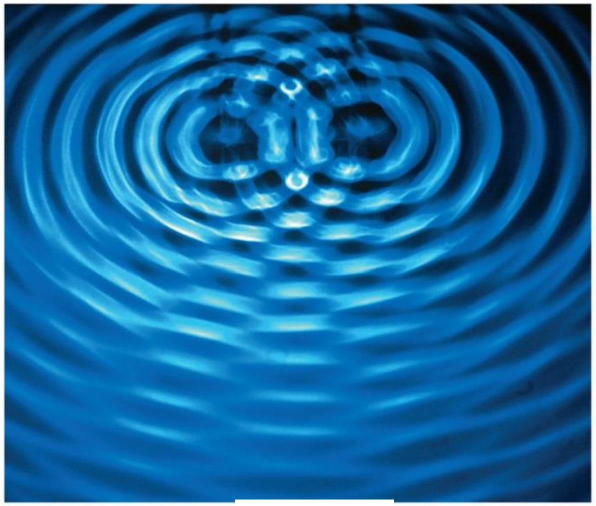
Petrucci • Harwood • Herring • Madura

Ninth Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 8: Electrons in Atoms

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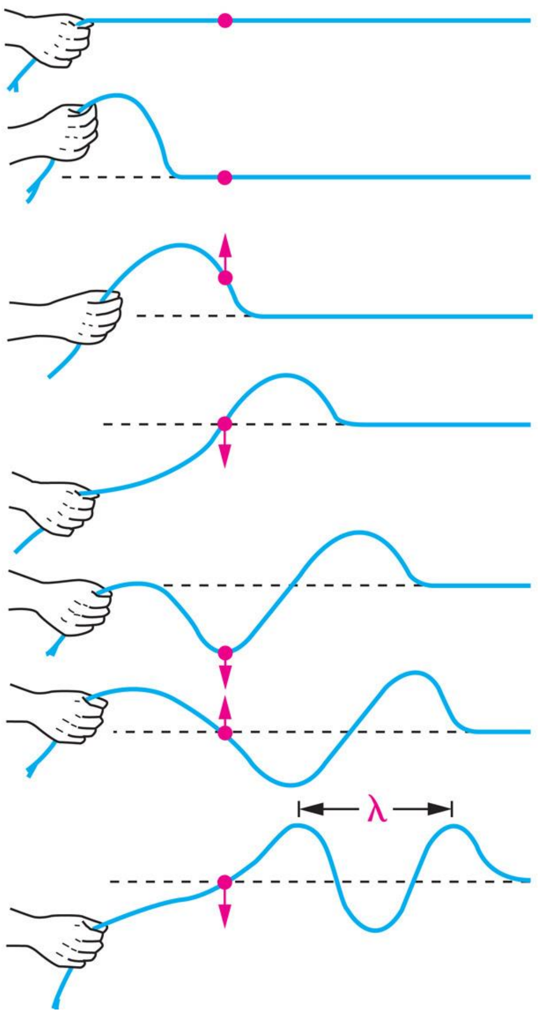
8-1 Electromagnetic Radiation

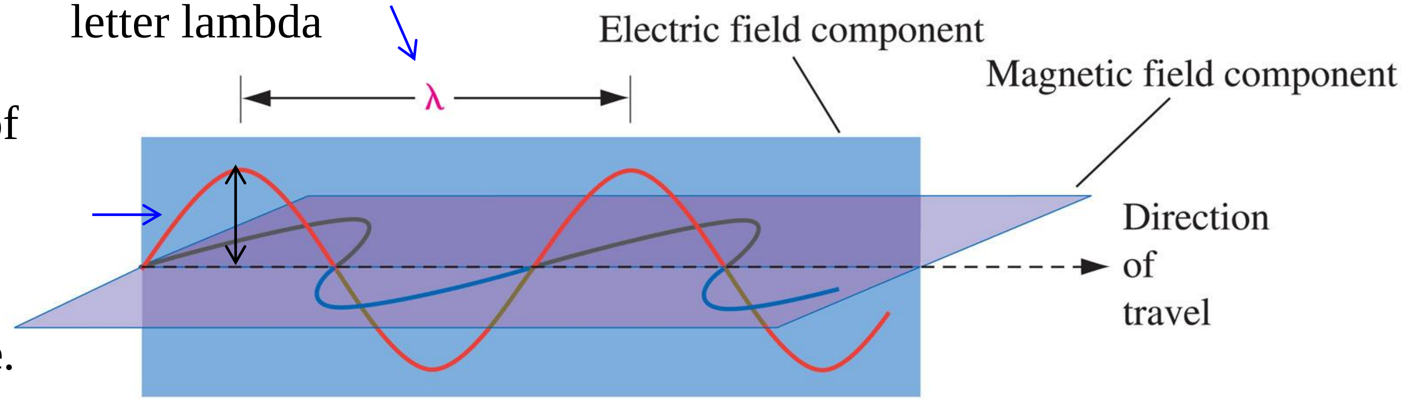
- **Electromagnetic radiation** is a form of energy transmission in which electric and magnetic fields are propagated as waves through empty space (a vacuum) or through a medium, such as glass.
- A wave transmits energy.



Electromagnetic Radiation

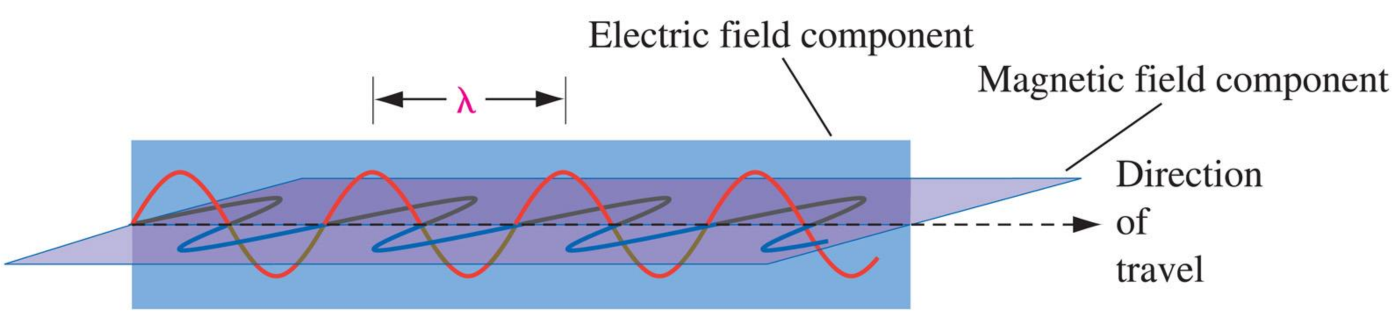
The distance between the tops of two successive crests (or the bottoms of two troughs) is called the **wavelength,** designated by the Greek letter lambda

The maximum height of the wave above the center line or the maximum depth below is called the **amplitude**.



