CH 431: INORGANIC CHEMISTRY

Atomic theory, orbitals and electron configuration

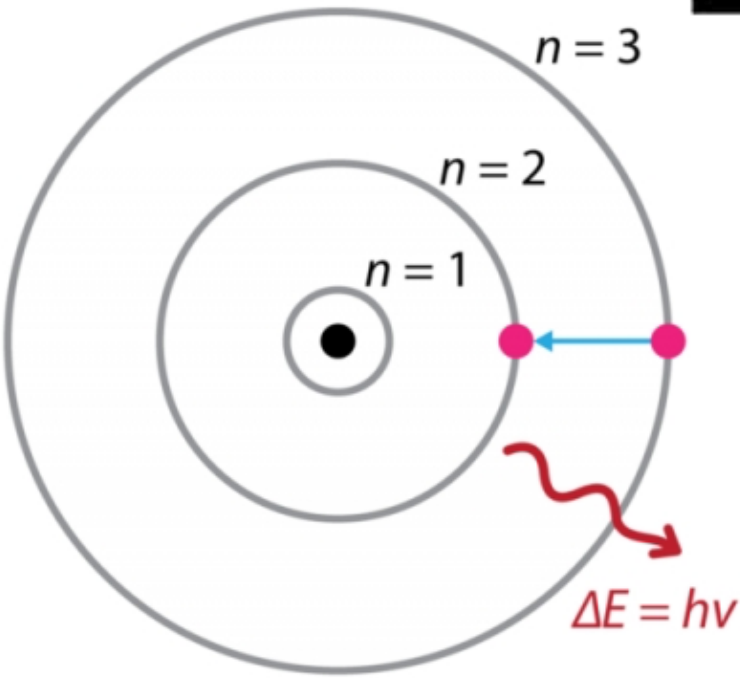
MFT Chapter 2

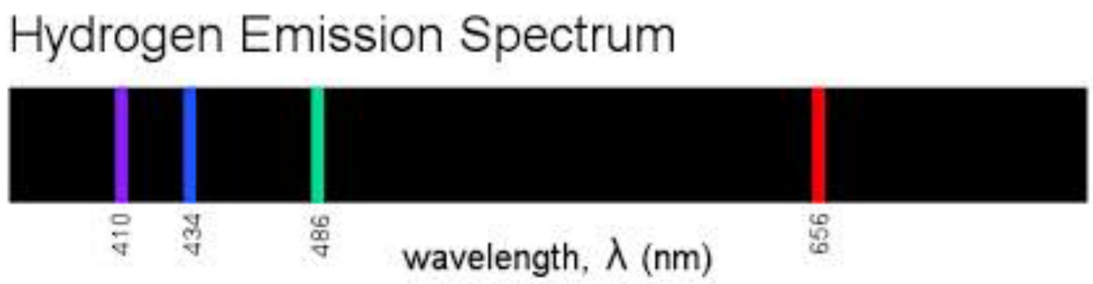
ATOMIC STRUCTURE

Being able to describe atomic structure, and more specifically, the electrons in an atom, is essential for understanding the bonding and properties of molecules

Atomic structure: the H atom

The Bohr Model





Rydberg formula

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

n: principal quantum number

Caveat: conflicts with Heisenberg's uncertainty principal

Atomic structure: the H atom

The Schrödinger equation (you will learn more about this in P Chem):
Describes wave properties of an electron in terms of its position, mass, total energy, and potential energy

$$H\Psi = E\Psi$$

H: Hamiltonian operator
E: Energy of the electron
Ψ: wave function

Wavefunctions (Ψ) are the solutions to the Schrödinger equation, these functions describe **atomic orbitals**.

