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Chapter 6
Electronic Structure and the Periodic Table

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Outline

- Light, photon energies and atomic spectra
- The hydrogen atom
- Quantum numbers
- Atomic orbitals, shapes and sizes
- Electron configurations in atoms
- Orbital diagrams of atoms
- Electron arrangements in monatomic ions
- Periodic trends in the properties of atoms

Review

- Chapter 2: Structure of the Atom
  - Nucleus: protons and neutrons
  - Surrounding the nucleus: electrons
- Electron Arrangements in Atoms
  - Energy levels
  - Spatial locations
- Considerations
  - Single electron in the hydrogen atom
  - Multiple electrons in other atoms

Arranging Electrons in Atoms

- Electron configuration
  - The electron configuration associates the energy level with the number of electrons in each level
- Orbital diagrams
  - Orbital diagrams show the arrangement of electrons within each energy level
- The periodic table
  - Electron configurations can be deduced from the periodic table
  - Properties of atoms can be related to the electron configuration

Atomic Spectra

- Under certain circumstances, atoms can generate light, which is transmitted through space
  - Fireworks displays
  - Neon lights
  - Sodium vapor streetlights

Fireworks

The Wave Nature of Light

- Wavelength (λ)
  - Distance between two successive crests or troughs in the light wave
  - Measured in nanometers (1 nm = 10^{-9} m)
- Frequency (ν)
  - Number of successive crests or troughs (wave cycles) that pass a point in a unit of time
  - If 10^8 cycles pass in one second, the frequency is 10^8/s or 10^8Hz
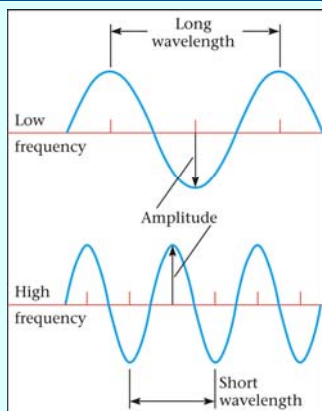
Wavelength-Frequency Relationship

- The speed at which a wave moves through space is found by multiplying the wavelength by the frequency:

$$\lambda \nu = c$$

- c is the speed of light in a vacuum, 2.998 X 10^8 m/s
- To use this equation,
  - Frequency must be in s^{-1}
  - Wavelength must be in m

Figure 6.1

Example 6.1

Table 6.1 – Color and Wavelength

TABLE 6.1 Relation Between Color and Wavelength

Wavelength (nanometers)	Color Absorbed	Color Transmitted
<400 nm	Ultraviolet	Colorless
400–450 nm	Violet	Red, orange, yellow
450–500 nm	Blue	Red, orange, yellow
500–550 nm	Green	Purple
550–580 nm	Yellow	Purple
580–650 nm	Orange	Blue, green
650–700 nm	Red	Blue, green
>700 nm	Infrared	Colorless

The Electromagnetic Spectrum

- The human eye can see light covering only a narrow region of the electromagnetic spectrum (400-700 nm)
  - We see the red glow of a barbecue grill, but most of the radiation is emitted above 700 nm as infrared radiation, also known as heat
  - We cannot see the radiation responsible for sunburn (ultraviolet, below 400 nm) or X-rays (even shorter wavelength)

Color and Wavelength

- Each color detected by the human eye has a wavelength correlated to it
- Color can arise from absorption or transmission of light

Color

- Some substances can be identified by color
- Color arises from the absorption and transmission of specific wavelengths of light
  - Copper sulfate is blue
  - Potassium permanganate is deep violet

Visible Light

- Visible light ranges from 400 to 700 nm
  - Below 400 nm is the ultraviolet
    - Ultraviolet light leads to sunburn
  - Above 700 is the infrared
    - Heat
    - Absorption of infrared light leads to warming up
    - Global warming and carbon dioxide

Figure 6.2
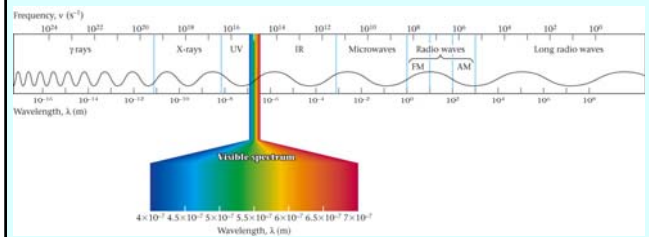
Figure 6.3 and 6.4
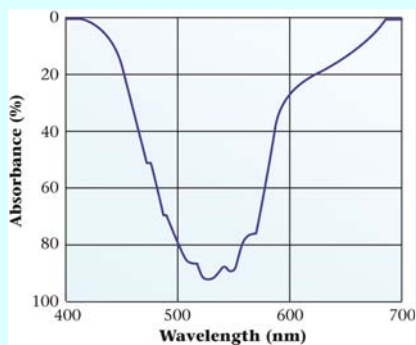
The Particle Nature of Light; Photon Energies

