Chapter 7 – Atomic Structure and Periodicity
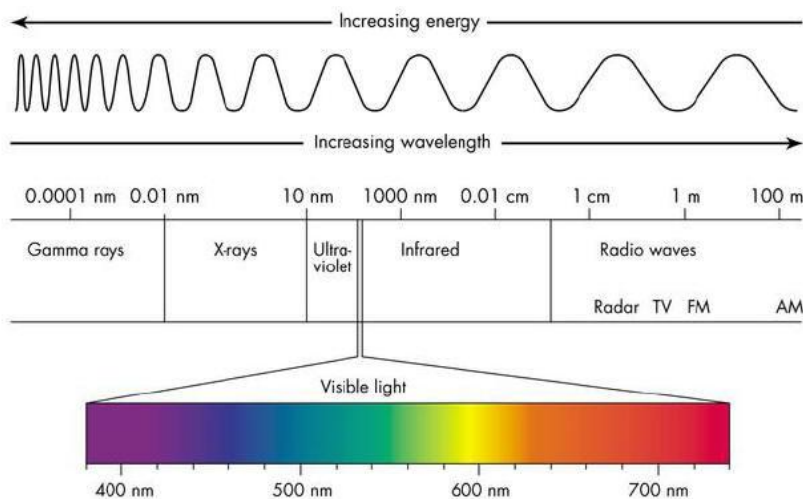
1. Electromagnetic Radiation
   a. Types of EM Radiation (wavelengths in meters)

Wavelength increases ———————▶
Frequency decreases ———————▶
Energy decreases ———————▶
Speed is constant = 2.9979 x 108 m/sec

   b. Properties of EM Waves
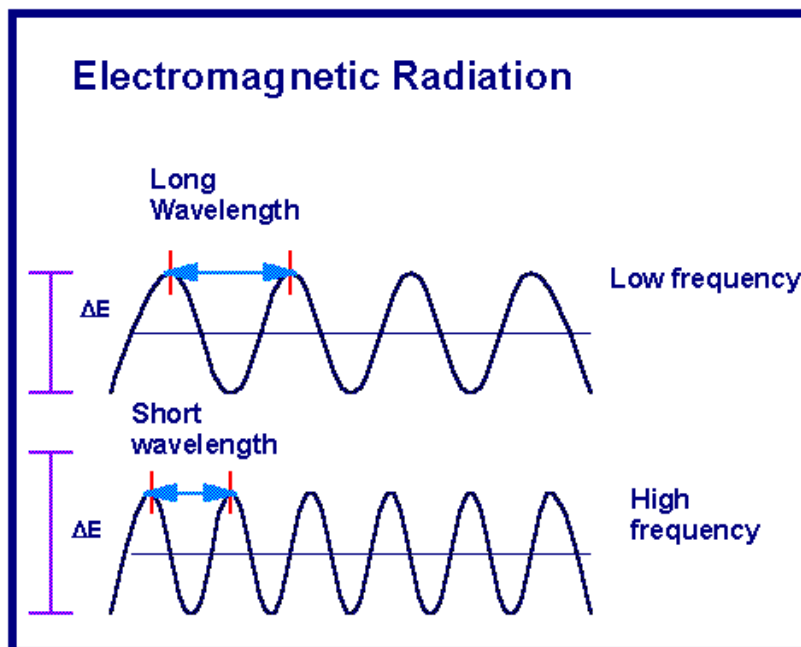   i. Wavelength (λ)
         1. Distance between two consecutive peaks or troughs in a wave
         2. Measured in meters (SI system)
      ii. Frequency (ν)
         1. Number of waves that pass a given point per second
         2. Measured in hertz (sec-1)
   c. Speed (c)
      i. Measured in meters/sec

   d. Relationship of properties
      i. $\lambda \ \nu = c$

2. The Nature of Matter
    a. Max Planck and Quantum Theory
        i. Energy is gained or lost in whole number multiples of the quantity hv
           Frequency = v
           Planck's constant = h = 6.626 x 10^{-34} J·S

$$\Delta E = nhv$$

    b. Energy is transferred to matter in packets of energy, each called a quantum
3. Einstein and the Particle Nature of Matter
    a. EM radiation is a stream of particles - "photons"