TABLE 2.2 Quantum Numbers and Their Properties

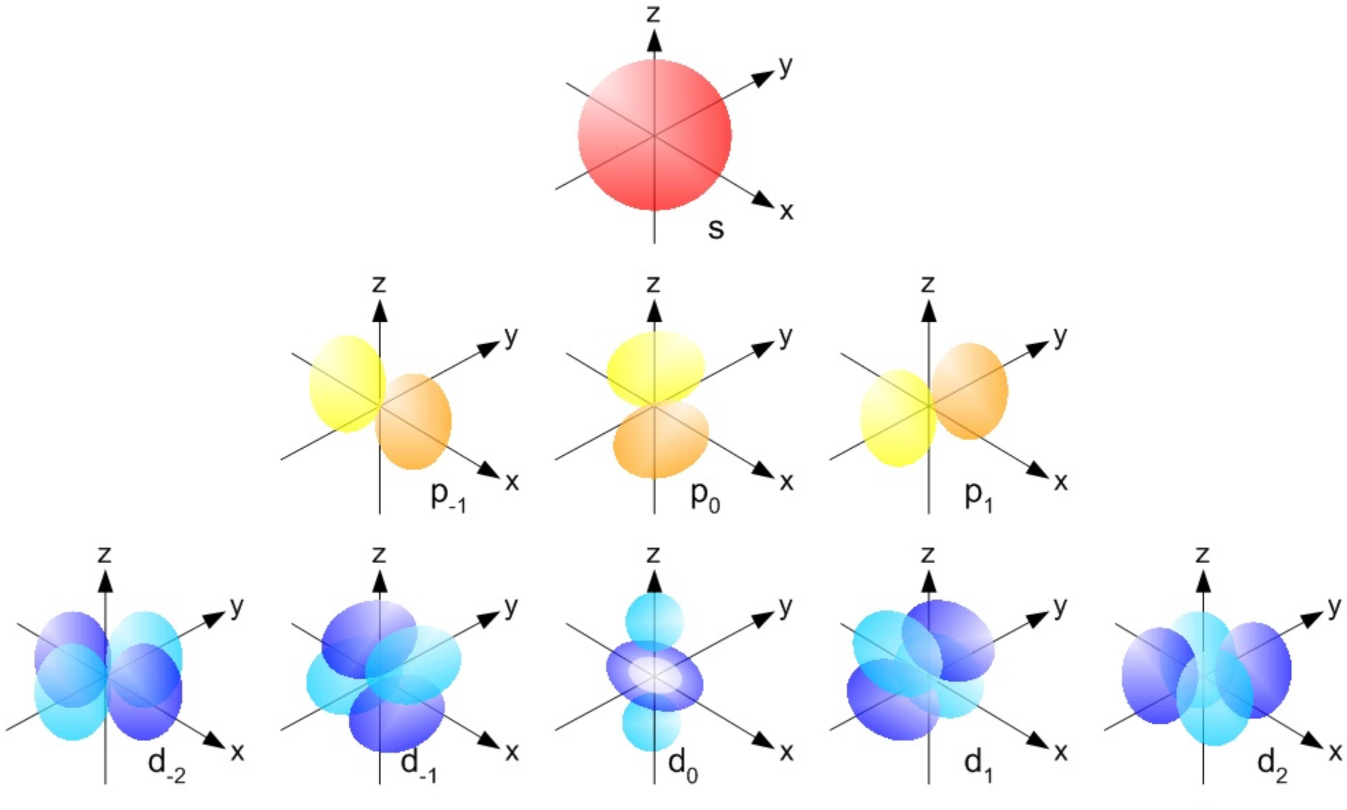
Symbol	Name	Values	Role
n	Principal	1, 2, 3, . . .	Determines the major part of the energy
l	Angular momentum*	0, 1, 2, . . ., $n-1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	0, ±1, ±2, . . ., $\pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm\frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, …
Label	*s*	*p*	*d*	*f*	*g*	continuing alphabetically

Quantum numbers come from wavefunctions

Basic shapes of atomic orbitals



These have the m_l values to differentiate different p and d orbitals, however we will use x,y,z nomenclature to differentiate orbitals