- Before the 20th century, light was explained in terms of waves only
- Experiments from 1900-1910 showed that light has properties not explained by waves
  - Max Planck, blackbody radiation
  - Albert Einstein, photoelectric effect
- Today, we consider light to be a stream of particles called photons, whose energy, E, is given by

$$E = h\nu = \frac{hc}{\lambda}$$

- h is Planck's constant, 6.626×10^{-34} J·s

Energy and Wavelength

- Note that energy and wavelength are inversely related
  - As the wavelength becomes longer, energy decreases
  - As the wavelength becomes shorter, energy increases
- Low energy
  - Infrared, microwave
- High energy
  - Ultraviolet, X-ray

Example 6.2

EXAMPLE 6.2 GRADED

Sodium vapor lamps are commonly used to illuminate highways because of their intense yellow-orange emissions at 589 nm.

a Calculate the energy, in joules, of one photon of this light.

b Calculate the energy, in kilojoules, of one mole of such photons.

c To sense visible light, the optic nerve needs at least 2.0×10^{-17} J of energy to trigger impulses that reach the brain. How many photons of the sodium lamp emissions are needed to "see" the yellow light?

a

ANALYSIS	
Information given:	wavelength of sodium vapor (589 nm)
Information implied:	speed of light (2.998×10^8 m/s); Planck's constant (6.626×10^{-34} J · s)
Asked for:	energy of one photon in J

STRATEGY	

Use Equation 6.2 to relate energy to wavelength.

$$E = \frac{hc}{\lambda}$$

SOLUTION	

| Energy for one photon | $E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{589 \times 10^{-9} \text{ m}} = 3.37 \times 10^{-19}$ J |

continued

Example 6.2, (Cont'd)

b

ANALYSIS	
Information given:	From part (a), the energy of one photon (3.37×10^{-19} J)
Information implied:	Avogadro's number (6.022×10^{23} units/mol)
Asked for:	energy of one mole of photons in kJ

STRATEGY	

Use the appropriate conversion factors to change nm to m, J to kJ, and one photon to one mole of photons.

SOLUTION	

| E/mol of photons | $E = 1 \text{ mol photons} \times \frac{3.37 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol photons}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 203 \text{ kJ}$ |

Example 6.2, (Cont'd)

c

ANALYSIS	
Information given:	Energy required by the optic nerve (2.0×10^{7} J) From part (a), the energy of one photon (3.37×10^{-19} J)
Asked for:	number of photons needed to "see" yellow light

STRATEGY	

Use the energy per photon for yellow light found in part (a) as a conversion factor.

$$\frac{3.37 \times 10^{-19} \text{ J}}{1 \text{ photon}}$$

SOLUTION	

| Photons needed | $2.0 \times 10^{-17} \text{ J} \times \frac{1 \text{ photon}}{3.37 \times 10^{-19} \text{ J}} = 59 \text{ photons}$ |

END POINTS	

1. In part (a), 3.37×10^{-19} J may seem like a tiny amount of energy, but bear in mind that it comes from a single photon.
2. In part (b), the energy calculated for one mole of photons, 203 kJ, is roughly comparable to the energy effects in chemical reactions. About 240 kJ of heat is evolved when a mole of hydrogen gas burns (more on this in Chapter 8).
3. In part (c), note that not too many photons are needed to sense light.

Atomic Spectra

- Sir Isaac Newton
  - 17th Century
  - Showed that white light from the sun can be separated into color components by a prism
  - The resulting spectrum is *continuous* (unbroken) from 400 to 700 nm

Gaseous Elements

- Elements can be put in to the gas phase at high energy
  - Resulting emission of light is *not continuous*
  - Consider sodium
    - Two strong lines in the yellow region: 589.0 and 589.6 nm
    - Light is colored only *yellow*
  - *Line Spectra*

Figure 6.5
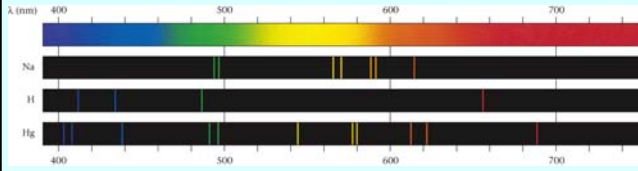
- The fact that photons making up atomic spectra have only certain discrete wavelengths implies that they can have only discrete energies because

$$E = h\nu = \frac{hc}{\lambda}$$

- Photons are produced when an electron moves from one energy level to another within the atom
- Electronic energies are *quantized*: they are limited to specific values

Atomic Spectrum of Hydrogen

- Hydrogen has a single electron and therefore a simple atomic spectrum
  - Multi-electron atoms have complex spectra
- When hydrogen is energized at high voltage, atoms emit radiation
  - Wavelengths can be grouped into series
  - First series was discovered by Johann Balmer (the Balmer Series)

Table 6.2

TABLE 6.2 Wavelengths (nm) of Lines in the Atomic Spectrum of Hydrogen

Ultraviolet (Lyman Series)	Visible (Balmer Series)	Infrared (Paschen Series)
121.53	656.28	1875.09
102.54	486.13	1281.80
97.23	434.05	1093.80
94.95	410.18	1004.93
93.75	397.01	
93.05		

