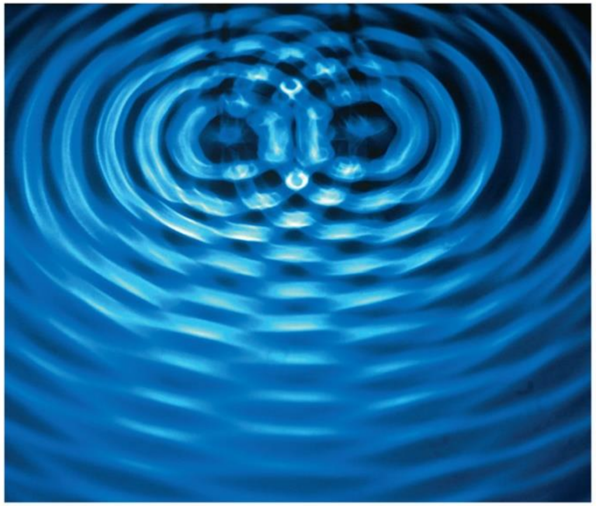
GENERAL CHEMISTRY I



Chapter 6: Electronic Structure of Atoms

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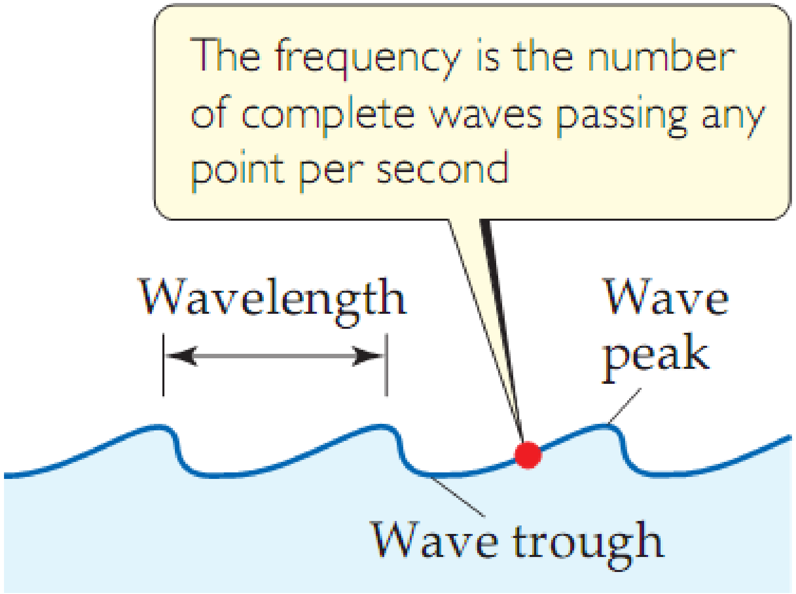
6-1 The Wave Nature of Light

A wave transmits energy.



λ: wavelength

υ: wave frequency

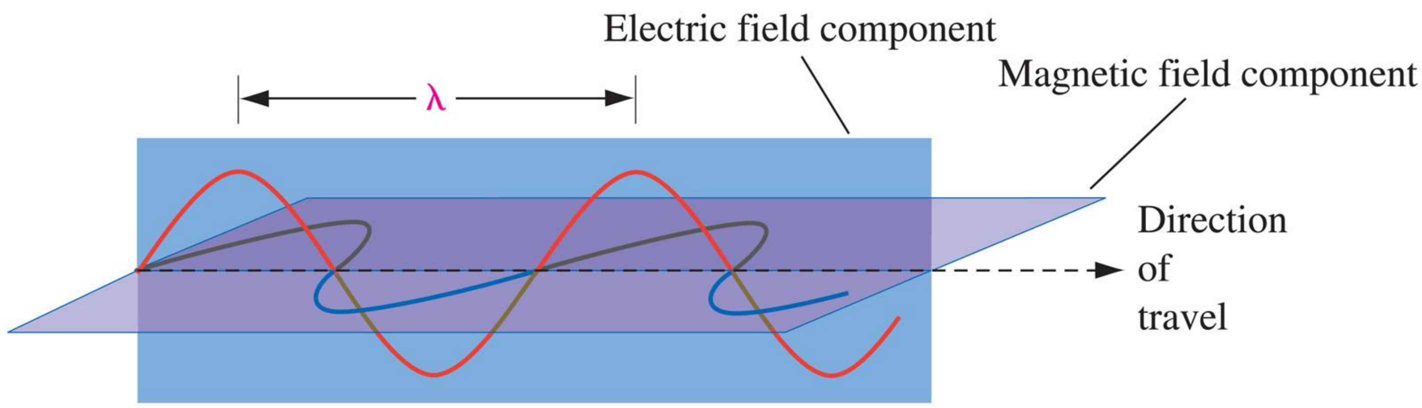
c: velocity

$c = \lambda \upsilon$

Electromagnetic Radiation

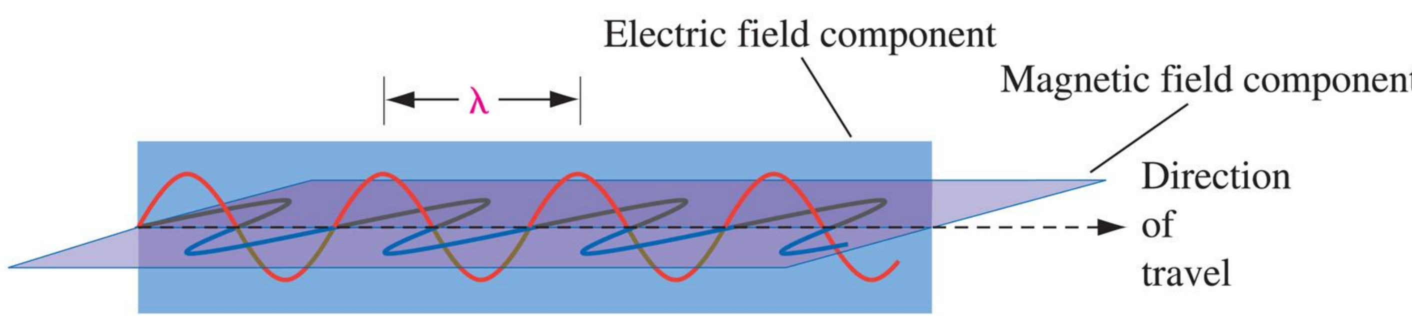
- Electric and magnetic fields propagate as waves through empty space or through a medium.