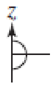
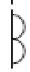
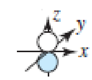
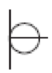
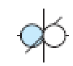
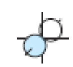
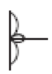
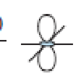
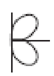
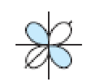
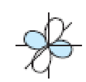
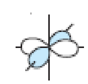
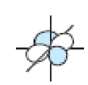
Atomic orbital wavefunctions (Ψ)

- $\Psi_{(n,l,ml)} = R_{(n,l)}(r) \times Y_{(l,ml)}(\Theta,\Phi)$

- Important components of atomic orbital wavefunctions:
  - **Radial function:** describes the electron density at different distances from the nucleus, depends on n, l
    - The square of the radial function describes the *probability* of finding an electron at a particular radius
  - **Angular function:** describes shape of orbital and its orientation in space, depends on l, m_l

Angular wavefunctions

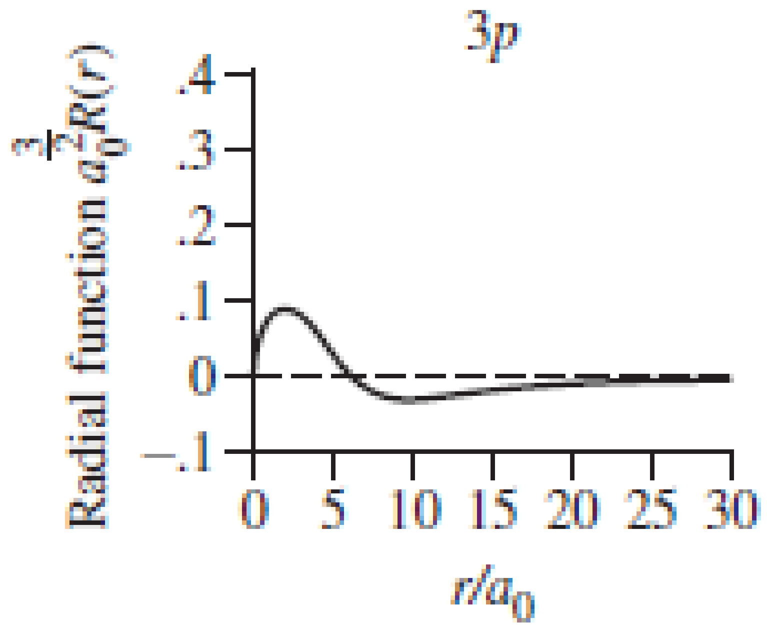
TABLE 2.3 Hydrogen Atom Wave Functions: Angular Functions

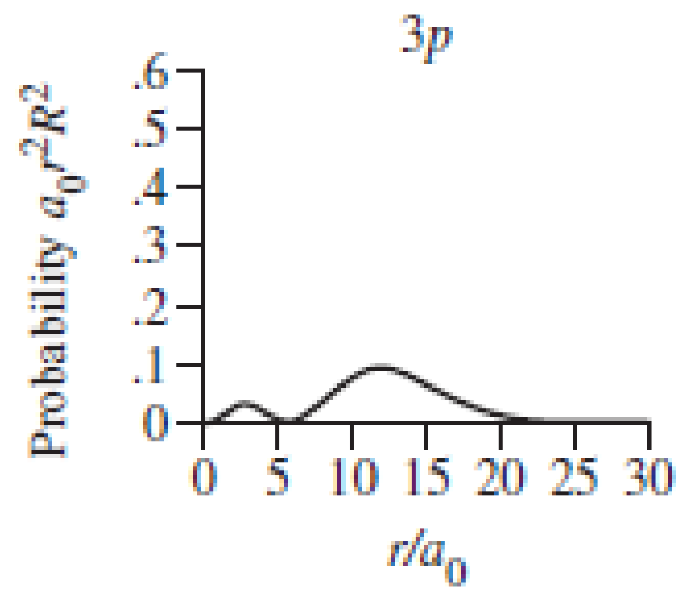
Angular Factors: Related to Angular Momentum				Angular Factors: Functions of θ	Real Wave Functions: In Polar Coordinates	Real Wave Functions: In Cartesian Coordinates	Shapes	Label
l	m_l	Φ	Θ		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$		
$0(s)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$		p_z
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r}$		p_x
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r}$		p_y
$2(d)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2}\sqrt{\frac{5}{2}}(3\cos^2\theta - 1)$		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2 - x^2 - y^2)}{r^2}$		d_{z^2}
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$		d_{xz}
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$		d_{yz}
	$+2$	$\frac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2 - y^2)}{r^2}$		$d_{x^2-y^2}$
	-2	$\frac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$		d_{xy}