The Hydrogen Atom

- Niels Bohr (1885-1962)
  - Theoretical explanation of the hydrogen spectrum
  - 1922 Nobel Prize in physics
- The Bohr Model
  - Hydrogen consists of a central proton about which moves the electron
  - Electrostatic attraction of proton for electron likened to centrifugal force of circular motion of the electron
  - Electrons occupy fixed orbits around the nucleus

Mathematics of the Bohr Model

- The energy of the hydrogen electron is given by

$$E_n = \frac{-R_H}{n^2}$$

  - E_n is the energy of the electron
  - R_H is the Rydberg constant, 2.180×10^{-18} J
  - n is an integer called the principal quantum number

Notes on the Bohr Model

1. Zero energy is the point at which the proton and electron are infinitely separated; energy must be absorbed to reach this state, so all states below it have negative energy.
2. The ground state is the lowest energy state for the hydrogen atom, where n = 1. Any n value above 1 corresponds to an excited state.
3. When an electron emits energy as a photon of light, it falls from a higher n to a lower n.

Energy Release

- The difference in energy between two states in the hydrogen atom is the energy of the photon released in the transition between those states

$$\Delta E = h\nu = E_{hi} - E_{lo}$$

- Combining Bohr's equation for two states produces the Rydberg equation for the hydrogen atom

$$\nu = \frac{R_H}{h}\left[\frac{1}{n_{lo}^2} - \frac{1}{n_{hi}^2}\right]$$

- h is Planck's constant, 6.626×10^{-34} J·s

Example 6.3

The Hydrogen Series

- The lines in the hydrogen spectrum are grouped by the value of n_{lo}:
  - Balmer series has n_{lo} = 2
  - Lyman series has n_{lo} = 1
  - Paschen series has n_{lo} = 3

The Balmer Series
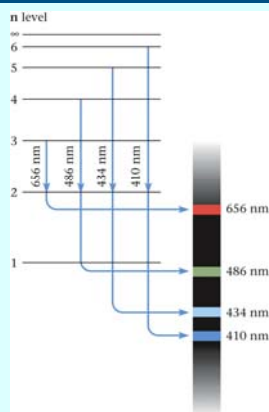
The Quantum Mechanical Model

- Bohr's theory explains the hydrogen atom very well
- When applied to atoms with two or more electrons, the theory gives only qualitative agreement with experimental data

Matter Waves

- deBroglie, 1892-1987
  - If light, which is ordinarily considered a wave, can have the properties of a particle, then electrons, which are ordinarily considered particles, can have the properties of a wave
  - The result was a new branch of physics called *wave mechanics*, which evolved into *quantum mechanics*

Fundamental Principles of Quantum Mechanics

- The kinetic energy of an electron is inversely related to the volume of the region in space to which it is confined
  - The kinetic energy increase from the shrinking volume of an electron moving toward the nucleus balances the electrostatic attraction to prevent the electron from falling into the nucleus
- It is impossible to specify the exact position of an electron at a given instant
  - We can only specify the probability of finding an electron in a particular region of space

Schrodinger

- Erwin Schrödinger (1887-1961)
  - 1926
  - Wrote a differential equation to express the wave properties of an atom
    - Ψ is called the wave function
    - It is possible to find the amplitude of the electron wave at various points in space
    - Ψ^2 is proportional to the probability of finding an electron at a particular point in space

Electron Cloud Diagrams

- Electron cloud diagrams are maps of electron density
  - The depth of color is proportional to Ψ^2, the probability of finding an electron
- Orbitals
  - The orbital represents the region in space where there is a 90% or higher probability of finding an electron
- Pictorial view follows

Figure 6.6

In this rendering the depth of color is proportional to the probability of finding the electron at a given point. The dotted line encloses the volume within which there is a 90% probability of finding the electron.

In this rendering the orbital encloses the volume within which there is a 90% probability of finding the electron; the electron density within the orbital is not shown.

Quantum Numbers

- The Schrödinger equation can be solved exactly only for the hydrogen atom
- Approximations allow for solutions of the equation relevant to atoms with two or more electrons
- The solutions result in orbitals, which have an energy, a shape and an orientation in space
- The solutions result in three *quantum numbers*:
  - n
  - ℓ
  - m_ℓ

First Quantum Number, n

- The principal energy level is specified by the first quantum number, n
- n = 1, 2, 3, 4, …
  - n = 1 is the first principal level
  - n = 2 is the second principal level, and so on …

The Second Quantum Number, ℓ

- Each principal energy level (specified by n) has one or more sublevels
  - The sublevel is specified by the quantum number ℓ
  - ℓ is derived from n:
    - ℓ = 0, 1, 2 … (n-1)
      - In the nth principal level, there are n sublevels
  - Instead of using numbers, the sublevels are given letter designations
    - For ℓ = 0, 1, 2, 3   we use   s, p, d, f

Combining n and ℓ

- n and ℓ are combined to indicate the principal and subsidiary levels
  - 1s means n = 1 and ℓ =0
  - 2s means n = 2 and ℓ = 0
  - 3p means n = 3 and ℓ = 1

TABLE 6.3 Sublevel Designations for the First Four Principal Levels

n	1	2		3			4			
ℓ	0	0	1	0	1	2	0	1	2	3
Sublevel	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f