$$E_{photon} = hv = \frac{hc}{\lambda}$$

    b. Energy and mass are inter-related
$$E = mc^2$$
    c. de Broglie and the Dual Nature of Light
        i. Light travels through space as a wave
        ii. Light transmits energy as a particle
        iii. Particle's have wavelength, exhibited by diffraction patterns
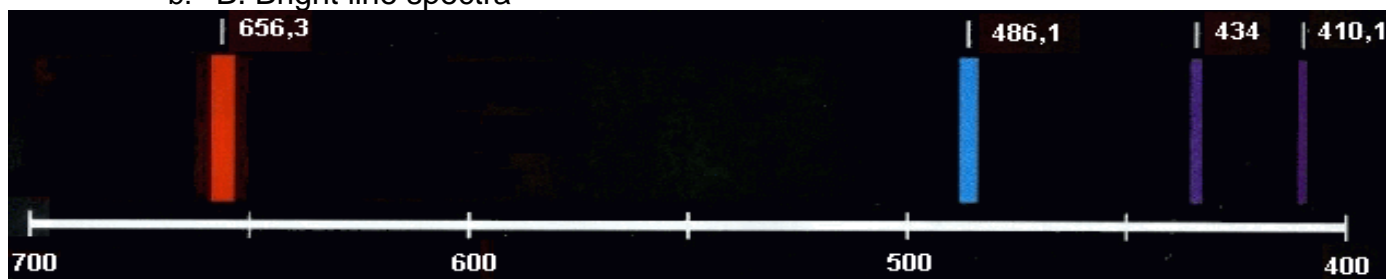
$$\lambda = \frac{h}{mv}$$

            1. large particles have very short wavelengths
            2. All matter exhibits both particle and wave properties

4. The Atomic Spectrum of Hydrogen
    a. Continuous spectra
        i. Contains all wavelengths of light
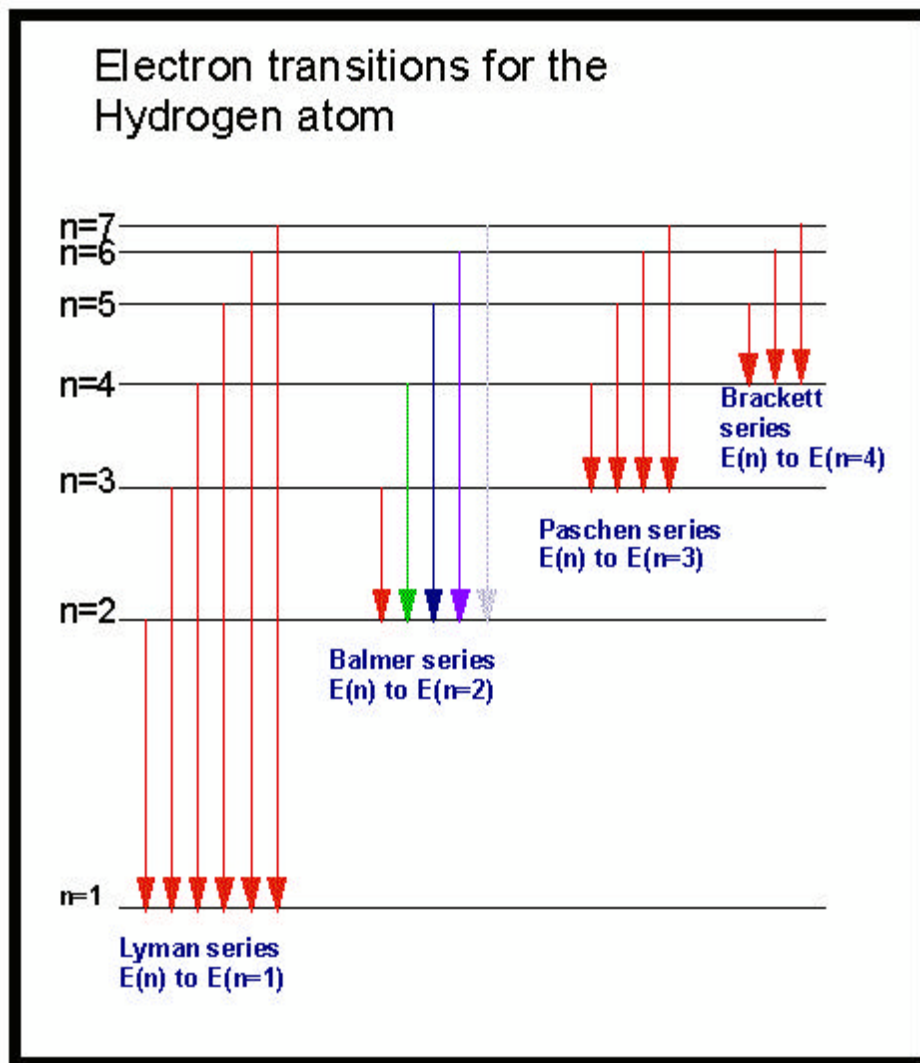   b. B. Bright line spectra