Source: Hydrogen Atom Wave Functions: Angular Functions, *Physical Chemistry*, 5th ed.,Gordon Barrow (c) 1988. McGraw-Hill Companies, Inc.

You are NOT responsible for these equations, just know shape and orientation of orbitals

A closer look at radial wavefunction





This radial wavefunction describes where a 3p electron can be in space as it relates to the distance from the nucleus (r).

Can be (+) or (-).

The square of the radial function describes the probability of finding an electron in a certain region in space.

Can only be (+) or zero

Nodes: regions of zero probability

- The total number of nodes in an orbital is equal to n-1
- These nodes can be made up of both angular and radial nodes

Angular nodes (# of angular nodes = l):

TABLE 2.5 Nodal Surfaces

Angular Nodes [$Y(\theta, \phi) = 0$]	
Examples (number of angular nodes)	
s orbitals	0
p orbitals	1 plane for each orbital
d orbitals	2 planes for each orbital except d_{z^2}
	1 conical surface for d_{z^2} (counts as 2 nodes)

More about nodes

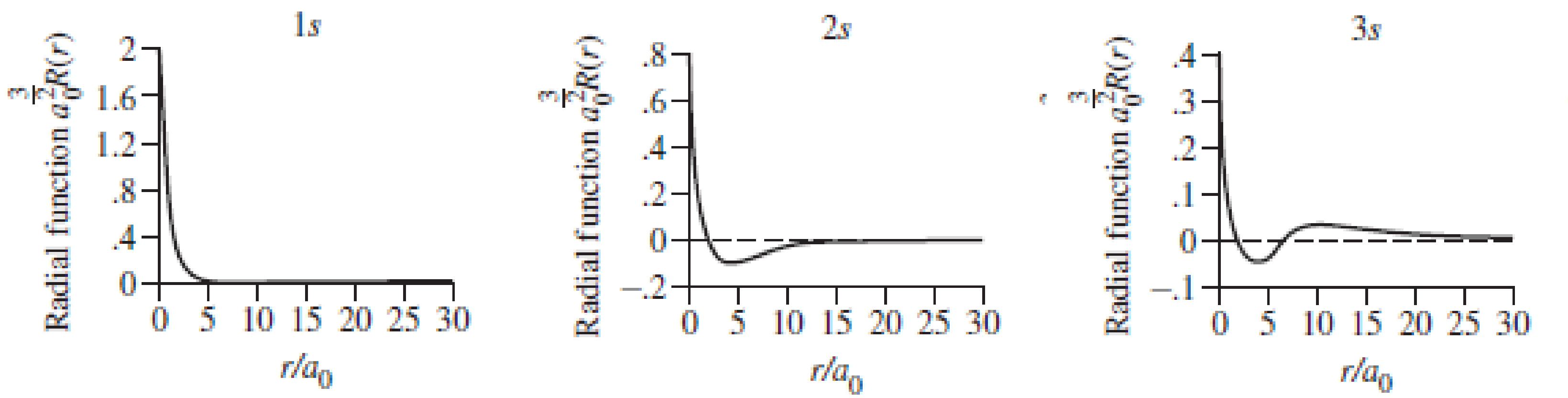
- The total number of nodes in an orbital is equal to n-1
- These nodes can be made up of both angular and radial nodes

Radial nodes (number of radial nodes = n-l-1):