Relative Energy

- For atoms with more than one electron, the energy is dependent on both n and ℓ
  - ns < np < nd < nf
- Recall that as n increases, energy increases
  - 2s is higher energy than 1s
- Combining both
  - 2p is higher energy than 2s

The Third Quantum Number, m_ℓ

- Each sublevel contains one or more orbitals, which differ from one another in the value of the third quantum number, m_ℓ
- Just as ℓ depends on n, m_ℓ depends on ℓ
  - m_ℓ = -ℓ … -1, 0, +1, … +ℓ
  - There are 2ℓ + 1 orbitals per sublevel

Sublevels s through f

- For an s sublevel, ℓ = 0, so m_ℓ = 0
- For a p sublevel, ℓ = 1 so m_ℓ = -1, 0, or 1
- For a d sublevel, ℓ = 2 so m_ℓ = -2, -1, 0, 1, or 2
- For an f sublevel, ℓ = 3 so m_ℓ = -3, -2, -1, 0, 1, 2 or 3

The Fourth Quantum Number, m_s

- The last quantum number is associated with the electron spin
  - Two spins are possible, clockwise and counterclockwise
  - There are two values of m_s, $+\frac{1}{2}$ and $-\frac{1}{2}$
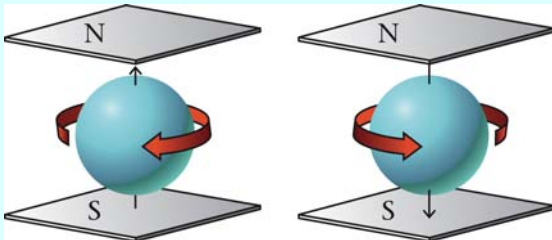
The Pauli Exclusion Principle

- No two electrons in the same atom may have the same set of four quantum numbers
  - Two electrons may occupy an orbital; these will differ in spin
  - The spins of two electrons in an orbital will be opposite to each other

Table 6.4

TABLE 6.4 Permissible Values of the Quantum Numbers Through n = 4

n	ℓ	m_ℓ	m_s
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (2p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (3p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
	2 (3d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ
4	0 (4s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (4p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
	2 (4d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ
	3 (4f)	−3, −2, −1, 0, +1, +2, +3	$\pm\frac{1}{2}$ for each value of m_ℓ

Example 6.4

EXAMPLE 6.4

Consider the following sets of quantum numbers (n, ℓ, m_ℓ, m_s). Which ones could not occur? For the valid sets, identify the orbital involved.

(a) 3, 1, 0, $+\frac{1}{2}$ (b) 1, 1, 0, $-\frac{1}{2}$ (c) 2, 0, 0, $+\frac{1}{2}$

(d) 4, 3, 2, $+\frac{1}{2}$ (e) 2, 1, 0, 0

STRATEGY

1. Use the selection rules to identify quantum numbers that are not valid.
2. Recall the letter and number designations for ℓ.

$\ell = 0 = s; \ell = 1 = p; \ell = 2 = d; \ell = 3 = f$

Example 6.4 (Cont'd)

SOLUTION

(a) 3, 1, 0, $+\frac{1}{2}$	valid; n = 3, ℓ = 1 = p; 3p
(b) 1, 1, 0, $-\frac{1}{2}$	not valid; n = 1, ℓ = 1, ℓ cannot equal n
(c) 2, 0, 0, $+\frac{1}{2}$	valid; n = 2, ℓ = 0 = s; 2s
(d) 4, 3, 2, $+\frac{1}{2}$	valid; n = 4, ℓ = 3 = f; 4f
(e) 2, 1, 0, 0	not valid; m_s can only be $+\frac{1}{2}$ or $-\frac{1}{2}$.

Example 6.5

EXAMPLE 6.5

(a) What is the capacity for electrons of an s sublevel? A p sublevel? A d sublevel? An f sublevel?

(b) What is the total capacity for electrons of the fourth principal level?

ANALYSIS

Information given:	sublevels
Information implied:	capacity of an orbital (2 e^-) number of orbitals in a sublevel
Asked for:	(a) number of electrons in each sublevel (b) number of electrons in n = 4

STRATEGY

1. Recall the number designations that correspond to the letter designation of sublevels.
2. Use the rule that tells you how many orbitals there are to a particular sublevel.

SOLUTION

(a) s sublevel	ℓ = s = 0; m_ℓ = 0; 1 orbital × 2e^-/orbital = 2e^-
p sublevel	ℓ = p = 1; m_ℓ = −1, 0, +1; 3 orbitals × 2e^-/orbital = 6e^-
d sublevel	ℓ = d = 2; m_ℓ = −2, −1, 0, +1, +2; 5 orbitals × 2e^-/orbital = 10e^-
f sublevel	ℓ = f = 3; m_ℓ = −3, −2, −1, 0, +1, +2, +3; 7 orbitals × 2e^-/orbital = 14e^-
(b) Number of e^- in n = 4	n = 4; ℓ = 0, 1, 2, 3
	From (a): (ℓ = 0 = 2e^-) + (ℓ = 1 = 6e^-) + (ℓ = 2 = 10e^-) + (ℓ = 3 = 14e^-) = 32e^-