(a)

Low ν



(b)

High ν

Frequency, Wavelength and Velocity

- Frequency (ν) is the number of crests or troughs that pass through a given point per unit of time. Frequency has the unit time^{-1} , usually s^{-1} or Hertz—Hz.
- Wavelength (λ) in meters—m.
    - cm μm nm Å pm

      (10^{-2} m) (10^{-6} m) (10^{-9} m) (10^{-10} m) (10^{-12} m)
- Velocity (c)—A distinctive feature of electromagnetic radiation is its *constant* speed of 2.997925×10^{8} m s^{-1} in a vacuum, often referred to as the **speed of light**.
- The speed of light is represented by the symbol *c*, and the relationship between this speed and the frequency and wavelength of electromagnetic radiation is

$$c = \lambda\nu \qquad \lambda = c/\nu \qquad \nu = c/\lambda$$

Electromagnetic Spectrum

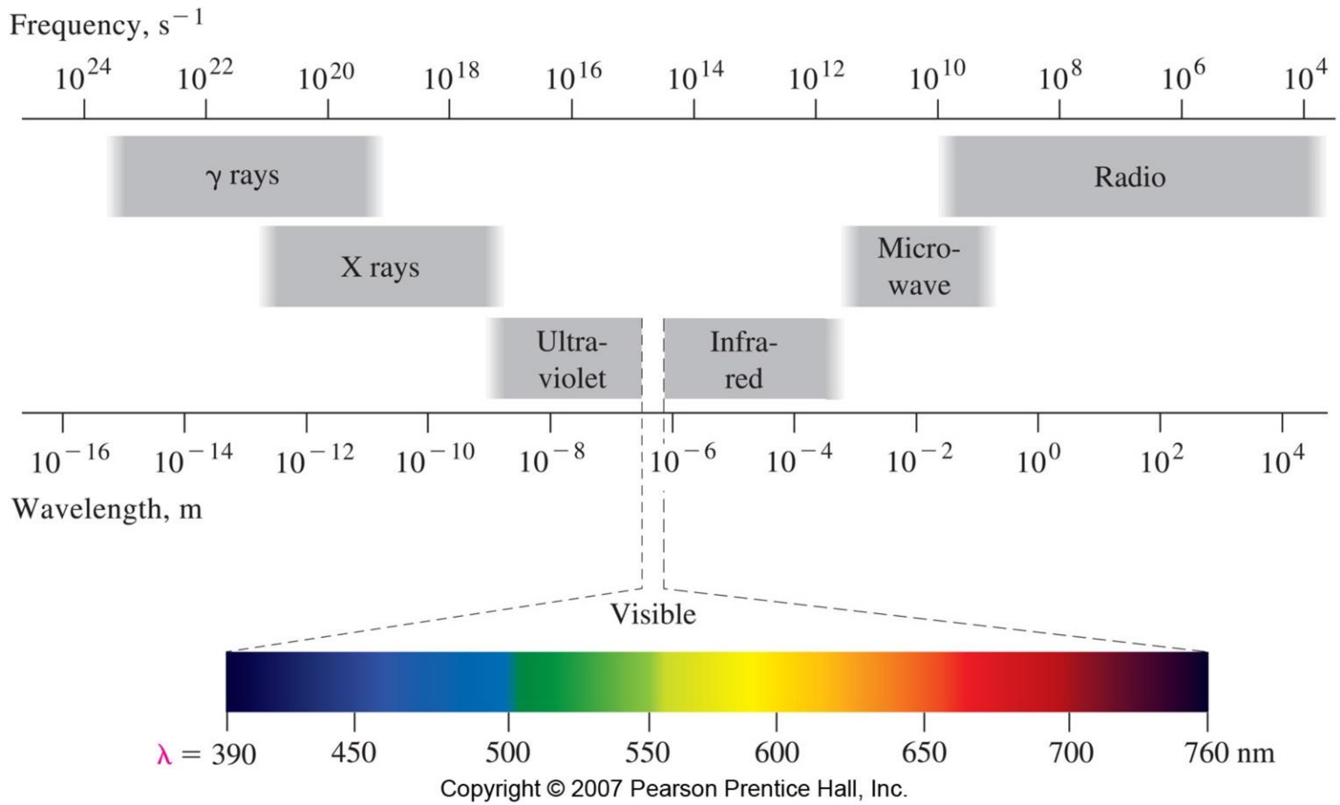


Figure indicates the wide range of possible wavelengths and frequencies for some common types of electromagnetic radiation and illustrates this important fact: The wavelength of electromagnetic radiation is shorter for high frequencies and longer for low frequencies.

EXAMPLE 8-1

Most of the light from a sodium vapor lamp has a wavelength of 589 nm. What is the frequency of this radiation?

Change the units of λ from nanometers to meters.

$$\lambda = 589 \text{ nm} \times \frac{1 \times 10^{-9} \text{ m}}{1 \text{ nm}} = 5.89 \times 10^{-7} \text{ m}$$

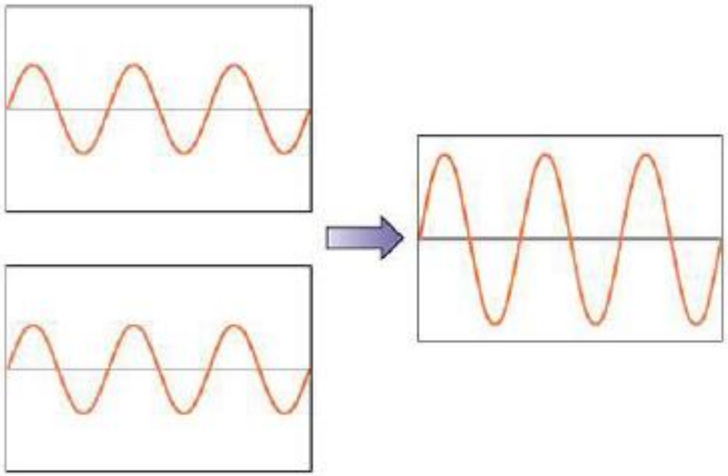
$$c = 2.998 \times 10^{8} \text{ m s}^{-1}$$

$$\nu = ?$$

Rearrange equation (8.1) to the form $\nu = c/\lambda$, and solve for ν.

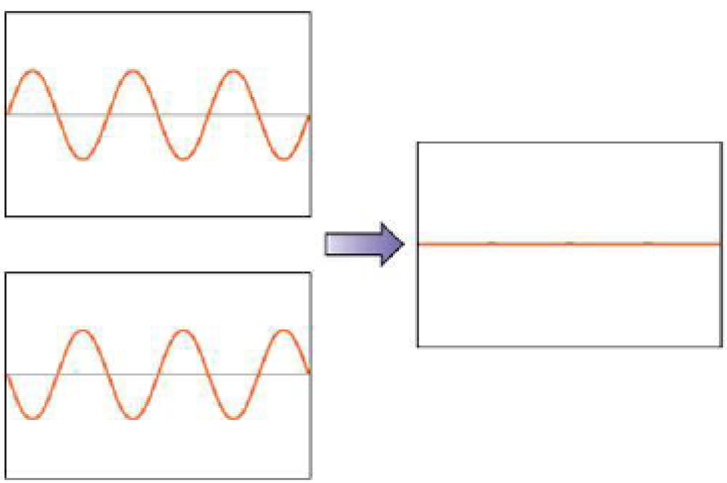
$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8} \text{ m s}^{-1}}{5.89 \times 10^{-7} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1} = 5.09 \times 10^{14} \text{ Hz}$$

Constructive and Destructive Interference



(a)

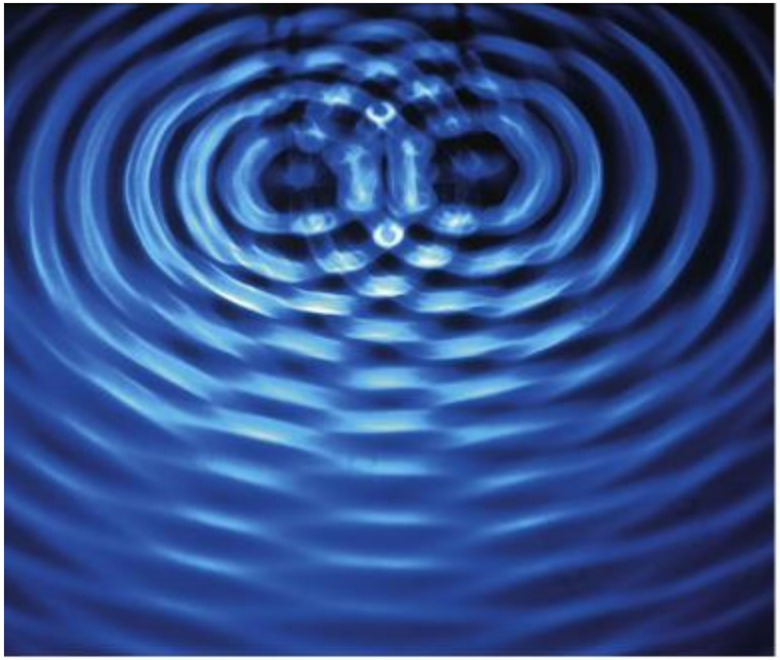
In the intensifying interference, the crests and troughs of both waves coincide (in phase) with the result that the crests and troughs of the two waves are added together.