Low ν



(a)

High ν



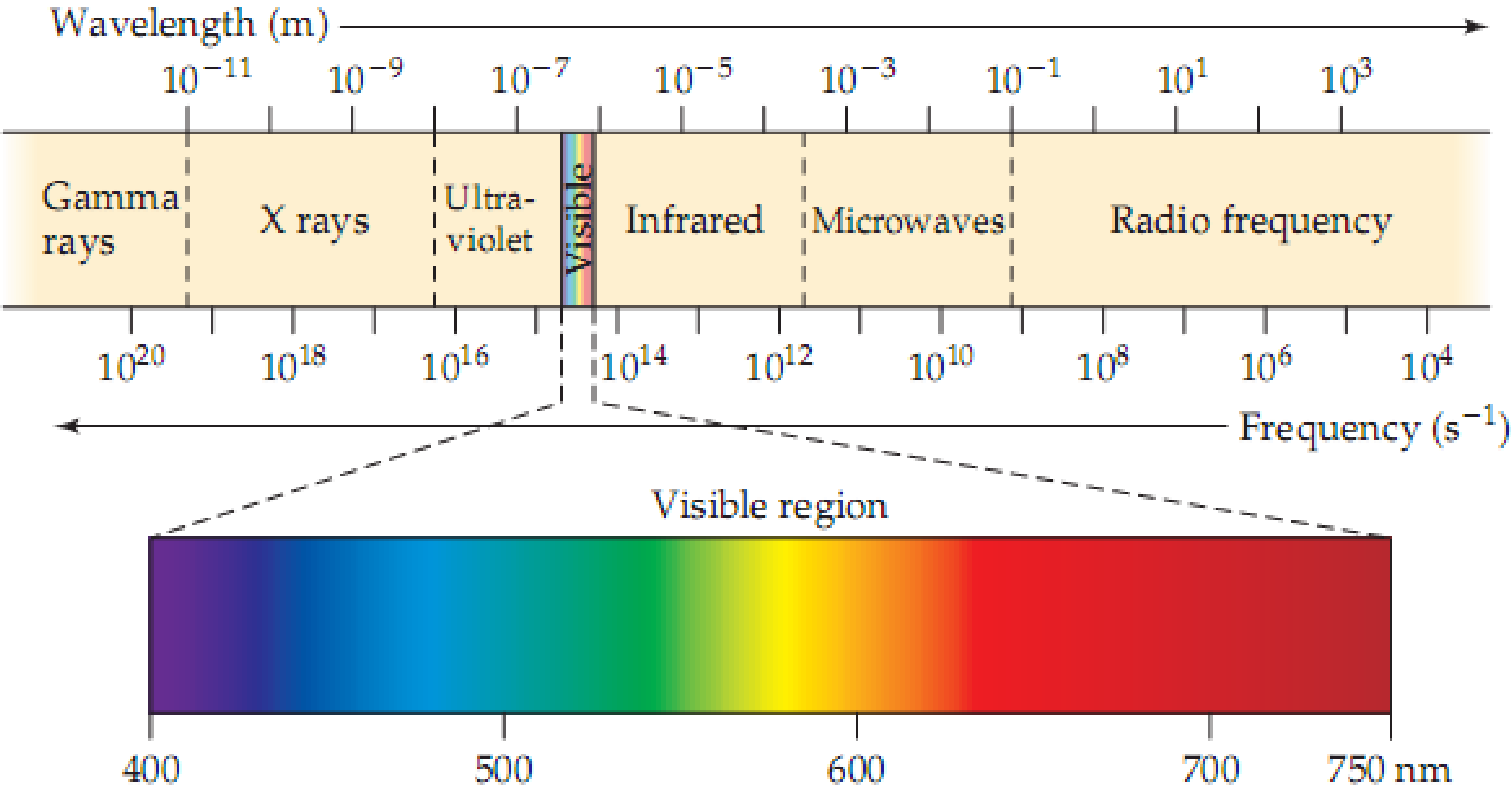
(b)

Frequency, Wavelength and Velocity

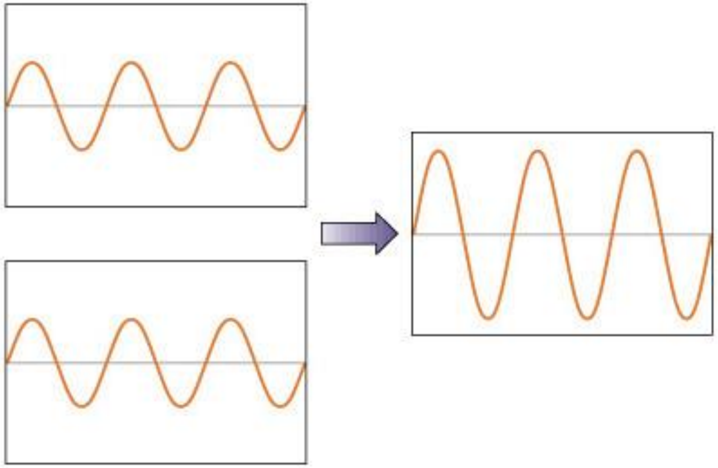
- Frequency (ν) in Hertz—Hz or s^{-1}.
- Wavelength (λ) in meters—m.
  - cm (10^{-2} m) µm (10^{-6} m) nm (10^{-9} m) Å (10^{-10} m) pm (10^{-12} m)
- Velocity (c)—2.997925×10^{8} m s^{-1}.