Atomic Orbital Shapes and Sizes

- Recall that an orbital is a physical representation of the region in space where there is a 90% probability of finding an electron
- We will consider the shapes of two types of orbitals in this chapter
  - s orbitals are spherical, differing only in size (they become larger as n increases)
  - p orbitals consist of two lobes along an axis
    - There are three axes – x, y and z
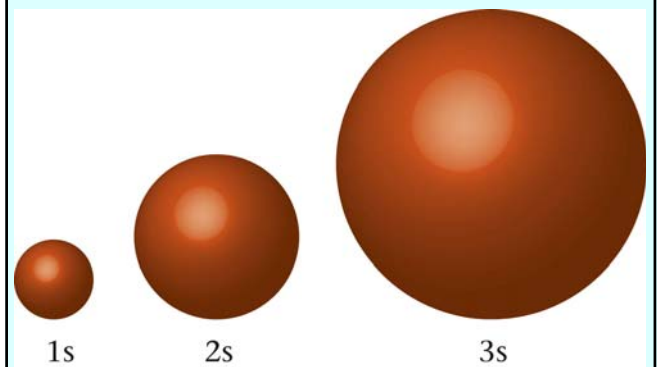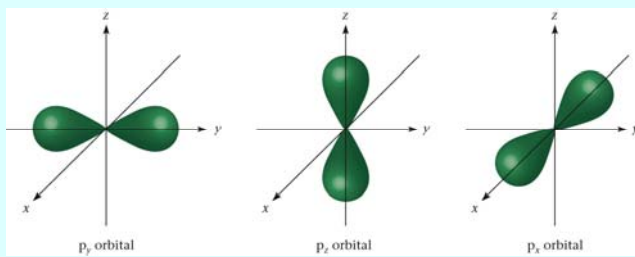   - There are three p orbitals – p_x, p_y, and p_z

Shape of s-orbital

1s   2s   3s

Figure 6.9: Shapes of p-orbitals

p_y orbital p_z orbital p_x orbital

Example 6.6

EXAMPLE 6.6

Find the electron configurations of the sulfur and iron atoms.

ANALYSIS	
Information given:	identity of the atoms
Information implied:	atomic number of the atoms Figure 6.10; energy diagram
Asked for:	electron configurations for (a) S and (b) Fe

continued

Example 6.6 (Cont'd)

STRATEGY
1. Find the atomic numbers of S and Fe in the periodic table.   S: atomic number = 16; Fe: atomic number = 26
2. Use Figure 6.10 and fill the appropriate sublevels.   Remember 4s fills before 3d.

SOLUTION	
(a) S	$1s^2 2s^2 2p^6 3s^2 3p^4$
(b) Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

END POINT
Use the periodic table to check your answer. See Figure 6.11 and the accompanying discussion.

Example 6.7

EXAMPLE 6.7

For the iodine atom, write

(a) the electron configuration.   (b) the abbreviated electron configuration.

ANALYSIS	
Information given:	Identity of the atom (I)
Information implied:	atomic number of I periodic table or Figure 6.11
Asked for:	(a) electron configuration (b) abbreviated electron cofiguration

continued

10

Example 6.7 (Cont'd)

STRATEGY

(a) Use Figure 6.11 or any periodic table. Go across each period in succession, noting the sublevels occupied until you get to I.

(b) Start with the preceding noble gas, krypton (Kr).

SOLUTION

|	
(a) Period 1	$1s^2$
Period 2	$2s^2 2p^6$
Period 3	$3s^2 3p^6$
Period 4	$4s^2 3d^{10} 4p^6$
Period 5	$5s^2 4d^{10} 5p^5$
Putting them together	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$
(b) $[_{36}Kr]$	Kr accounts for periods 1–4
Abbreviated electron configuration	$[_{36}Kr]$ + period 5 = $[Kr]5s^2 4d^{10} 5p^5$

END POINT

Check your answer by adding all the electrons (superscripts) in your electron configuration. Your answer must equal the atomic number, which is the number of electrons in the atom.

Electron Configuration in Atoms

- By applying the rules from which quantum numbers derive, it is possible to assign quantum numbers to each electron in an atom
  - Electron configuration: $1s^2 2s^2 2p^5$
  - Coefficient is n
  - Letter is m_ℓ
  - Superscript is the number of electrons

Predicting Electron Configurations

- Predictions apply to gaseous atoms in the ground state
- Energy of sublevel determines order of assignment
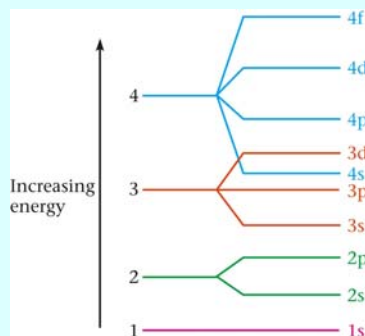
Electron Configuration from Sublevel Energies

- Once the order of filling of sublevels is known, the electron configuration is readily obtained
  - Experimental evidence provides the relative energies of sublevels
  - Sublevels are ordinarily filled before proceeding to the next energy sublevel
- Examples

  H, $1s^2$ He, $1s^2$

  Li, $1s^2 2s^1$ Be, $1s^2 2s^2$

  B, $1s^2 2s^2 2p^1$ C $1s^2 2s^2 2p^2$

The Transition Metals

- Consider Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$
  - The next electron enters the 4s
    - K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
    - Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
  - With the transition metals, the 3d fills after the 4s
    - Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
  - Following the transition metals, the 4p fills
    - Ga: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