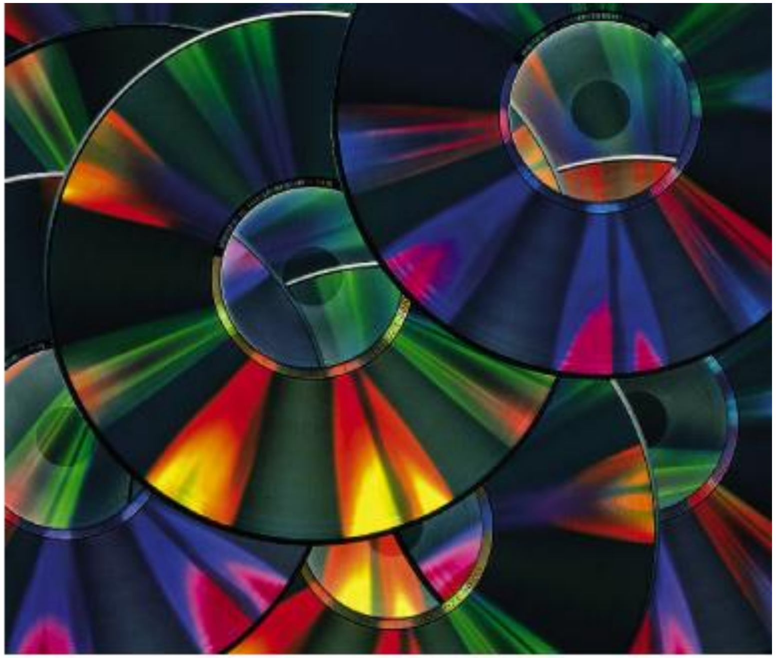
(b)

In destructive interference, the crests and troughs of the two waves do not coincide (not in phase) and the waves are extinguished.

Examples of Interference

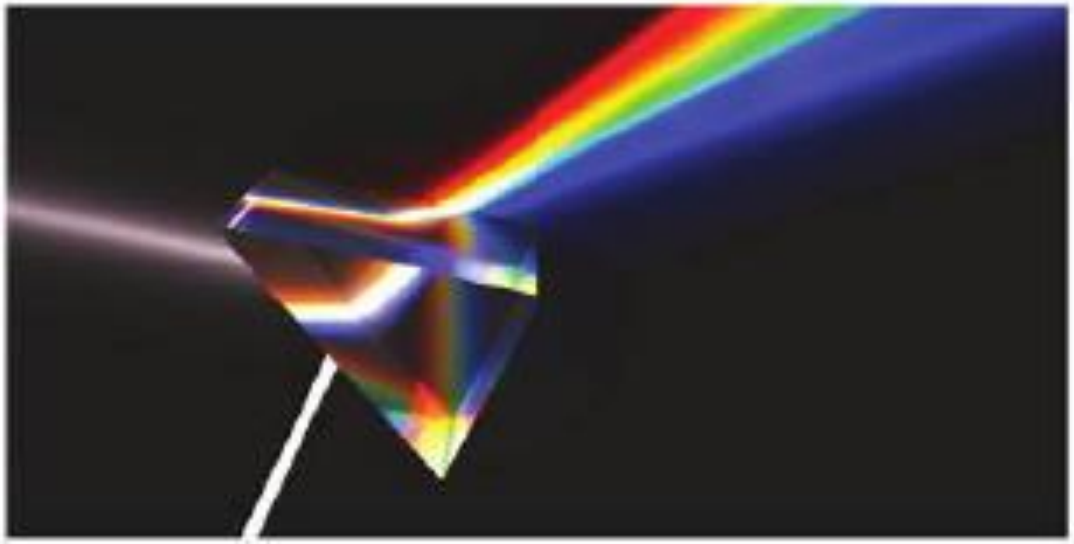


(a)



(b)

Refraction of Light



The speed of light is lower in any medium than it is in a vacuum. Also, the speed is different in different media. As a consequence, light is refracted, or bent, when it passes from one medium to another. When a beam of white light is passed through a transparent medium, the wavelength components are refracted differently. The light is dispersed into a band of colors, a *spectrum*. In figure a beam of white light (for example, sunlight) is dispersed by a glass prism into a continuous band of colors corresponding to all the wavelength components from red to violet. This is the **visible spectrum** shown in figure and also seen in a rainbow, where the medium that disperses the sunlight is droplets of water.

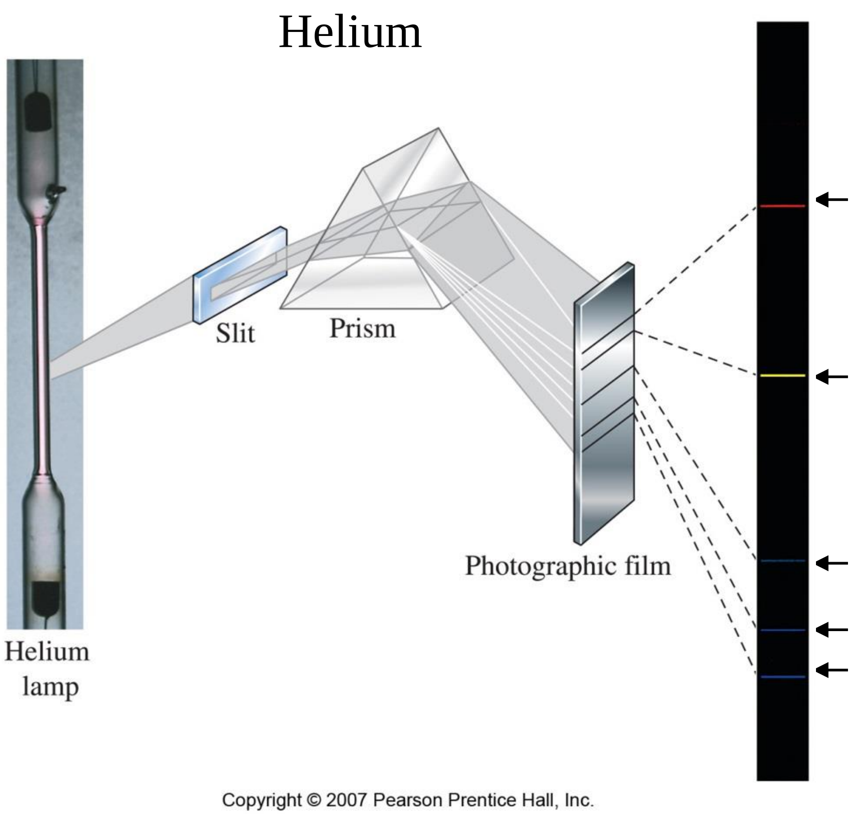
8-2 Atomic Spectra

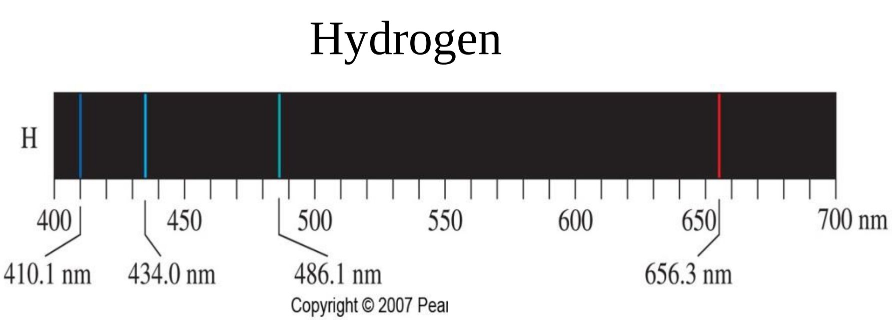
(a) (b) (c) (d) (e)

Sources for light emission

Light emitted by an electric discharge through **(a)** hydrogen gas and **(b)** neon gas. Light emitted when compounds of the alkali metals are excited in the gas flames: **(c)** lithium, **(d)** sodium, and **(e)** potassium.