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

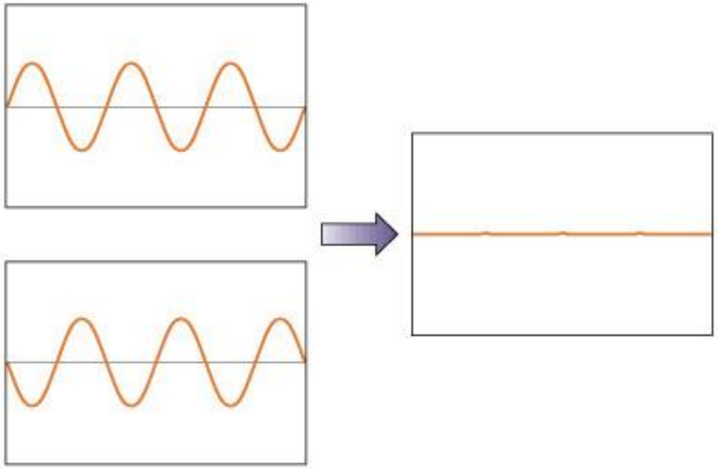
Electromagnetic Spectrum



Constructive and Destructive Interference



(a)



(b)

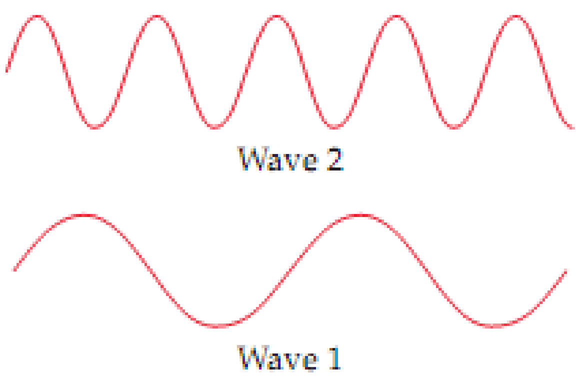
EXAMPLE

Two electromagnetic waves are represented in the diagram.

(a) Which wave has the higher frequency?

(b) If one wave represents visible light and the other represents infrared radiation, which wave is which?

(a) Wave 1 has a longer wavelength (greater distance between peaks). The longer the wavelength, the lower the frequency ($\nu = c/\lambda$). Thus, Wave 1 has the lower frequency, and Wave 2 has the higher frequency.



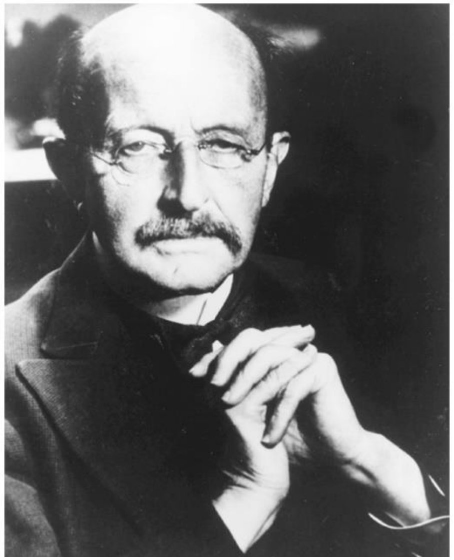
(b) The electromagnetic spectrum indicates that infrared radiation has a longer wavelength than visible light. Thus, Wave 1 would be the infrared radiation.

6-2 Quantized Energy and Photons

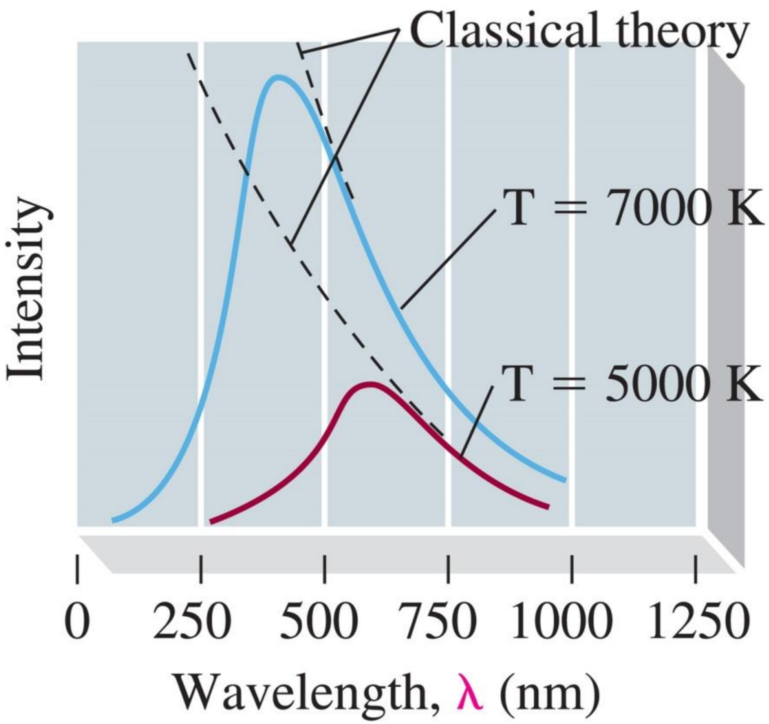
The wavelength distribution of the radiation depends on temperature

Example: a red-hot object, for is cooler than a yellowish or white-hot one

Blackbody Radiation:



Max Planck, 1900

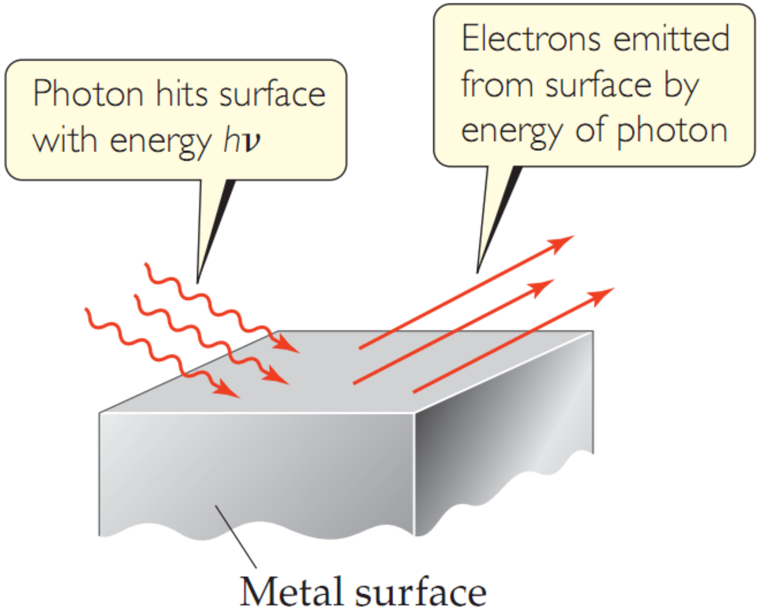


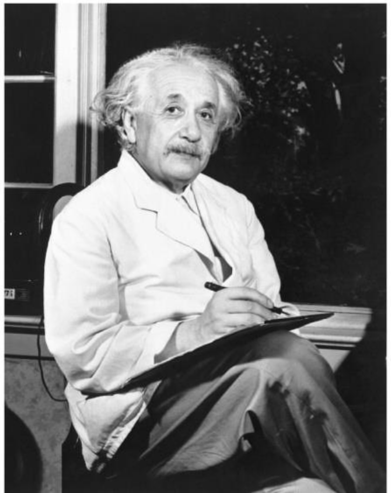
Energy, like matter, is discontinuous.

$$E = h\nu$$

h is called Planck constant and has a value of 6.626×10^{-34} J.s

The Photoelectric Effect and Photons





- Albert Einstein, 1905
  - The radiant energy striking the metal surface behaves like a stream of tiny energy packets.
  - Each packet is like a "particle" of energy
  - Each packet is called a photon
  - Energy of photon = $E = h\upsilon$

- Heinrich Hertz, 1888
  - Light striking the surface of certain metals causes ejection of electrons.