Abbreviated Electron Configurations

- To save writing, abbreviated electron configurations are written
  - Start with the preceding noble gas
  - Complete the configuration with the rest of the electrons in the element
    - S is $[Ne]3s^2 3p^4$
    - Ni is $[Ar]4s^2 3d^8$

Filling of Sublevels and the Periodic Table

- By using the periodic table, it is possible to quickly write an electron configuration for any element
  - Consider the Group 1 elements
    - All have the outer configuration s^1
  - Consider the Group 2 elements
    - All have the outer configuration s^2
- Atoms of elements in a group have the same distribution of electrons in the outermost principal energy level

Table 6.5

TABLE 6.5 Abbreviated Electron Configurations of Group 1 and 2 Elements

Group 1		Group 2	
$_3$Li	[He] **2s¹**	$_4$Be	[He] **2s²**
$_{11}$Na	[Ne] **3s¹**	$_{12}$Mg	[Ne] **3s²**
$_{19}$K	[Ar] **4s¹**	$_{20}$Ca	[Ar] **4s²**
$_{37}$Rb	[Kr] **5s¹**	$_{38}$Sr	[Kr] **5s²**
$_{55}$Cs	[Xe] **6s¹**	$_{56}$Ba	[Xe] **6s²**

Notes on The Periodic Table

1. Elements in Group 1 and 2 fill an *s sublevel*
2. Elements in Groups 13-18 fill a *p sublevel*
3. Elements of the transition metals fill a *d sublevel*
4. The two sets of 14 elements each at the bottom of the periodic table fill f sublevels with a principal quantum number *two less than the period number*
   - First row: lanthanides
   - Second row: actinides

Example 6.8

EXAMPLE 6.8

Construct orbital diagrams for atoms of sulfur and iron.

ANALYSIS	
Information given:	identity of the atoms (S and Fe)
Information implied:	periodic table number designations for ℓ number of orbitals in each sublevel
Asked for:	orbital diagram for (a) S and (b) Fe

STRATEGY

1. Write the electron configurations for S and Fe.
   See Example 6.6 where the electron configuration for these atoms is obtained.
2. Recall the number of orbitals per sublevel and the number of electrons allowed in each orbital.
   $m_\ell = 2\ell + 1$; $2e^-$ per orbital
3. Apply Hund's rule.
   Electrons enter singly in parallel spins when several orbitals of equal energy are available.

Example 6.8 (Cont'd)

SOLUTION

(a) S electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^4$
Number of orbitals	s = 0; 2(0) + 1 = 1 orbital for s sublevels
	p = 1; 2(1) + 1 = 3 orbitals for p sublevels
Orbital diagram	1s 2s 2p 3s 3p
	(↑↓) (↑↓) (↑↓)(↑↓)(↑↓) (↑↓) (↑↓)(↑)(↑)
(b) Fe electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Number of orbitals	s = 0; 2(0) + 1 = 1 orbital for s sublevels
	p = 1; 2(1) + 1 = 3 orbitals for p sublevels
	d = 2; 2(2) + 1 = 5 orbitals for p sublevels
Orbital diagram	1s 2s 2p 3s 3p 4s 3d
	(↑↓) (↑↓) (↑↓)(↑↓)(↑↓) (↑↓) (↑↓)(↑↓)(↑↓) (↑↓) (↑↓)(↑)(↑)(↑)(↑)

END POINT

You can't write an orbital diagram without knowing: (a) the number designations for ℓ, (b) the number of orbitals in each sublevel, (c) the electron configuration, and (d) Hund's rule.

Exceptions

- Some elements have electron configurations that differ from those expected from the application of the rules we have seen
  - Cr is actually [Ar]$4s^1 3d^5$
  - Cu is actually [Ar]$4s^1 3d^{10}$
- These difference arise because
  - The energy levels of the orbitals are close to each other
  - There is a gain in stability by producing a half-filled or a filled shell where possible

Figure 6.11: The Periodic Table
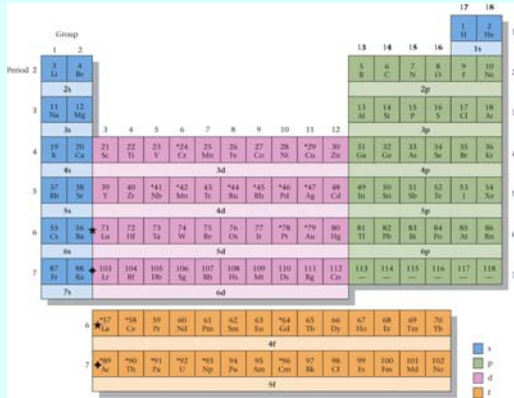
Orbital Diagrams of Atoms

- One step beyond the assignment of electrons to orbitals is the depiction of electrons in orbitals
  - Parentheses indicate orbitals (___)
  - Arrows, up and down, indicate electrons ($\uparrow\downarrow$)
    - Recall the m_s quantum number
    - One electron in an atom has $m_s = \frac{1}{2}$ and the other has $m_s = -\frac{1}{2}$
  - Hund's Rule
    - Maximize unpaired spins where possible