Atomic Spectra





The visible spectrum is said to be a continuous spectrum because the light being diffracted consists of many wavelength components.

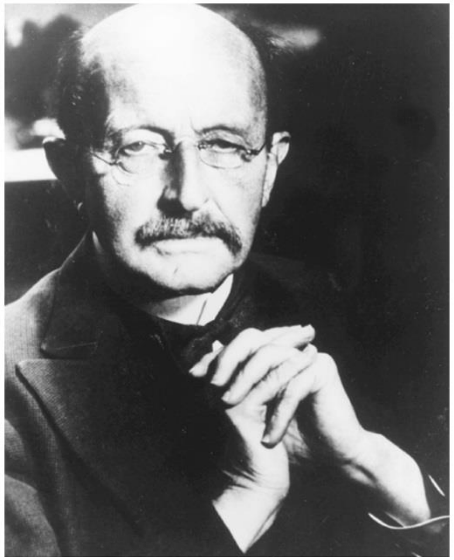
If the source of a spectrum produces light having only a relatively small number of wavelength components, then a discontinuous spectrum is observed.

For example, if the light source is an electric discharge passing through a gas, only certain colors are seen in the spectrum. Or, if the light source is a gas flame into which an ionic compound has been introduced, the flame may acquire a distinctive color indicative of the metal ion present.

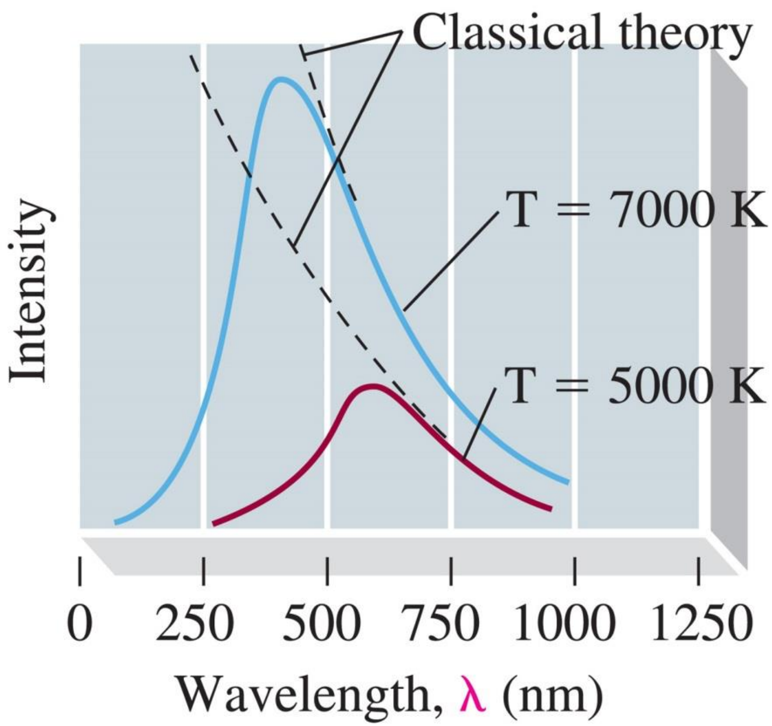
In each of these cases, the emitted light produces a spectrum consisting of only a limited number of discrete wavelength components, observed as colored lines with dark spaces between them. These discontinuous spectra are called **atomic, or line, spectra.**

8-3 Quantum Theory

Blackbody Radiation:



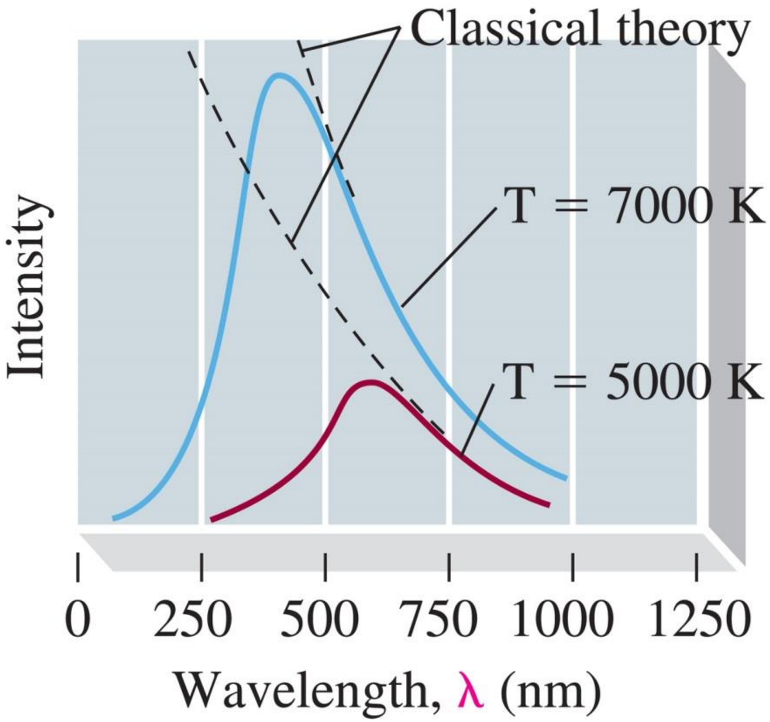
Max Planck, 1900



Energy, like matter, is discontinuous.

$$\epsilon = h\nu$$

8-3 Quantum Theory



- We are aware that hot objects emit light of different colors, from the dull red of an electric-stove heating element to the bright white of a light bulb filament. Light emitted by a hot radiating object can be dispersed by a prism to produce a continuous color spectrum.

As seen in the figure, the light intensity varies smoothly with wavelength, peaking at a wavelength fixed by the source temperature. As with atomic spectra, classical physics could not provide a complete explanation of light emission by heated solids, a process known as blackbody radiation. Classical theory predicts that the intensity of the radiation emitted would increase indefinitely, as indicated by the dashed lines in Figure.

8-3 Quantum Theory

- In 1900, to explain the fact that the intensity does not increase indefinitely, Max Planck (1858 -1947) made a revolutionary proposal: *Energy, like matter, is discontinuous*.
- Here, then, is the essential difference between the classical physics of Planck s time and the new quantum theory that he proposed: Classical physics places no limitations on the amount of energy a system may possess, whereas quantum theory limits this energy to a discrete set of specific values.
- The *difference* between any two allowed energies of a system also has a specific value, called a **quantum** of energy.
- This means that when the energy increases from one allowed value to another, it increases by a tiny jump, or quantum.
- Here is a way of thinking about a quantum of energy: It bears a similar relationship to the total energy of a system as a single atom does to an entire sample of matter.

- Planck's postulate can be phrased in this: The energy of a quantum of electromagnetic radiation is proportional to the frequency of the radiation the higher the frequency, the greater the energy. This is summarized by what we now call Planck's equation.

$$E = h\nu$$

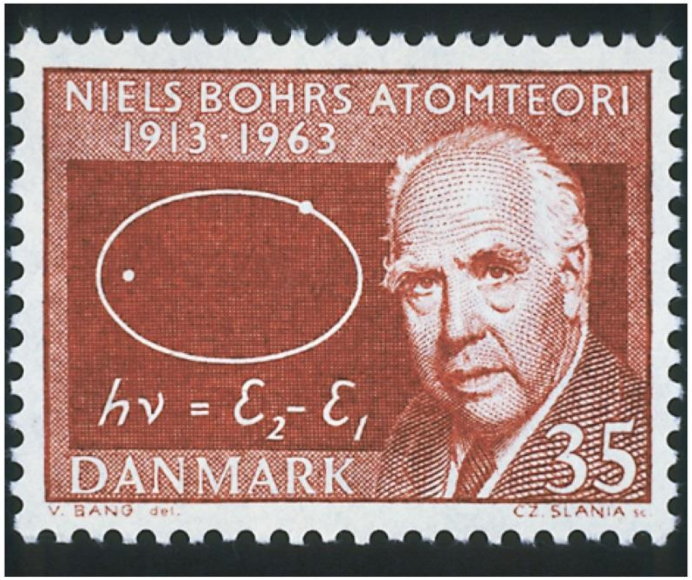
The term ***h*** is called ***Planck's constant***, equal to 6.626×10^{-34} Js.