Emission spectrum of hydrogen.

    c. Excited electrons in an atom return to lower energy states
    d. Energy is emitted in the form of a photon of definite wavelength
    e. Definite change in energy corresponds to:
        i. Definite frequency
        ii. Definite wavelength

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

    f. Only certain energies are possible within any atom

Electron transitions for the Hydrogen atom

5. Bohr Model (Neils Bohr, 1913)
    a. Quantum Model
        i. The electron moves around the nucleus only in certain allowed circular orbits
        ii. Bright line spectra confirms that only certain energies exist in the atom, and atom emits photons with definite wavelengths when the electron returns to a lower energy state
        iii. Energy levels available to the electron in the hydrogen atom

$$E = -2.178E^{-18} \, J(\frac{Z^2}{n^2})$$

n = integer   Z = nuclear charge   J = energy in Joules

b. Calculating the energy of the emitted photon
  i. Calculate electron energy in outer level
  ii. Calculate electron energy in inner level
  iii. Calculate the change in energy (ΔE)
       ΔE = energy of final state - energy of initial state
  iv. Use the equation:

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

  to calculate the wavelength of the emitted photon
c. Energy Change in Hydrogen atoms
  i. Calculate energy change between any two energy levels

$$\Delta E = -2.178E^{-18} \, J \, (\frac{1}{n^2_{Final}} - \frac{1}{n^2_{initial}})$$

d. Shortcomings of the Bohr Model
  i. Bohr's model does not work for atoms other than hydrogen
  ii. Electron's do not move in circular orbits

6. The Quantum Mechanical Model of the Atom
   a. The Electron as a standing wave
     i. Standing waves do not propagate through space
     ii. Standing waves are fixed at both ends
     iii. Only certain size orbits can contain whole numbers of half wavelengths
        1. fits the observation of fixed energy quantities - "quanta"
   b. The Schrödinger Equation (Erwin Schrödinger)
     i. For the motion of one particle, in the along the x axis in space:

$$-\frac{h^2}{8\pi^2 m} \frac{d^2 \Psi}{dx^2} + V\Psi = E\Psi$$

     ii. Solution of the equation has demonstrated that E (energy) must occur in integer multiples
     iii. Your book has done you the favor of greatly simplifying this and presents the general equation:

$$\hat{H}\Psi = E\Psi$$

       $\hat{H}$=a set of mathematical functions called an "operator"
       Ψ=a wave function. Specific wave functions are called "orbitals"
     iv. Orbitals
       1. Orbitals are not circular orbits for electron
       2. Orbitals are areas of probability for locating electrons

c. Heisenberg Uncertainty Principle (Werner Heisenberg)
    i. "There is a fundamental limitation on how precisely we can know both the position and momentum of a particle at a given time"

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

Δx = uncertainty in the particle's position
$\Delta(mv)$ = uncertainty in the particle's momentum

    ii. The more accurately we know the position of any particle, the less accurately we can know its momentum, and vice-versa

d. Physical Meaning of a Wave Function
    i. Square of the absolute value of the wave function gives a probability distribution.