Figure 6.12

Notes

- In all filled orbitals, the two electrons have opposed spins
- Within a given sublevel there are as many half-filled orbitals as possible
  - This is a direct consequence of Hund's Rule
- Hund's rule is based on experiment
  - Substances with *unpaired* electrons are *paramagnetic*
  - Substances with *all paired* electrons are *diamagnetic*

Electron Arrangements in Monatomic Ions

- In forming an ion, electrons are *removed from (cation)* or *added to (anion)* sublevels in the highest principal energy level

Main Group Ions and Noble Gas Structures

- Cations of Group 1 form +1 ions
- Cations of Group 2 from +2 ions
- Nitrogen forms a -3 ion
- Elements in the oxygen family form -2 ions
- Halogens form -1 ions

Figure 6.13 – Noble Gas Configurations

						H^-	He
Li^+	Be^{2+}			N^{3-}	O^{2-}	F^-	Ne
Na^+	Mg^{2+}	Al^{3+}			S^{2-}	Cl^-	Ar
K^+	Ca^{2+}	Sc^{3+}			Se^{2-}	Br^-	Kr
Rb^+	Sr^{2+}	Y^{3+}			Te^{2-}	I^-	Xe
Cs^+	Ba^{2+}	La^{3+}					

Transition Metal Cations

- Transition metal cations do not usually form ions with noble-gas configurations
  - Cations do form, with charges ranging from +1 to higher numbers
  - The outer s electrons are lost before the d electrons; this is the first-in, first-out rule
- Consider Mn
  - Mn is $[Ar]4s^23d^5$
  - Mn^{2+} is $[Ar]3d^5$

Example 6.9

EXAMPLE 6.9

Give the electron configuration of
(a) Fe^{2+} (b) Br^-

ANALYSIS

Information given:	Identity of the ions and their charge: (Fe^{2+}, Br^-)
Information implied:	atomic number of the atoms; electron configuration of the atoms
Asked for:	electron configuration of the ions

STRATEGY

1. Write the electron configuration of each atom.
2. Add electrons (for anions) or subtract electrons (for cations) from sublevels of the highest **n**. If there is more than one sublevel in the highest **n**, add or subtract electrons in the highest **ℓ** of that **n**.

continued

Example 6.9 (Cont'd)

SOLUTION

(a) Fe electron configuration	$1s^22s^22p^63s^23p^64s^23d^6$
Cation with +2 charge	subtract 2 electrons
Highest **n**	4 with only one sublevel
Fe^{2+} electron configuration	$1s^22s^22p^63s^23p^64s^{2-2}3d^6 = 1s^22s^22p^63s^23p^63d^6$
(b) Br electron configuration	$1s^22s^22p^63s^23p^64s^23d^{10}4p^5$
Anion with −1 charge	add 1 electron
Highest **n**	4 with 2 sublevels (s and p)
Highest **ℓ** in **n**	p
Br^- electron configuration	$1s^22s^22p^63s^23p^64s^23d^{10}4p^{5+1} = 1s^22s^22p^63s^23p^64s^23d^{10}4p^6$

END POINT

The electron configuration for Br^- is the same as that for the noble gas closest to it, krypton.

Periodic Trends

- The chemical and physical properties of elements are a periodic function of atomic number
  - Recall that the number of electrons is equal to the atomic number of an element
  - Properties to be considered
    - Atomic radius (and ionic radius)
    - Ionization energy
    - Electronegativity

Atomic Radius

- The "size" of an atom is a difficult to define term
- The radius of an atom can be defined and measured, assuming the atom is a sphere
- The trend for the radius of the atom is
  - A decrease in radius across a period
  - An increase in radius down a group

Figure 6.14

Atomic radius = $\frac{0.256 \text{ nm}}{2}$ = 0.128 nm

0.256 nm

Cu
a

Atomic radius = $\frac{0.198 \text{ nm}}{2}$ = 0.099 nm

0.198 nm

Cl_2
b
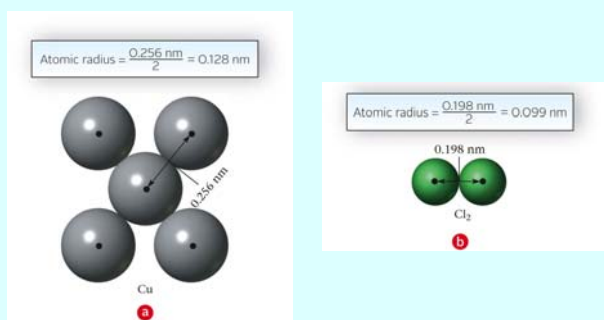
Trends in Atomic Radius

- The increase in radius down a group can be explained by the screening of the electron from the positive charge on the nucleus in the outer shell by the inner electrons; *the effective nuclear charge decreases*
- The decrease in radius across a period can be explained by the fact that electrons are being added to the same principal energy level and do not screen as well; the *effective nuclear charge increases*

Ionic Radius

- *Cations are smaller than the atoms from which they form*
  - Fewer electrons mean increased effective nuclear charge on those that remain
- *Anions are larger than the atoms from which they form*
  - More electrons mean that there is more electron-electron repulsion so the size of the ion increases relative to that of the atom

Figure 6.15

Example 6.10

EXAMPLE 6.10

Using only the periodic table, arrange each of the following sets of atoms and ions in order of increasing size.