The Photoelectric Effect

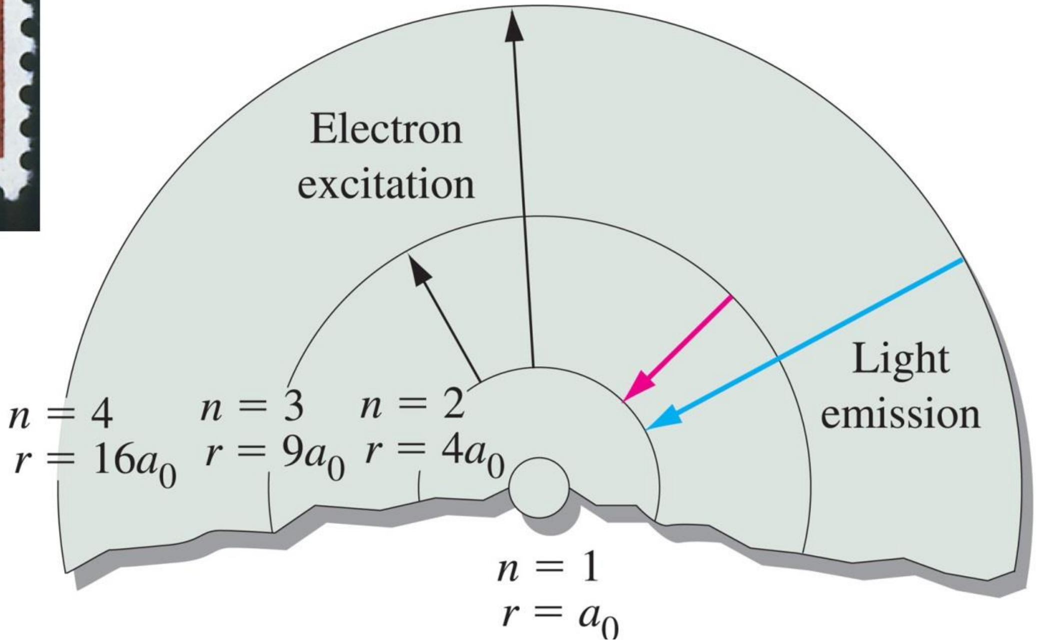
In 1888, H. Herz discovered that when light hits the surface of certain metals, there is a discharge of electrons from the metal. This phenomenon is called the photoelectric effect, and the notable phenomena in this phenomenon are:

- Electron emission occurs only when the frequency of the incident light rises above a certain threshold $(\nu > \nu_o)$
- When the above condition is met, the e- number emitted depends on the intensity of the incident light (e- $\approx$ I).
- The kinetic energy of the emitted electrons depends on the frequency of the light $(ek \approx \nu)$

8-4 The Bohr Atom



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



$R_H = 2.179 \times 10^{-18}$ J

8-4 The Bohr Atom

1. The electron moves in a circular orbit around the nucleus, as described by classical physics.
2. The electron can be found in a fixed set of allowed orbitals, and this is called the "stationary state". Permissible orbitals are orbitals in which the electron receives specific values from certain properties. No matter how long an electron stays in a certain orbital, it does not emit energy and its energy remains constant. The property of the electron that leads to a certain set of orbitals and can only take permissible values is called "angular momentum".
3. The electron can only move from one allowed orbit to another allowed orbit. In this type of transition, an energy packet (quanta) with a certain value, which can be calculated with the Planck equation, is received or given.

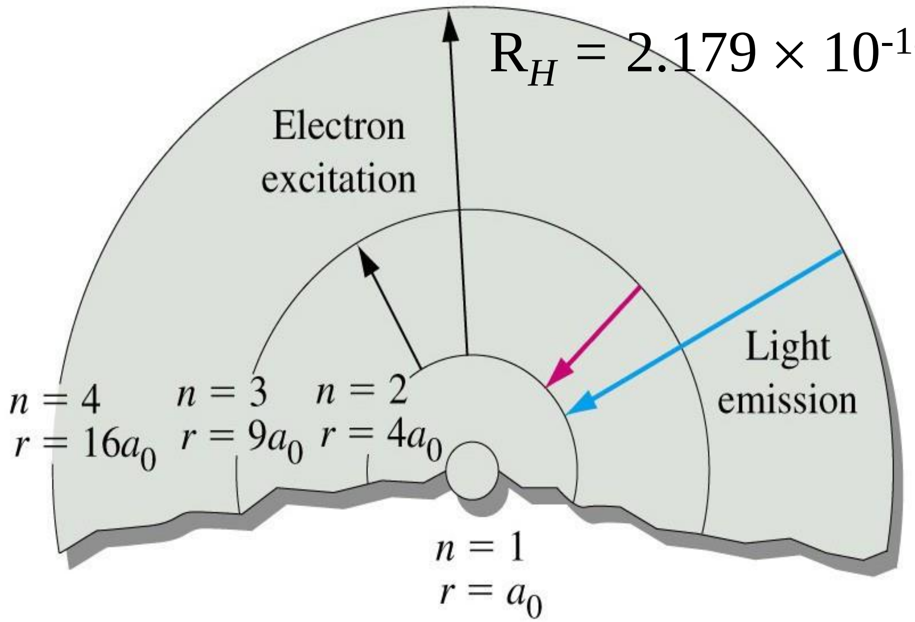
8-4 The Bohr Atom

- The nucleus is in the center and the electron is in one of the independent orbitals. n = 1,2,…
- When the atom is excited, the electron moves to higher number orbitals as indicated by the black arrows. Light is emitted as the electron returns to a lower number orbital.
- The Bohr theory predicts the radii of the allowed orbits in a hydrogen atom.

$r_n = n^2 a_0$, where $n = 1, 2, 3, \ldots$ and $a_0 = 53$ pm (0.53 Å)

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

$R_H = 2.179 \times 10^{-18}$ J



Bohr model of the hydrogen atom

- The theory also allows us to calculate the energy in these orbits:

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

8-4 The Bohr Atom

- Normally, the electron in the hydrogen atom is in the orbit closest to the nucleus (n=1). This is the lowest allowable energy level, the "ground state".