$$\left| \Psi \right|^2$$

    ii. Electron density map indicates the most probable distance from the nucleus
    iii. Wave functions and probability maps do not describe:
        1. How an electron arrived at its location
        2. Where the electron will go next
        3. When the electron will be in a particular location

7. Quantum Numbers
    a. Principal Quantum Number (n)
        i. Integral values: 1, 2, 3, ….
        ii. Indicates probable distance from the nucleus
            1. Higher numbers = greater distance
            2. Greater distance = less tightly bound = higher energy
    b. Angular Momentum Quantum (*l*)
        (this was called the "orbital quantum number" in your general chem book)
        i. Integral values from 0 to n - 1 for each principal quantum number n
        ii. Indicates the shape of the atomic orbitals

Table Angular momentum quantum numbers and corresponding atomic orbital numbers					
Value of *l*	0	1	2	3	4
Letter used	s	p	d	f	g

    c. Magnetic Quantum Number (m_l)
        i. Integral values from *l* to -*l*, including zero
        ii. Magnetic quantum number relates to the orientation of the orbital in space relative to the other orbitals
    d. Spin Quantum Number
        i. Covered in section 7.8

Table Quantum numbers for the first four levels of orbitals in the hydrogen atom				
n	**l**	**Orbital designation**	**m$_l$**	**# of orbitals**
1	0	1s	0	1

2	0	2s	0	1
	1	2p	-1, 0, 1	3

3	0	3s	0	1
	1	3p	-1, 0, 1	3
	2	3d	-2, -1, 0, 1, 2	5

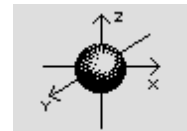|				
4	0	4s	0	1
	1	4p	-1, 0, 1	3
	2	4d	-2, -1, 0, 1, 2	5
	3	4f	-3, -2, -1, 0, 1, 2, 3	7

8. Orbital Shapes and Energies
   a. Size of orbitals
      i. Defined as the surface that contains 90% of the total electron probability
      ii. Orbitals of the same shape (s, for instance) grow larger as n increases
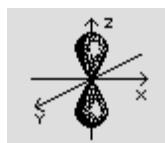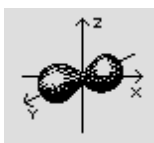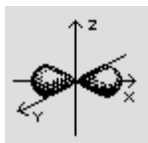   b. s Orbitals
      i. Spherical shape
      ii. Nodes (s orbitals of n=2 or greater)
         1. Internal regions of zero probability

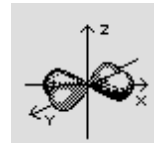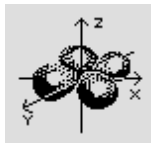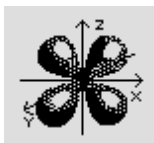   c. p Orbitals
      i. Two lobes each
      ii. Occur in levels n=2 and greater
      iii. Each orbital lies along an axis (2p$_x$, 2p$_y$, 2p$_z$)
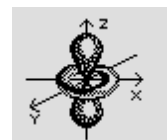

   d. d Orbitals
      i. Occur in levels n=3 and greater
      ii. Two fundamental shapes
         1. Four orbitals with four lobes each, centered in the plane indicated in the orbital label
            d$_{xz}$ d$_{yz}$ d$_{xy}$ d$_{x^2-y^2}$

         2. Fifth orbital is uniquely shaped - two lobes along the z axis and a belt centered in the xy plane
            dz^2

e. f Orbitals
   i. Occur in levels n=4 and greater
   ii. Highly complex shapes
   iii. Not involved in bonding in most compounds
f. Orbital Energies
   i. All orbitals with the same value of n have the same energy
      1. "degenerate orbitals" (hydrogen only!)
   ii. The lowest energy state is called the "ground state"
   iii. When the atom absorbs energy, electrons may move to higher energy orbitals - "excited state"

9. Electron Spin and the Pauli Principle
   a. Electronic Spin Quantum Number
      i. An orbital can hold only two electrons, and they must have opposite spins
      ii. Spin can have two values, +1/2 and -1/2
   b. Pauli Exclusion Principle (Wolfgang Pauli)
      i. "In a given atom no two electrons can have the same set of four quantum numbers"