EXAMPLE

Calculate the energy of one photon of yellow light that has a wavelength of 589 nm.

$E = h\upsilon$

$\nu = c/\lambda$

$\Rightarrow E = hc/\lambda =$

$= (6.626 \times 10^{-34}\ \mathrm{J.s}) \times (2.997925 \times 10^{8}\ \mathrm{m\ s^{-1}})/(589 \times 10^{-9}\mathrm{m})$

$= 3.37 \times 10^{-19}\ \mathrm{J}$

PRACTICE

1. A laser emits light that has a frequency of $4.69 \times 10^{14}\ s^{-1}$

(a) What is the energy of one photon of this radiation?

(b) If the laser emits a pulse containing 5.0×10^{17} photons of this radiation, what is the total energy of that pulse?

(c) If the laser emits 1.3×10^{-2} J of energy during a pulse, how many photons are emitted?

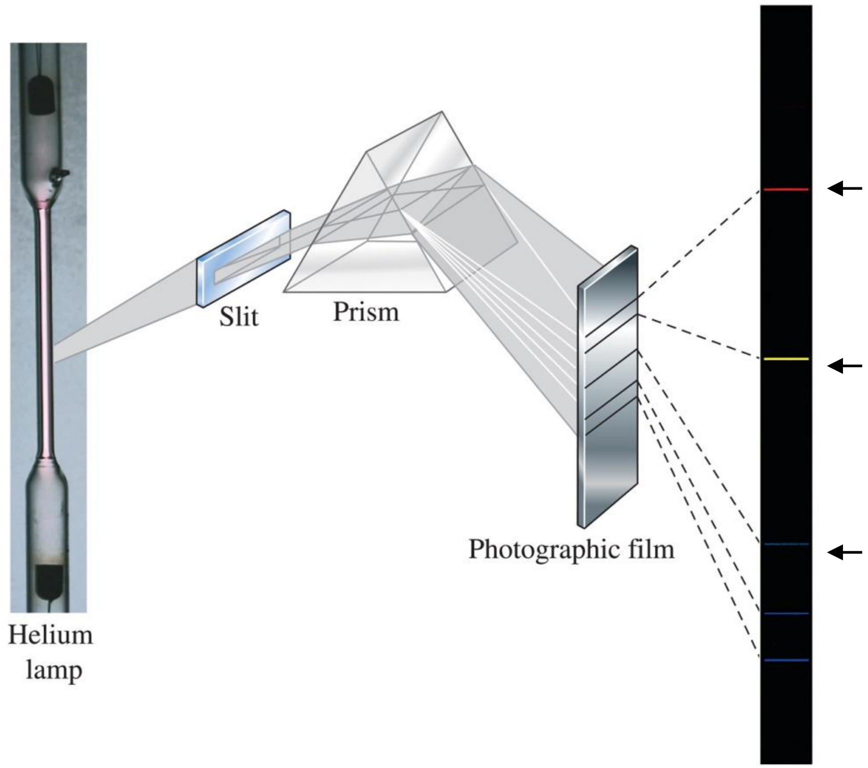
6.3 Line Spectra and the Bohr model

(a) (b)

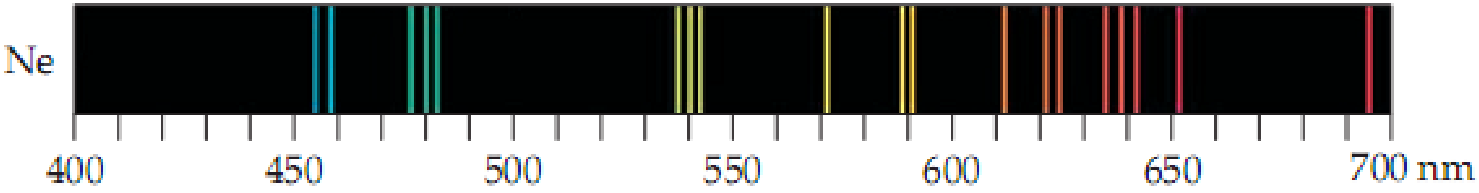
A continuous visible spectrum is produced when a narrow beam of white light is passed through a prism

Atomic Spectra

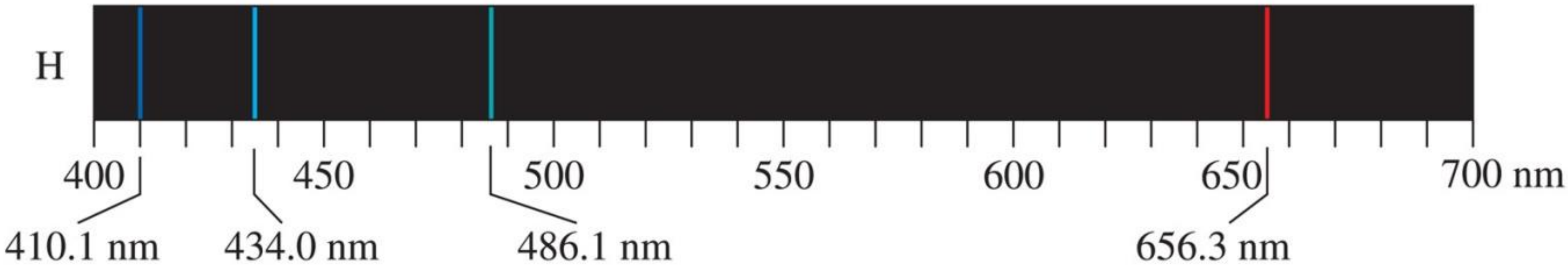
Helium



Neon



Hydrogen Atomic Spectra



The wavelengths of four lines of hydrogen fit an intriguingly simple formula that relates the wavelengths to integers