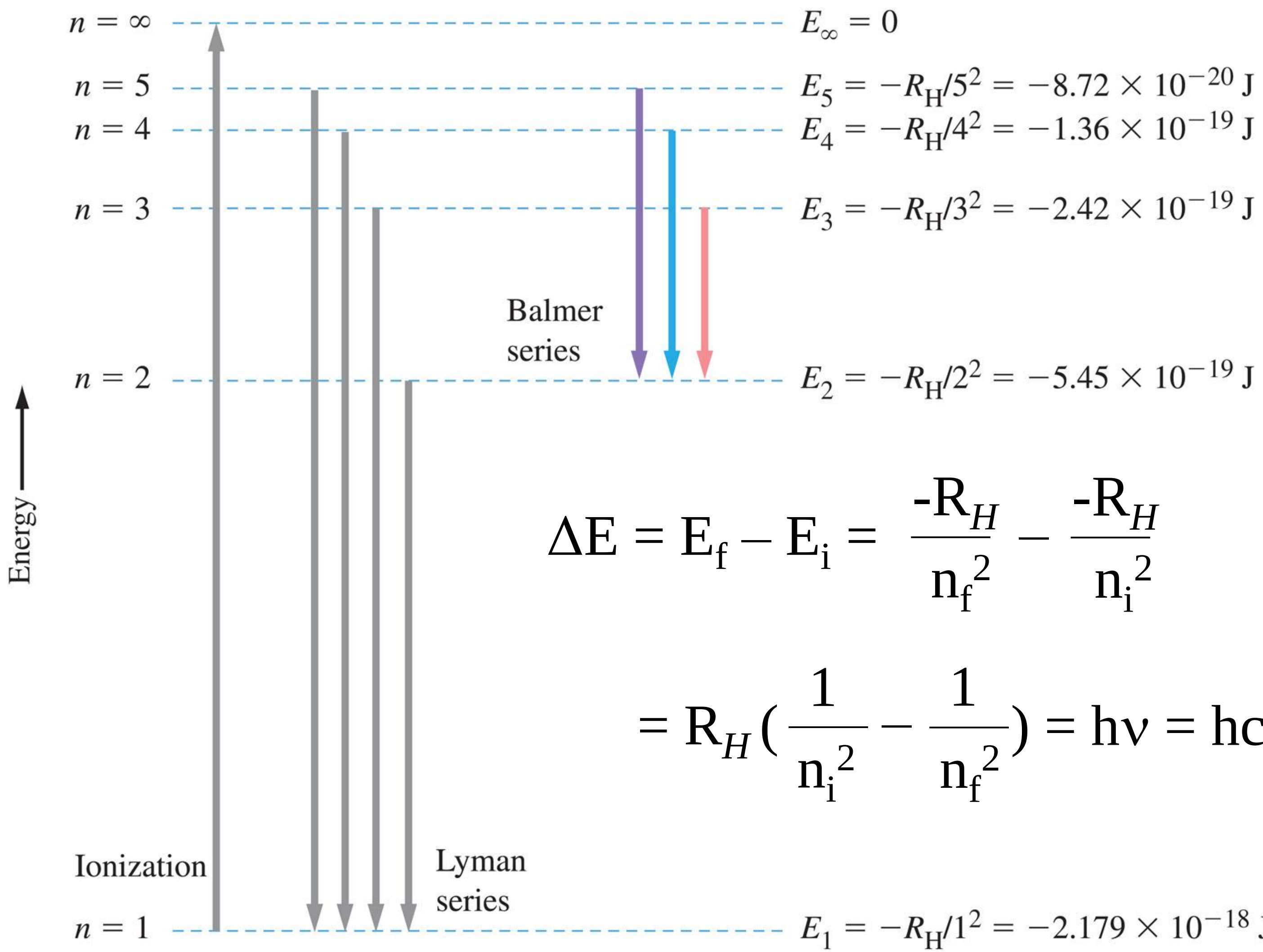
- When the electron gains an energy quantum, it moves to a higher energy level (n=2,3,..) and the hydrogen atom becomes "excited".

- When the electron lands in an orbit close to the nucleus, the energy is emitted as much as the difference between the two energy levels.

- The energy of the photon, E_{photon} , either absorbed or emitted, is equal to the magnitude of this energy difference. Because $E_{photon}=h\nu$ and $E_{photon}= |\Delta E|$ we can write:

$$\boxed{|\Delta E| = E_{\text{photon}} = h\nu}$$

Energy-Level Diagram



$$\Delta E = E_f - E_i = \frac{-R_H}{n_f^2} - \frac{-R_H}{n_i^2}$$

$$= R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = h\nu = hc/\lambda$$

Energy-Level Diagram

- If the electron gains an energy of 2,179 x 10^{-18} J, it moves to the n=∞ orbital, that is, the hydrogen atom is ionized (black arrow).

- If the electron descends from a high number orbital to the n=1 orbital, it emits energy in the form of ultraviolet light, producing a spectral series called the Lyman series (gray lines).

- If the electron transition occurs in the n=2 orbital, the resulting lines will be in the Balmer series. Three of these lines are seen here (in color).

- Transitions to the n=3 orbital form spectral lines in the infrared region.

Ionization Energy of Hydrogen

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

n_f is the last energy level and n_i is the first energy level. The energy of the emitted and absorbed photon is calculated by the Planck equation. As n_f goes to infinity for hydrogen starting in the ground state:

$$h\nu = R_H\left(\frac{1}{n_i^2}\right) = R_H$$

This also works for hydrogen-like species such as He^+ and Li^{2+}.

$$h\nu = \frac{-Z^2 R_H}{n^2}$$

Z: Effective core load

EXAMPLE 8-4

Determine the wavelength of the line in the Balmer series of hydrogen corresponding to the transition from $n = 5$ to $n = 2$.

The specific data for equation (8.6) are $n_i = 5$ and $n_f = 2$.

$$\Delta E = 2.179 \times 10^{-18}\,\text{J}\left(\frac{1}{5^2} - \frac{1}{2^2}\right)$$
$$= 2.179 \times 10^{-18} \times (0.04000 - 0.25000)$$
$$= -4.576 \times 10^{-19}\,\text{J}$$

Rearranging $E_{\text{photon}} = \Delta E = h\nu$ gives the frequency

$$\nu = \frac{E_{\text{photon}}}{h} = \frac{4.576 \times 10^{-19}\,\text{J photon}^{-1}}{6.626 \times 10^{-34}\,\text{J s photon}^{-1}} = 6.906 \times 10^{14}\,\text{s}^{-1}$$

Rearranging $c = \lambda\nu$ for the wavelength gives the following result:

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\,\text{m s}^{-1}}{6.906 \times 10^{14}\,\text{s}^{-1}} = 4.341 \times 10^{-7}\,\text{m} = 434.1\,\text{nm}$$

8-5 Two Ideas Leading to a New Quantum Mechanics

- Wave-Particle Duality
  - Einstein suggested particle-like properties of light could explain the photoelectric effect.
  - Diffraction patterns suggest photons are wave-like.
- deBroglie, 1924
  - Small particles of matter may at times display wavelike properties.

Louis de Broglie
Nobel Prize 1918

de Broglie and Matter Waves

$$E = mc^2$$

$$h\nu = mc^2$$

$$h\nu/c = mc = p$$

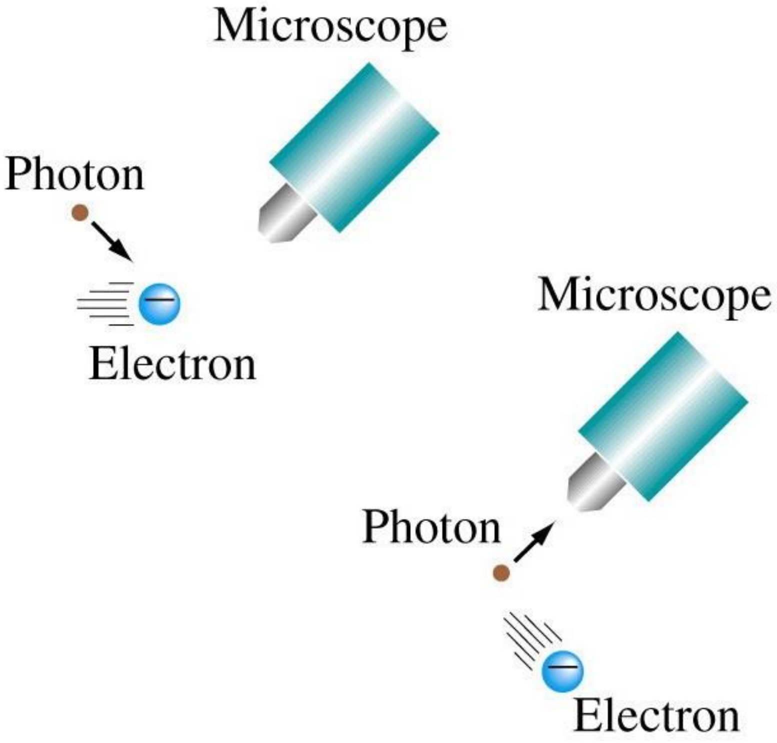
$$p = h/\lambda$$

$$\lambda = h/p = h/mu$$

The Uncertainty Principle

- The German physicist Werner Heisenberg proposed that because subatomic (really tiny) particles have both dual wavelike and particle-like natures, it's impossible to precisely calculate both their locations and momentums. This is called the **Heisenberg uncertainty principle.**

$$\Delta x \, \Delta p \geq \frac{h}{4\pi}$$



8-7 Quantum Numbers

- Each electron can be described by using four different numbers, called ***quantum numbers***. These numbers are kind of like an electron's address. I'll now describe each of these four numbers:

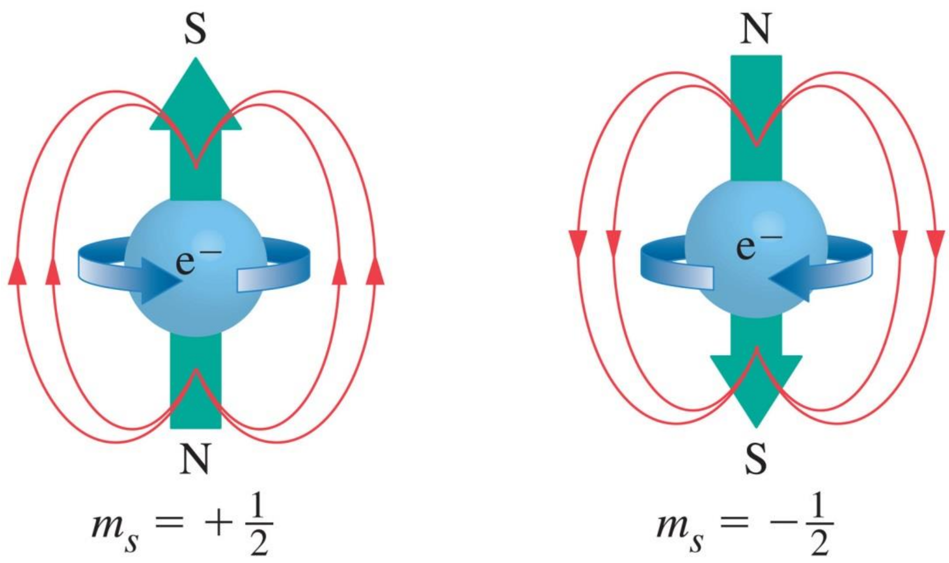
8-7 Quantum Numbers

- *n* (the principle quantum #): This number can be any integer 1, 2, 3, 4, etc., and describes how far an electron is away from the nucleus.
- ***l*** (the angular momentum quantum #): This number describes what *kind* of orbital (*s*, *p*, *d*, or *f*) the electron is in. An electron in an *s* orbital has an ***l*** value of 0. An electron in a *p* orbital has an ***l*** value of 1. An electron in a *d* orbital has an ***l*** value of 2, and an electron in an *f* orbital has an ***l*** value of 3.

Value of *l*	0	1	2	3
Letter used	*s*	*p*	*d*	*f*

8-7 Quantum Numbers

- m_l (the magnetic quantum #): This number can be any integer from –*l* to +*l*, including zero. The magnetic quantum number, m_l, describes the orbital's three-dimensional orientation in space. For example, you should remember from our previous slide that that ***l*** quantum number for p orbitals is 1. This means that the m_l number for ***p*** orbitals can be –1, 0, or +1.
- m_s (the spin #): The spin number is the last quantum number and is equal to ±½. That is, for any two electrons occupying the same orbital, one is assigned a +½ spin and the other a –½ spin.



8-7 Quantum Numbers

In summary, then, there are four different ***quantum numbers***, which we can assign to electrons, and which function kind of like an electron's address:

1. $\boldsymbol{n}$ = 1, 2, 3, 4, etc. (electron's distance from the nucleus)
2. $\boldsymbol{l}$ = 0 (*s* orbitals), 1 (*p* orbitals), 2 (*d* orbitals), 3 (*f* orbitals)
3. $\boldsymbol{m_l}$ = all integer values from $-l$ to $+l$, including 0 (describes the orbital's orientation)
4. $\boldsymbol{m_s}$ = ±1/2 (electron's spin)

Principle Shells and Subshells

- Principle electronic shell, $n = 1, 2, 3\ldots$
- Angular momentum quantum number,
  $\ell = 0, 1, 2\ldots(n-1)$