Radial Nodes [$R(r) = 0$]					
Examples (number of radial nodes)					
1*s*	0	2*p*	0	3*d*	0
2*s*	1	3*p*	1	4*d*	1
3*s*	2	4*p*	2	5*d*	2

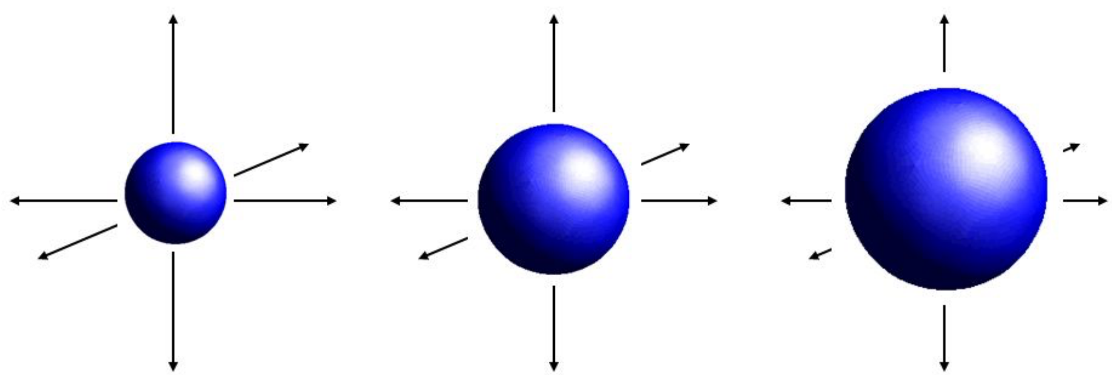
Case study: 1s vs 2s vs 3s orbitals

Radial wave functions for 1s, 2s, and 3s orbitals



As n gets bigger, functions extend further along x axis