$$\frac{1}{\lambda} = (R_H)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

λ = wavelength of a spectral line,

R_H = the Rydberg constant = 11.096776 x 10^7 m^{-1}

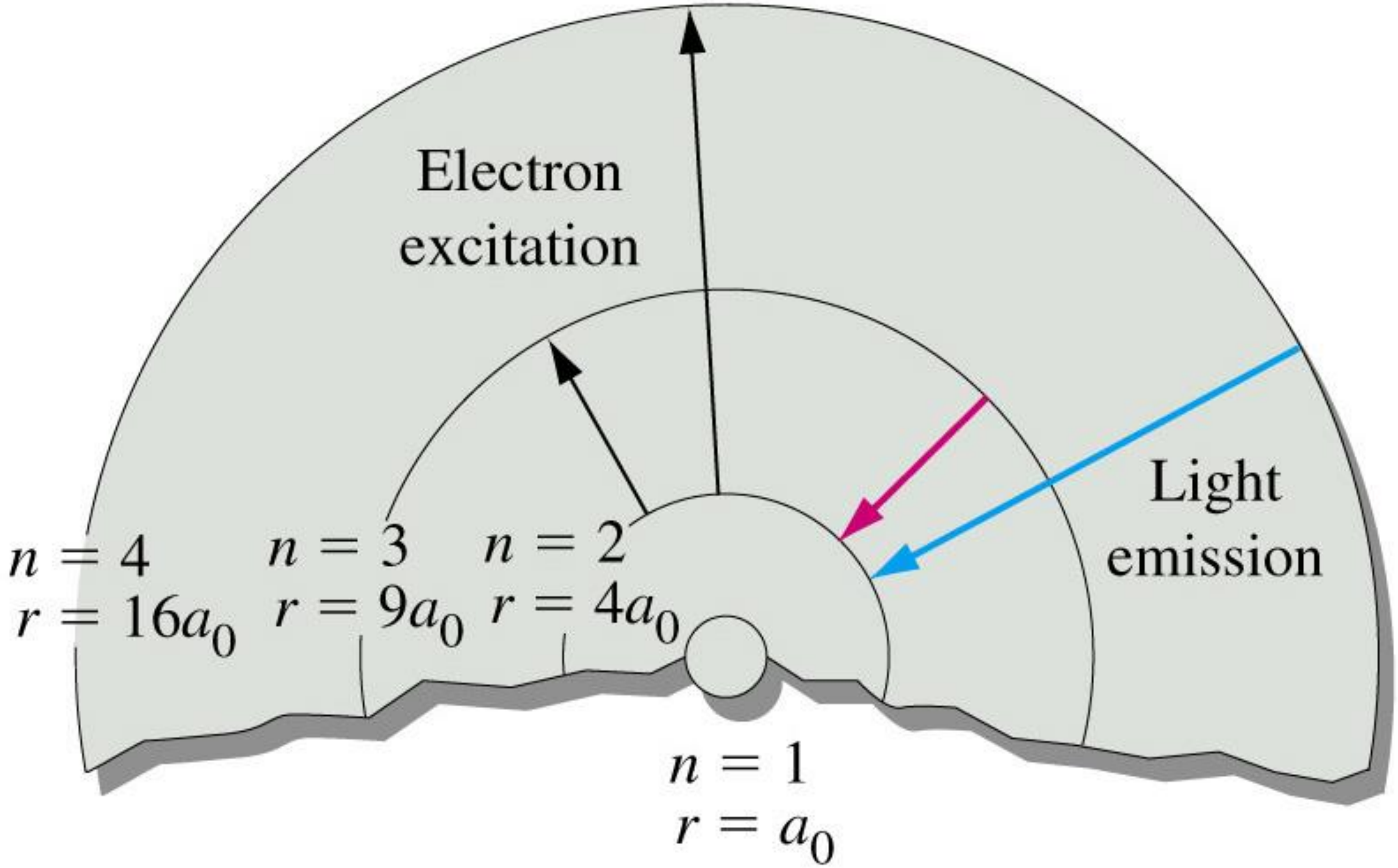
n_1 and n_2 are positive integers, with $n_2 > n_1$.

Bohr’s Model

1. Only orbits of certain radii, corresponding to certain specific energies, are permitted for the electron in a hydrogen atom.

2. An electron in a permitted orbit is in an “allowed” energy state. An electron in an allowed energy state does not radiate energy and, therefore, does not spiral into the nucleus.

3. Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. This energy is emitted or absorbed as a photon that has energy $E = h\upsilon$.



$$E = (-hcR_H)\left(\frac{1}{n^2}\right)$$

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

n = principal quantum number

n = 1 is the ground state

n > 1 are excited state

Energy-Level Diagram

$$\Delta E = E_f - E_i$$

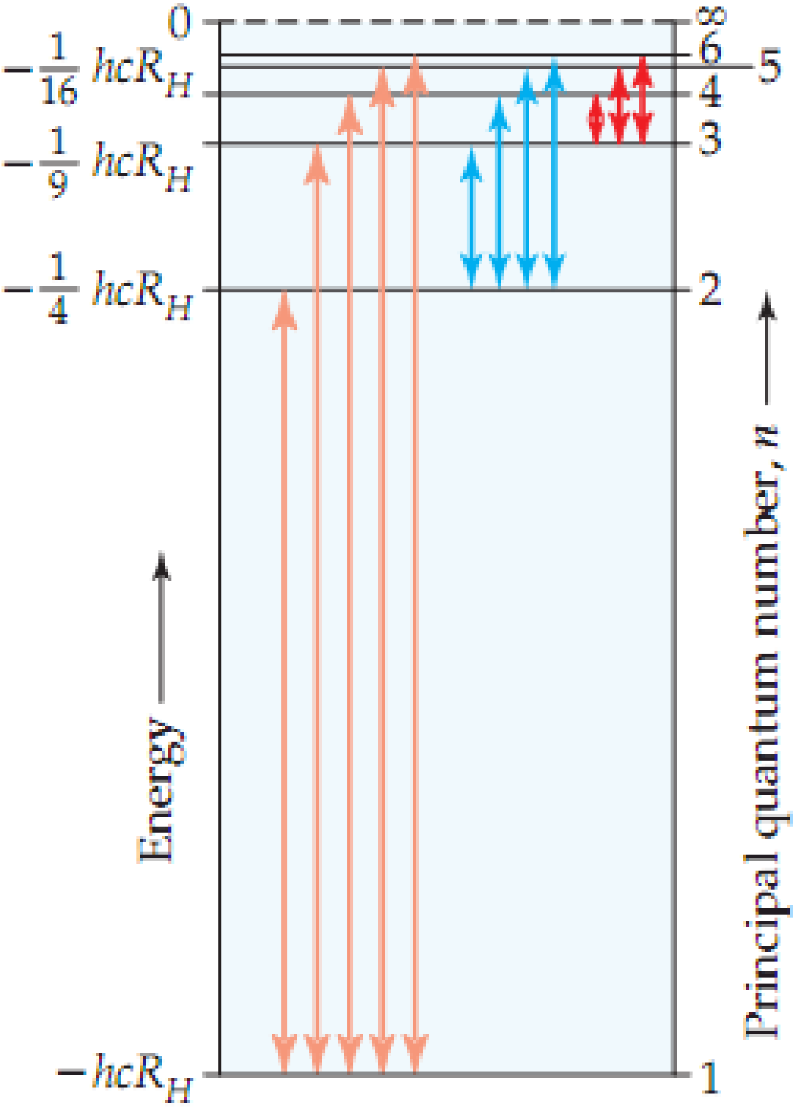
$$= (-hcR_H)\left(\frac{1}{n_f^2}\right) - (-hcR_H)\left(\frac{1}{n_i^2}\right)$$