(a) Mg, Al, Ca   (b) S, Cl, S^{2-} (c) Fe, Fe^{2+}, Fe^{3+}

STRATEGY

Recall the following:
- The definition of a period and a group in the periodic table.
- The radius decreases across a period and increases going down a group.
- An atom is larger than its cation but smaller than its anion.

continued

Example 6.10 (Cont'd)

SOLUTION

(a) Mg, Al, Ca

Mg and Al belong to the same period: Al < Mg.
Mg and Ca belong to the same group: Mg < Ca.
Thus Al < Mg < Ca.

(b) S, Cl, S^{2-}

S and Cl belong to the same period: Cl < S.
An atom is smaller than its anion: S < S^{2-}.
Thus Cl < S < S^{2-}.

(c) Fe, Fe^{2+}, Fe^{3+}

A cation is smaller than its atom: Fe^{2+} < Fe, Fe^{3+} < Fe
Increasing the charge of cations of the same atom decreases size:

Fe^{3+} < Fe^{2+}.

Thus Fe^{3+} < Fe^{2+} < Fe (Figure 6.16).

Figure 6.16

Fe
Fe^{2+}
Fe^{3+}
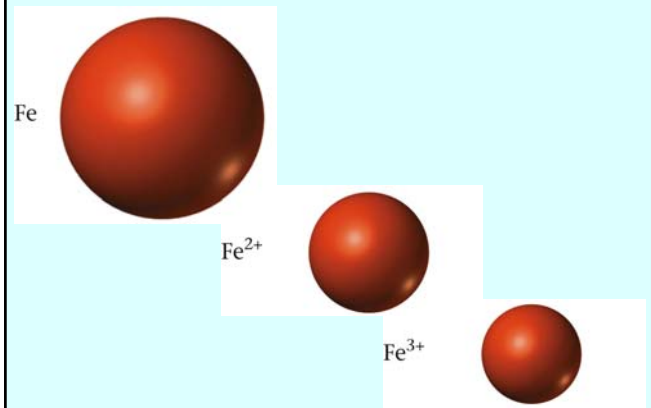
Ionization Energy

- The ionization energy is a measure of difficulty in removing an electron from a gaseous atom
- M (g) → M$^+$ (g) + e$^-$
  - Ionization energy increases across a period from left to right
  - Ionization energy decreases down a family from top to bottom

Figure 6.17

	1	2	13	14	15	16	17	18
							H 1312	He 2372
	Li 520	Be 900	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
	Na 496	Mg 738	Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1520
	K 419	Ca 590	Ga 579	Ge 762	As 944	Se 941	Br 1140	Kr 1351
	Rb 403	Sr 550	In 558	Sn 709	Sb 832	Te 869	I 1009	Xe 1170
	Cs 376	Ba 503	Tl 589	Pb 716	Bi 703	Po 812	At	Rn 1037

Ionization energy decreases

Ionization energy increases

Example 6.11

EXAMPLE 6.11

Consider the three elements C, N, and Si. Using only the periodic table, predict which of the three elements has
(a) the largest atomic radius; the smallest atomic radius.
(b) the largest ionization energy; the smallest ionization energy.

STRATEGY

1. Because these three elements form a block (N next to C and Si below C), in the periodic table, it is convenient to compare both silicon and nitrogen to carbon.
2. Recall the trends for atomic radius and ionization energy.

SOLUTION

(a) atomic radius	C > N; C < Si
	Si is the largest atom, N is the smallest.
(b) ionization energy	C < N; C > Si
	Si has the smallest first ionization energy.
	N has the largest first ionization energy.

END POINT

Check your answers against Figures 6.15 and 6.17.

Electronegativity

- Electronegativity is the ability of an atom to attract electrons
  - Linus Pauling
    - Fluorine is the most electronegative element
    - Cs is the least electronegative element
  - As electronegativity increases, the formation of an anion becomes more likely
- Trends
  - Electronegativity increases across a period
  - Electronegativity decreases down a family

Table 6.6

TABLE 6.6 Electronegativity Values

H 2.2							—*
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	—*
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	—*
K 0.8	Ca 1.0	Sc 1.4	Ge 2.0	As 2.2	Se 2.5	Br 3.0	Kr 3.3
Rb 0.8	Sr 0.9	Y 1.2	Sn 1.9	Sb 2.0	Te 2.1	I 2.7	Xe 3.0
Cs 0.8	Ba 0.9						

*The noble gases He, Ne, and Ar are not listed because they form no stable compounds.

Key Concepts

1. Relate wavelength, frequency and energy
2. Use the Bohr model to identify lines in the hydrogen spectrum
3. Identify the quantum numbers of electrons in atoms
4. Derive the electron capacity of energy levels
5. Write electron configurations, full and abbreviated, for atoms and ions
6. Draw orbital diagrams for atoms and ions
7. Identify periodic trends in radii, ionization energy and electronegativity