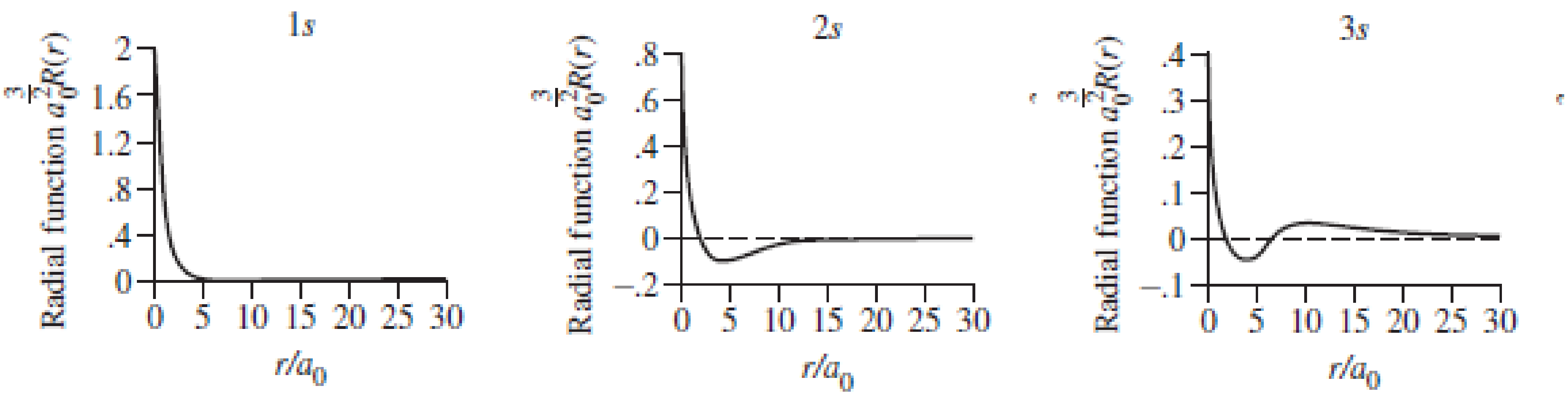
Surface view of 1s, 2s, 3s orbitals



1s 2s 3s

Case study: 1s vs 2s vs 3s orbitals

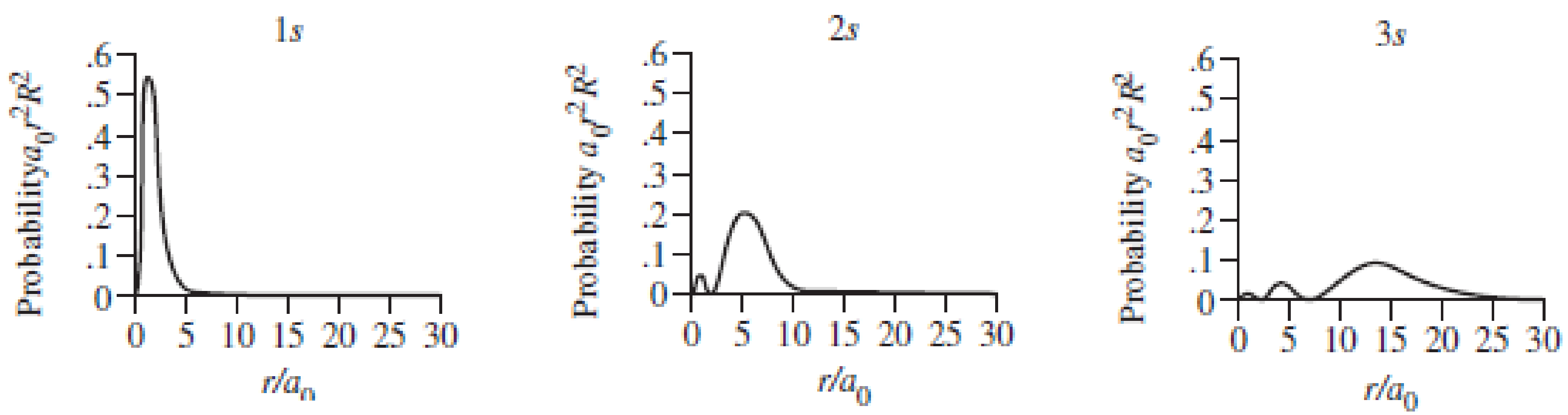
Radial wave functions for 1s, 2s, and 3s orbitals



1s orbital is only positive in sign, 2s and 3s cross between positive and negative