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

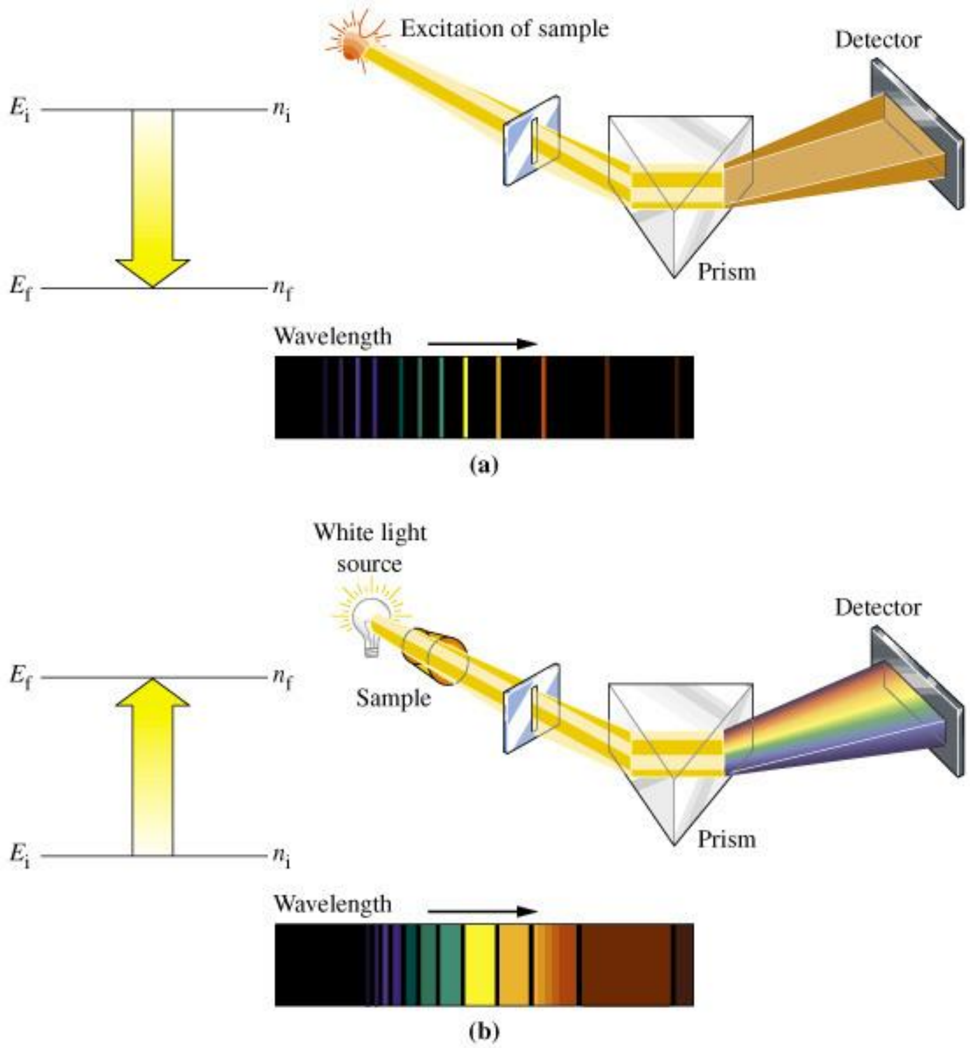
$$= 2.179 \times 10^{-18}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$\Delta E > 0$ ($n_f > n_i$) : Photon ***absorbed***
with $E_{photon} = h\upsilon = \Delta E$

$\Delta E < 0$ ($n_f < n_i$) : Photon ***emitted***
with $E_{photon} = h\upsilon = -\Delta E$



Emission and Absorption Spectroscopy



EXAMPLE

Using the diagram, predict which of these electronic transitions produces the spectral line having the longest wavelength:

a) n = 2 to n = 1,

b) n = 3 to n = 2,

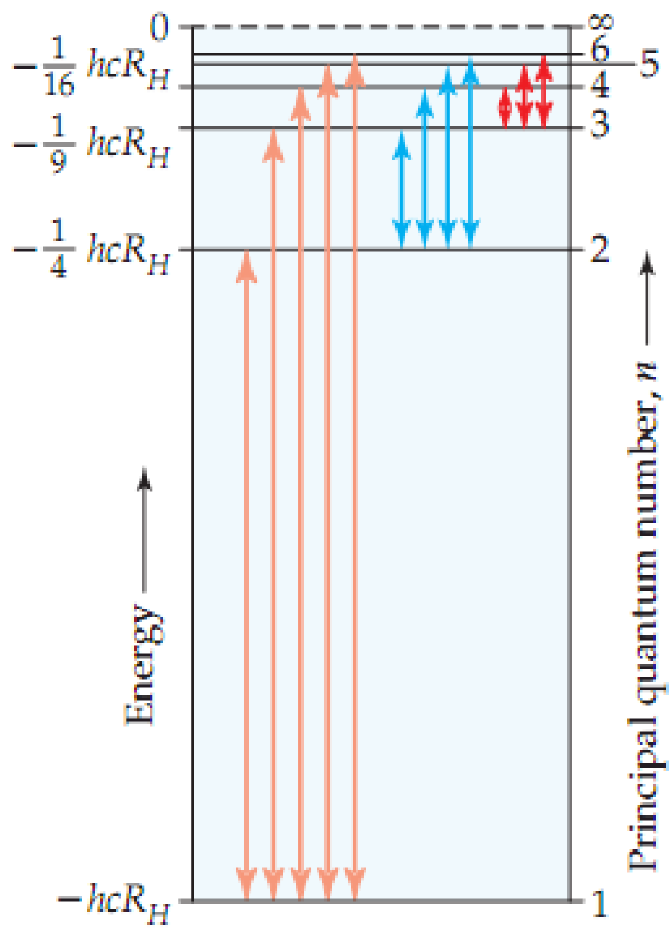
c) n = 4 to n = 3

$\lambda = c/\upsilon$

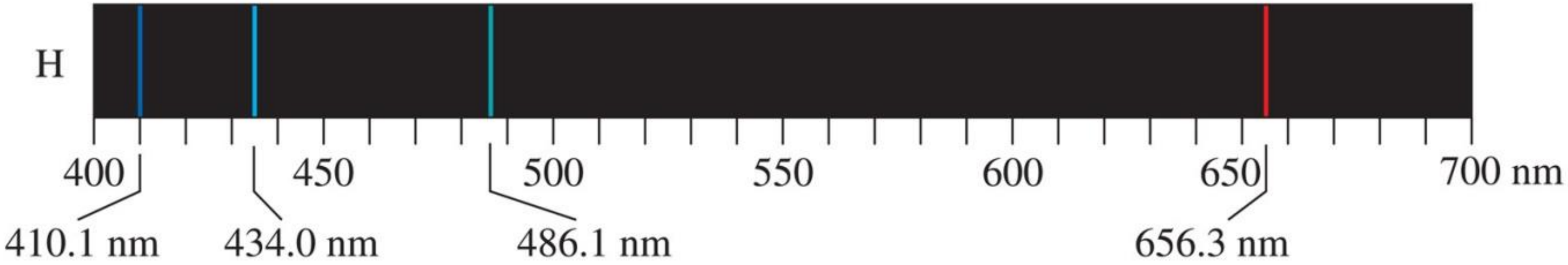
$E = h\upsilon$

Shortest vertical line represents the smallest energy change.

Thus, the n = 4 to n = 3 transition produces the longest wavelength (lowest frequency) line.



PRACTICE



1. The four lines in the H atom spectrum are due to transitions from a level for which $n_i > 2$ to the $n_f = 2$ level. What is the value of n_i for the blue-green line in the spectrum?

(a) 3

(b) 4

(c) 5

(d) 6

(e) 7

6.4 The Wave Behavior of Matter

Louis de Broglie

(1892–1987)

The wavelength of the electron, or of any other particle, depends on its mass, m, and on its velocity, v:

$$\lambda = \frac{h}{mv}$$

h is Planck constant

mv for any object is called its momentum

EXAMPLE

What is the wavelength of an electron moving with a speed of 5.97×10^6 m/s? The mass of the electron is 9.11×10^{-31} kg

$$h = 6.626 \times 10^{-34}\ \text{J-s}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{(6.626 \times 10^{-34}\ \text{J-s})}{(9.11 \times 10^{-31}\ \text{kg})(5.97 \times 10^{6}\ \text{m/s})}\left(\frac{1\ \text{kg-m}^2/\text{s}^2}{1\ \text{J}}\right)$$

$$= 1.22 \times 10^{-10}\ \text{m} = 0.122\ \text{nm} = 1.22\ \text{Å}$$

The Uncertainty Principle

Werner Heisenberg

(1901–1976)

The dual nature of matter places a fundamental limitation on how precisely we can know both the location and the momentum of an object at a given instant.

The limitation becomes important only when we deal with matter at the subatomic level (that is, with masses as small as that of an electron).

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

Δx = uncertainty in position

Δ(mυ) = uncertainty in momentum,

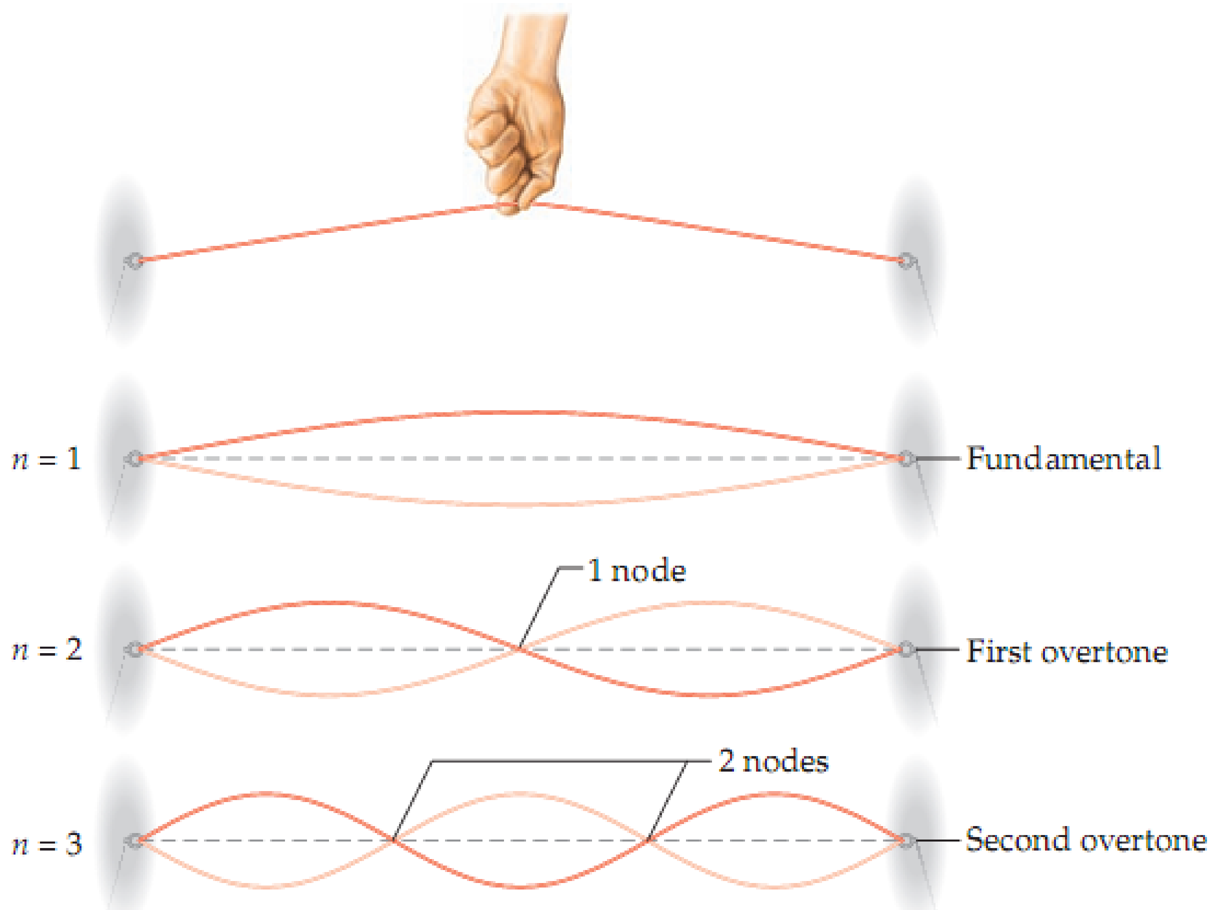
6.5 Quantum Mechanics and Atomic Orbitals