10. Polyelectronic Atoms
    a. Internal Atomic energies
       i. Kinetic energy of moving electrons
       ii. Potential energy of attraction between nucleus and electrons
       iii. Potential energy of repulsion between electrons
    b. The Electron Correlation Problem
       i. Electron pathways are not known, so electron replusive forces cannot be calculated exactly
       ii. We approximate the average repulsions of all other electrons
    c. Screening or Shielding
       i. Electrons are attracted to the nucleus
       ii. Electrons are repulsed by other electrons
       iii. Electrons would be bound more tightly if other electrons weren't present
    d. Variations in energy within the same quantum level
       i. Atoms other than hydrogen have variations in energy for orbitals having the same principal quantum number
       ii. Electrons fill orbitals of the same n value in preferential order
          $$E_{ns} < E_{np} < E_{nd} < E_{nf}$$
       iii. Electron density profiles show that s electrons penetrate to the nucleus more than other orbital types
          1. Closer proximity to the nucleus = lower energy

11. The History of the Periodic Table
    No notes. Read this section. The periodic table is as useful for predicting properties of undiscovered elements today as it was in Mendeleev's time

12. The Aufbau Principle and the Periodic Table
    a. The Aufbau Principle
       i. "As protons are added one by one to the nucleus to build up elements, electrons are similarly added to these hydrogen-like orbitals
    b. Hund's Rule
       i. "The lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerate orbitals

***Note: We will review configuration and orbital notation in class. This was covered extensively in General Chem, and will come back to you quickly

c. Period Table Vocabulary
    i. Valence Electrons
        1. Electrons in the outermost principal quantum level of an atom
        2. Elements in the same group (vertical column) have the same valence electron configuration
    ii. Transition metals
        1. What we have called the "d" block
    iii. Lanthanide and Actinide Series
        1. The sets of 14 elements following lanthanum and actinium
        2. What we have called the "f" block\
    iv. Main-group, or Representative Elements
        1. Groups 1A through 8A
        2. Configurations are consistent
    v. Metalloids (semi-metals)
        1. Found along the border between metals and nonmetals
        2. Exhibit properties of metals and nonmetals

13. Periodic Trends in Atomic Properties
    a. Ionization Energy - the energy required to remove an electron from an atom
        i. Ionization energy increases for successive electrons
        ii. Ionization energy tends to increase across a period
            1. electrons in the same quantum level do not shield as effectively as electrons in inner levels
            2. irregularities at half filled and filled sublevels due to extra repulsion of electrons paired in orbitals, making them easier to remove
        iii. Ionization energy decreases with increasing atomic number within a group
   1. electrons farther from the nucleus are easier to remove
    b. Electron Affinity - the energy change associated with the addition of an electron
        i. Affinity tends to increase across a period
        ii. Affinity tends to decrease as you go down in a period
            1. electrons farther from the nucleus experience less nuclear attraction
            2. Some irregularities due to repulsive forces in the relatively small p orbitals
    c. Atomic Radius
        i. Determination of radius
            1. half of the distance between radii in a covalently bonded diatomic molecule - "covalent atomic radii"
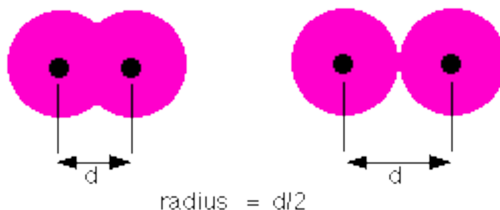
radius = d/2

        ii. Periodic Trends
            1. Radius decreases across a period (1) increased effective nuclear charge due to decreased shielding
            2. Radius increases down a group
                (1) addition of principal quantum levels

14. The Properties of a Group: the Alkali Metals
    a. Easily lose valence electron (Reducing agents)
        i. React with halogens to form salts
        ii. React violently with water
            1. Lithium is not the most reactive because the heat of reaction is insufficient to melt lithium and expose all of its surface area
    b. Large hydration energy
        i. Positive ionic charge makes ions attractive to polar water molecules
    c. Radius and Ionization energy follow expected trends

    See textbook for other properties of the Alkali metal group