$\ell = 0$, s

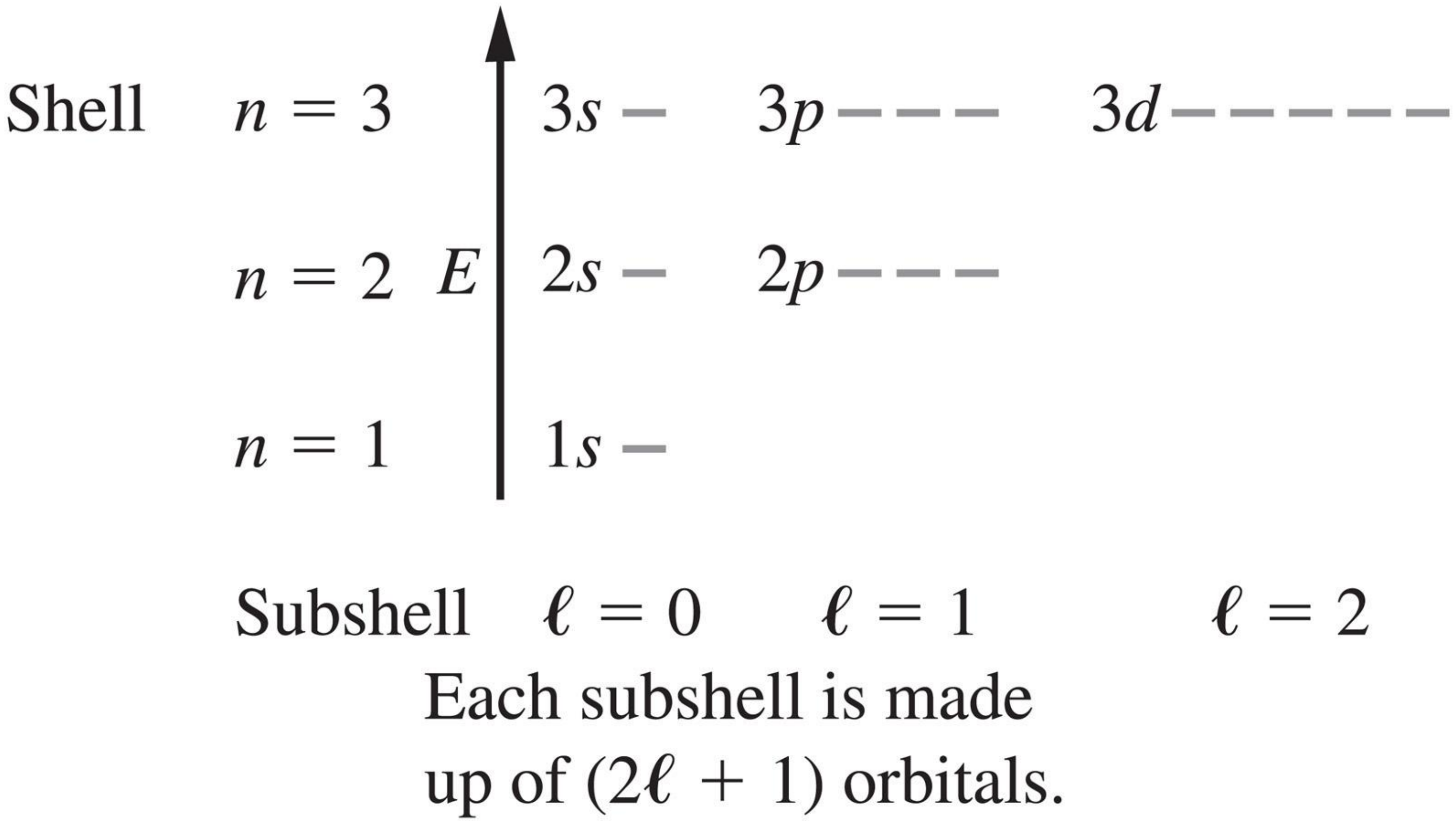
$\ell = 1$, p

$\ell = 2$, d

$\ell = 3$, f

- Magnetic quantum number,
  $m_l = -\ell\ldots-2, -1, 0, 1, 2\ldots+\ell$

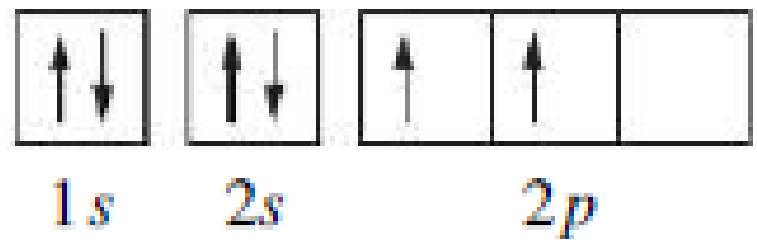
Orbital Energies



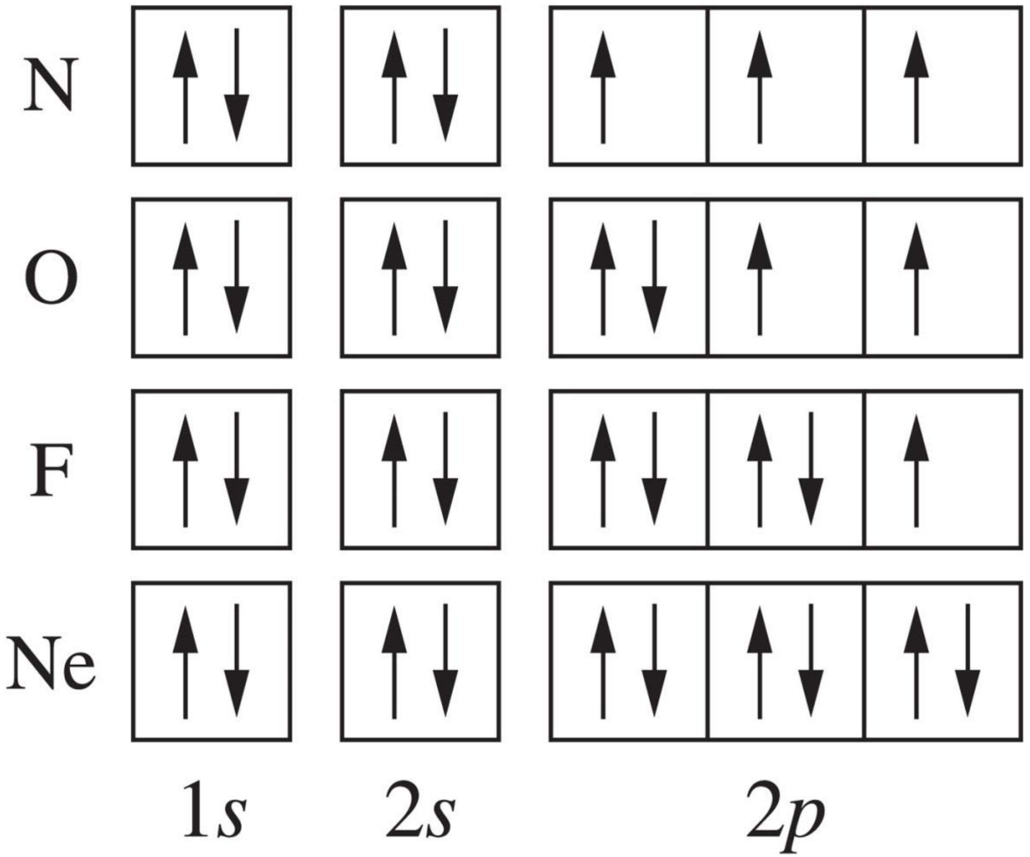
8-11 Electron Configurations

- Aufbau process.
  - Build up and minimize energy.
- Pauli exclusion principle.
  - No two electrons can have all four quantum numbers alike.
- Hund's rule.
  - Degenerate orbitals are occupied singly first.

Aufbau Process and Hunds Rule

spdf notation (condensed):	C	$1s^2 2s^2 2p^2$
spdf notation (expanded):	C	$1s^2 2s^2 2p_x^1 2p_y^1$
orbital diagram:	C	

Filling p Orbitals



Filling the d Orbitals

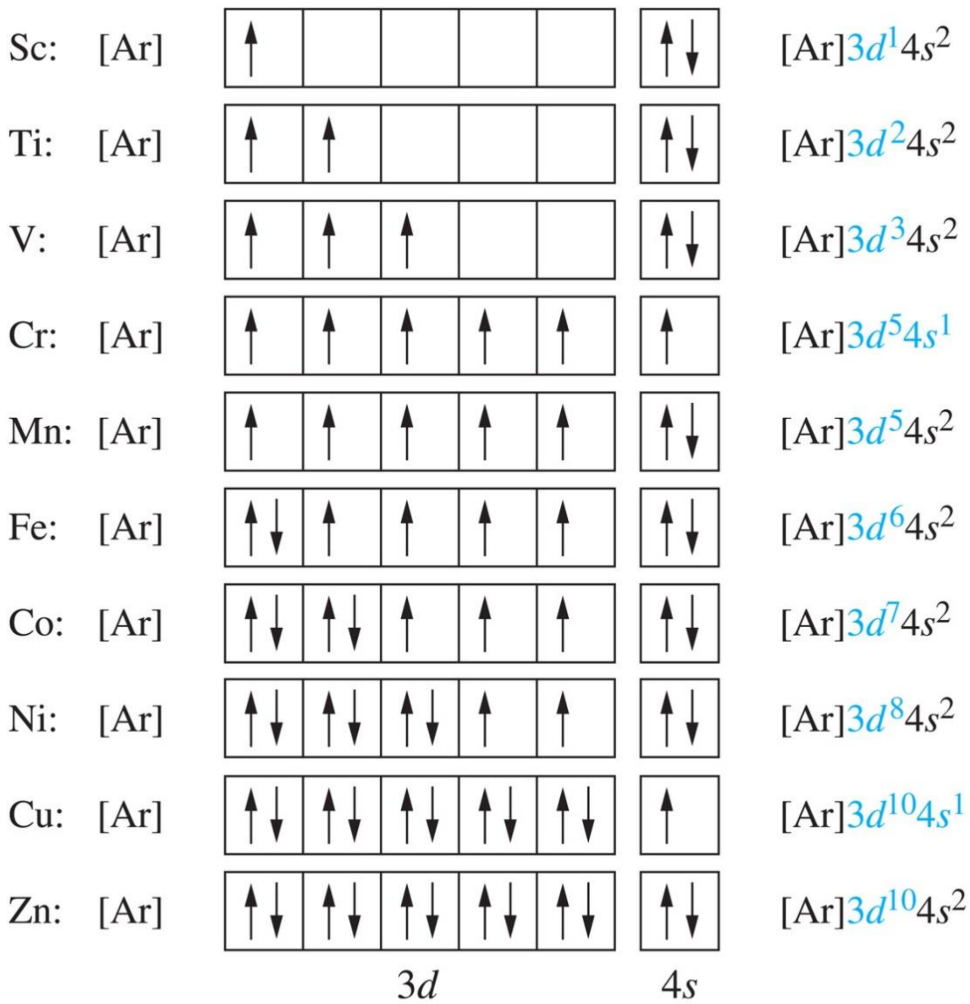


TABLE 8.2 Electron Configurations of Some Groups of Elements

Group	Element	Configuration
1	H	$1s^1$
	Li	$[He]2s^1$
	Na	$[Ne]3s^1$
	K	$[Ar]4s^1$
	Rb	$[Kr]5s^1$
	Cs	$[Xe]6s^1$
	Fr	$[Rn]7s^1$
17	F	$[He]2s^2 2p^5$
	Cl	$[Ne]3s^2 3p^5$
	Br	$[Ar]3d^{10} 4s^2 4p^5$
	I	$[Kr]4d^{10} 5s^2 5p^5$
	At	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$
18	He	$1s^2$
	Ne	$[He]2s^2 2p^6$
	Ar	$[Ne]3s^2 3p^6$
	Kr	$[Ar]3d^{10} 4s^2 4p^6$
	Xe	$[Kr]4d^{10} 5s^2 5p^6$
	Rn	$[Xe]4f^{14} 5d^{10} 6s^2 6p^6$

8-12 Electron Configurations and the Periodic Table