Case study: 1s vs 2s vs 3s orbitals

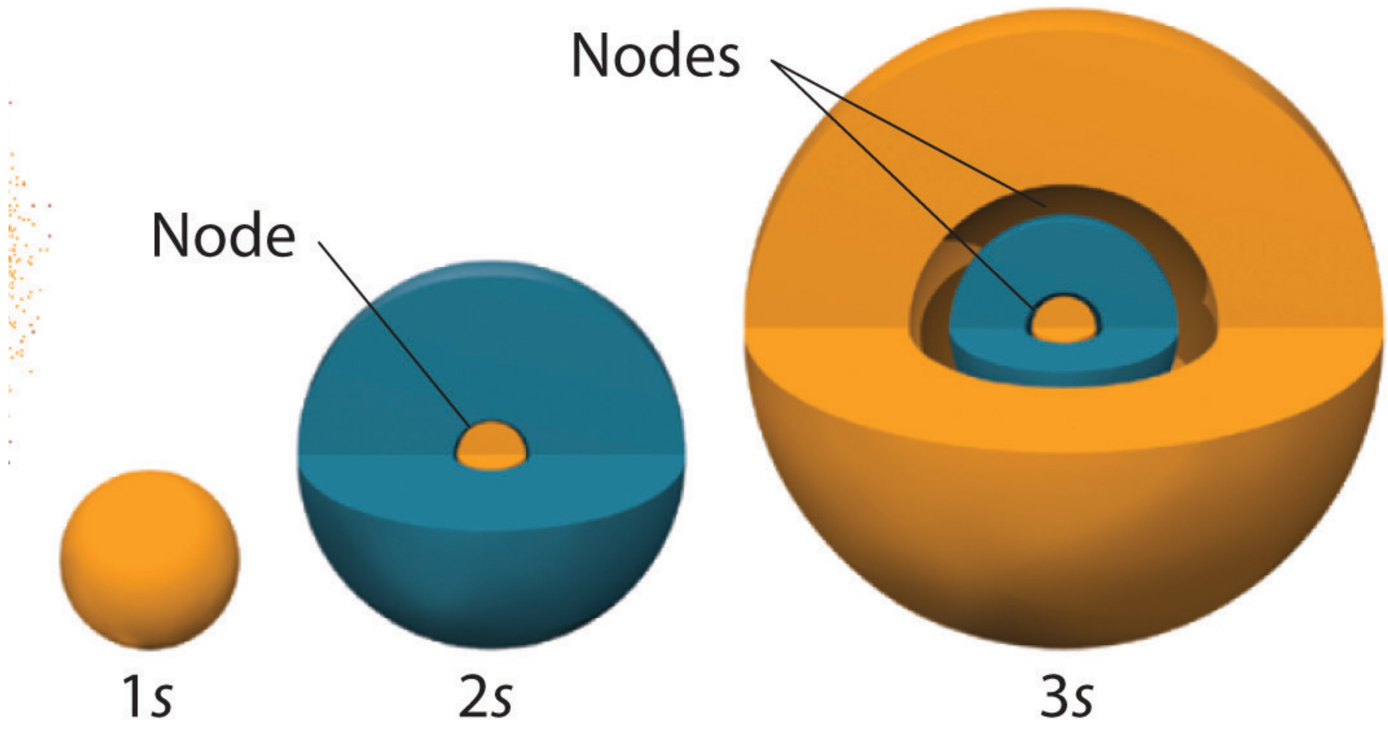
Probability functions for 1s, 2s, and 3s orbitals



Different patterns of zero probability in the three orbitals

Case study: 1s vs 2s vs 3s orbitals

Inside view of the 1s, 2s, and 3s orbitals



What do you need to know about orbitals?

