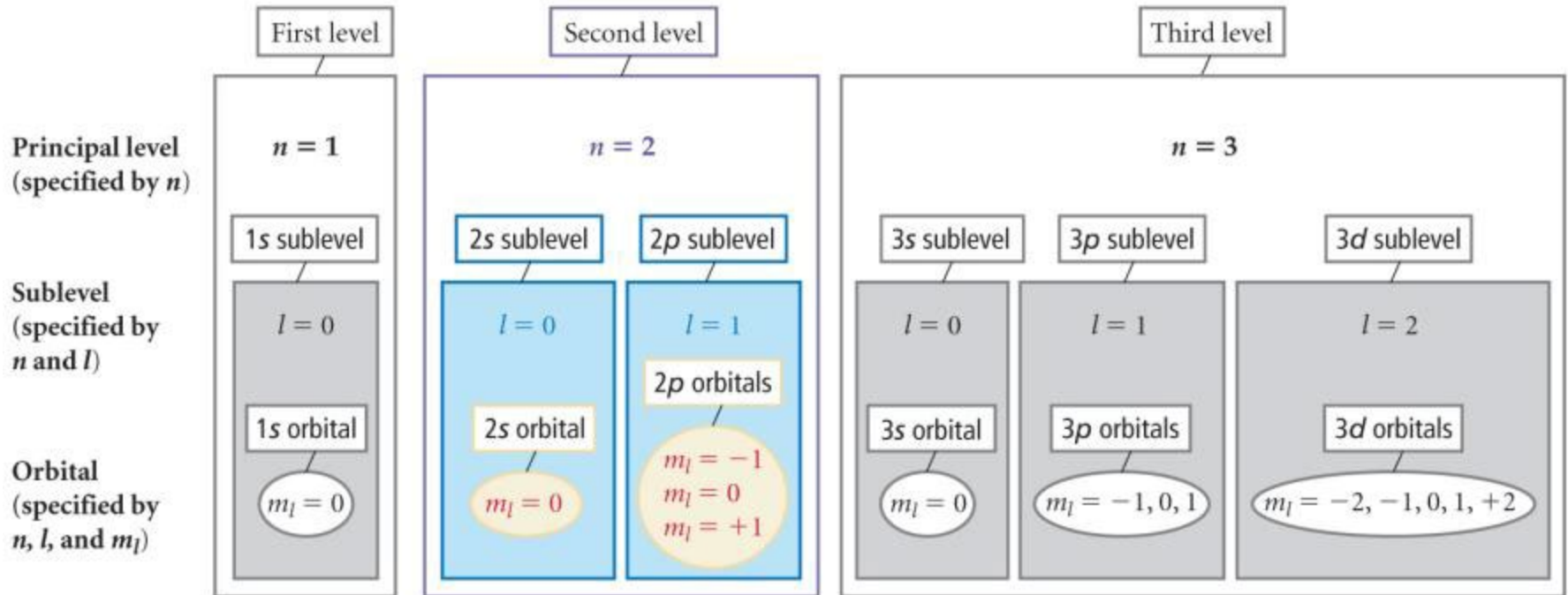
$m_\ell = 0$

So the quantum numbers associated with the n=1 energy level or 1s sublevel are:

$1, 0, 0 +{}^1/_2$ and $1, 0, 0, -{}^1/_2$

3. Magnetic Quantum Number (m_l): identifies the individual orbitals of a subshell of an atom and determines the orientation in space

4a. Spin Quantum Number (m_s): distinguishes the two spin states of an electron

n	l	Orbital Designation	m_l	# of orbital
1	0	s	0	2
2				
3				
4				

4b. Pauli Exclusion Principle: No two electrons can have the same four sets of identical quantum numbers. Moreover, when two electrons (and NO MORE THAN TWO!) occupy the same given orbital, their spins must be different. This is due to the spin number.

20

Lecture Questions on Quantum Mechanics

1. Determine the quantum numbers associated with the following energy levels:

a) n= 3   b) n = 5

n = 5

ℓ = 4, 3, 2, 1, 0

m_ℓ = 4,3,2,1,0,-1,-2,-3,-4 & 3,2,1,0,-1,-2,-3 & 2, 1, 0, -1, -2 & 1, 0, -1 & 0

Quantum numbers are:

5, 4, +4, ±½ **5, 3, +3, ±½** **5, 2, +2, ±½**   5, 1, -1, ±½   5, 0, 0, ±½

5, 4, +3, ±½ **5, 3, +2, ±½** 5, 2, +1, ±½   5, 1, 0, ±½

5, 4, +2, ±½ **5, 3, +1, ±½** 5, 2, 0, ±½   5, 1, +1, ±½

5, 4, +1, ±½ 5, 3, 0, ±½   5, 2, -1, ±½

5, 4, 0, ±½ 5, 3, -1, ±½   5, 2, -1, ±½

5, 4, -1, ±½ 5, 3, –2, ±½

5, 4, -2, ±½ 5, 3, -3, ±½   **total of 6 e-**   total of 2 e-

5, 4, -3, ±½   **p** orbital   **s** orbital

5, 4, -4, ±½

Total of 10 e-

d orbital

Now you try

2. **Determine the sublevel names & quantum numbers:**

   a) n = 3, l = 1   **b) n = 4, l = 2**   **c) n = 2, l = 0**

a) 3p $(3, 1, 1, \pm\frac{1}{2})$ **&** $(3, 1, -1, \pm\frac{1}{2})$ **&** $(3, 1, 0, \pm\frac{1}{2})$

b) 4d $(4, 2, -2, \pm\frac{1}{2})$ & $(4, 2, -1, \pm\frac{1}{2})$ & $(4, 2, 0, \pm\frac{1}{2})$ & $(4, 2, 1, \pm\frac{1}{2})$ & $(4, 2, 2, \pm\frac{1}{2})$

c) 2s $(2, 0, 0, \pm\frac{1}{2})$

3. **What is the maximum number of electrons in an atom that can have these quantum numbers?**

   A. $n = 3$ 18

   B. $n = 2, l = 0, m_l = 0$ 2

   C. $n = 5, m_s = +\frac{1}{2}$ 25   9 (4g) 7(3f) 5(2d) 3(1p) 1(0s)

   D. $n = 2, l = 1$ 6   **For the 2p subshell**