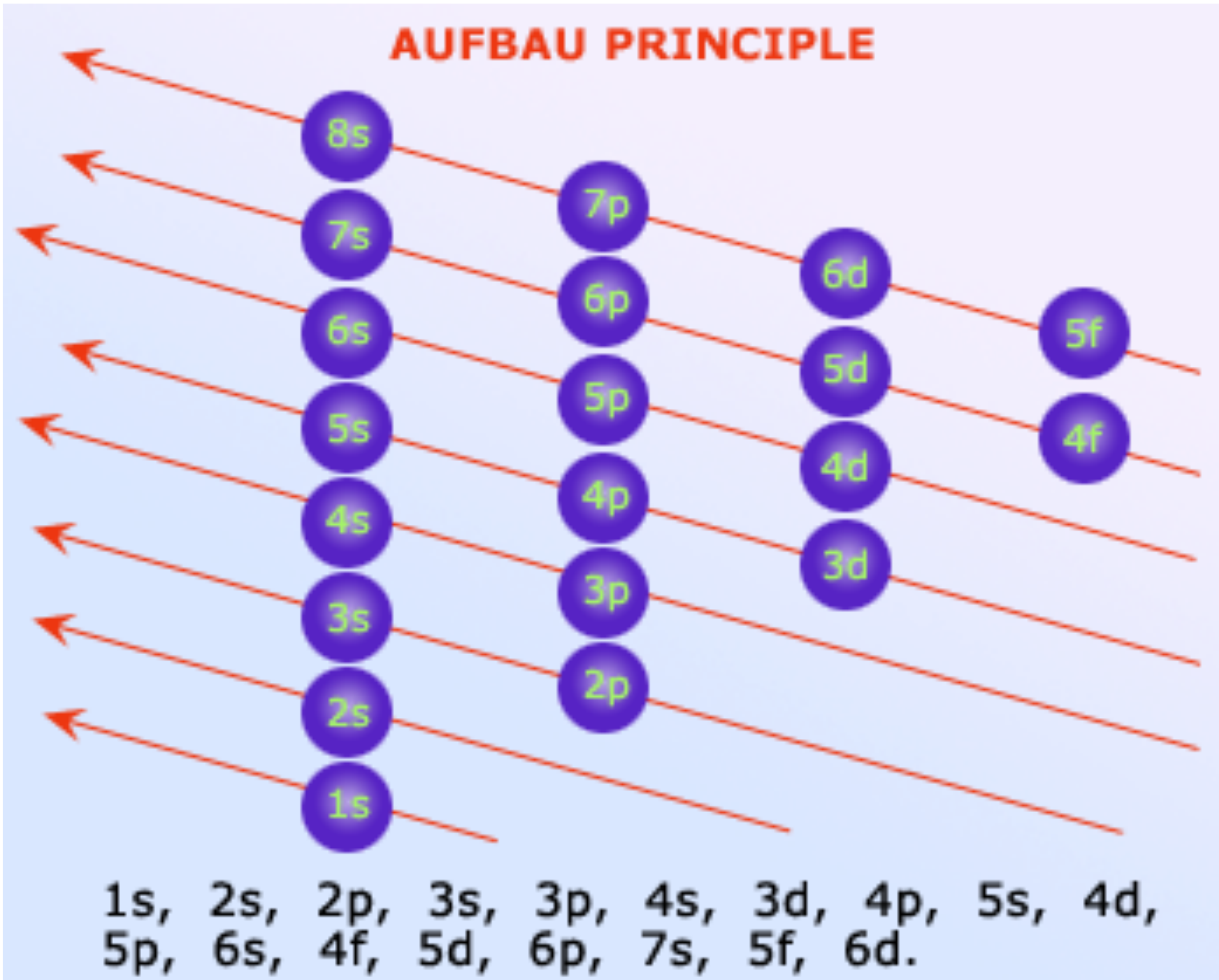
- You MUST know what basic shapes, orientations, and labels of s, p, and d orbitals
- You should be able to roughly sketch an orbital, including its nodes, based on its quantum numbers or specific label (or vice versa)
- You do NOT need to know the wavefunction equations
- Resource for atomic orbitals: Orbitron http://winter.group.shef.ac.uk/orbitron/
- Examples:

ELECTRONIC CONFIGURATION

Aufbau principle

- Electrons fill orbitals from the lowest to the highest energy
  - Lowest values of n and l fill first
  - Note: 4s typically fills before 3d (follow periodic table), some exceptions apply
  - m_l and m_s have no effect
  - See Table 2.7

Aufbau principle



Aufbau principle

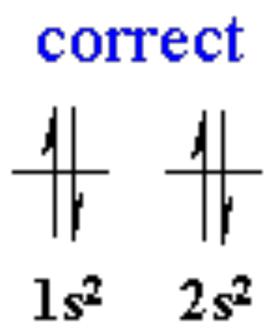
- However, there are some exceptions due to the fact that d^5 (half filled) and d^{10} (filled) configurations are particularly stable
- Examples: Cr and Cu

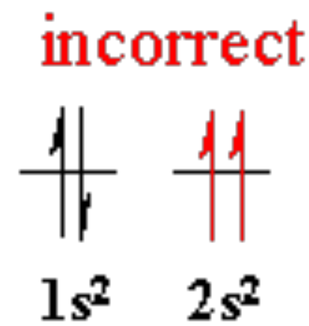
Aufbau principle

- When determining electron configuration of a positively charged metal ion, first consider the neutral configuration. When ionized, the species will lose the 4s (or equivalent) electrons first, followed by the 3d
  - Examples: Cu^{+} and Cu^{2+}

Pauli exclusion principle

- Each electron in an atom must have a unique set of quantum numbers (n, l, m_l, m_s)





Hund's rule

- Electrons must be placed in degenerate orbitals (orbitals with the same energy) to give maximum possible spin