Two Ideas Leading to a New Quantum Mechanics:

- Wave-Particle Duality.
  - Einstein suggested particle-like properties of light could explain the photoelectric effect.
  - But diffraction patterns suggest photons are wave-like.

- Wave Behavior of Matter
  - deBroglie suggested that small particles of matter may at times display wavelike properties.

Standing waves in a vibrating string



Nodes do not undergo displacement.

Orbitals and Quantum Numbers

1. **The principal quantum number, n, can have positive integral values 1, 2, 3, ...**

   As n increases, the orbital becomes larger, and the electron spends more time farther from the nucleus.

   An increase in n also means that the electron has a higher energy and is therefore less tightly bound to the nucleus.

2. **The second quantum number—the angular momentum quantum number, l, can have integral values from 0 to (n – 1) for each value of n**

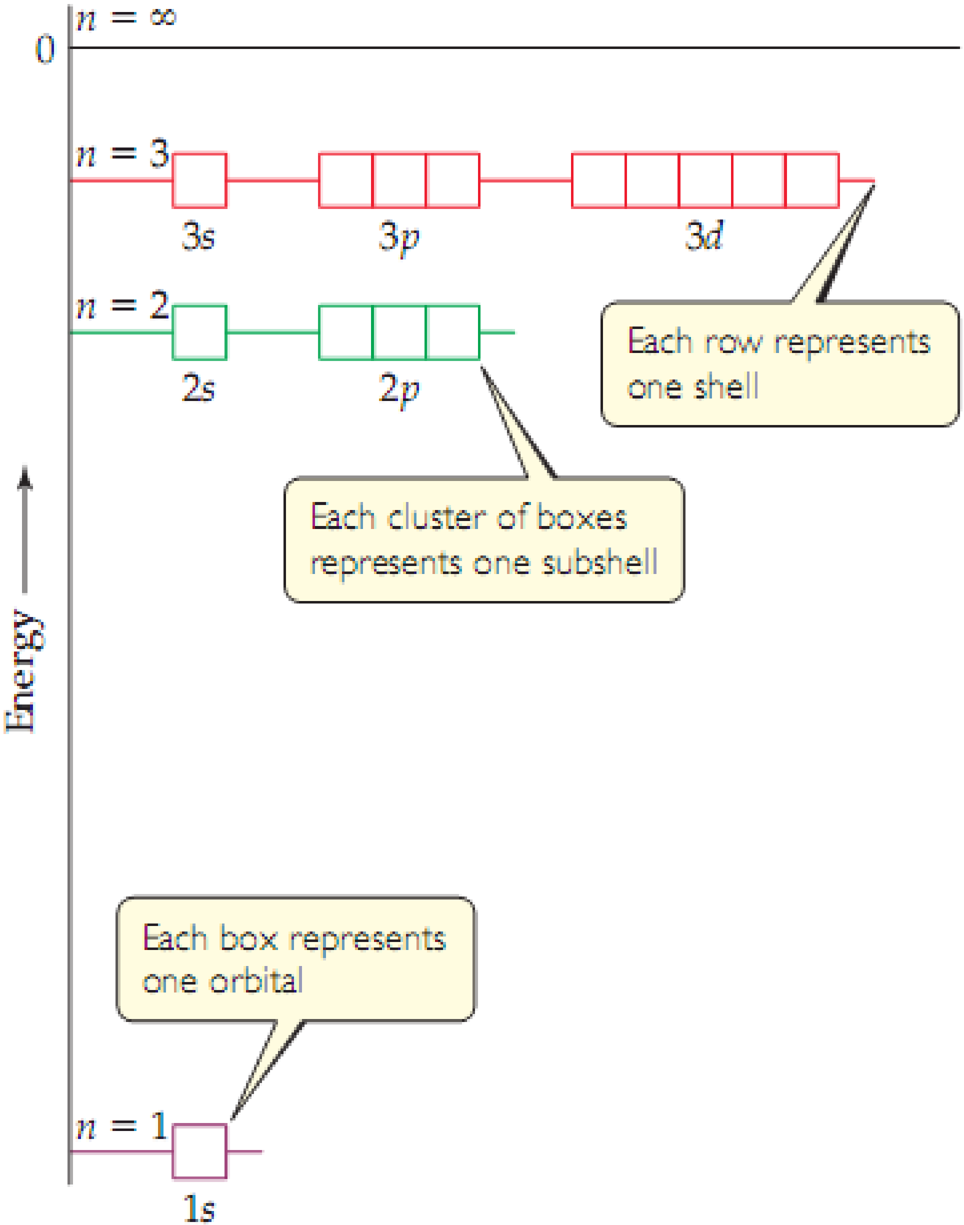
   This quantum number defines the shape of the orbital. The value of l for a particular orbital is generally designated by the letters s, p, d, and f,* corresponding to l values of 0, 1, 2, and 3:

3. **The magnetic quantum number, m_l, can have integral values between -*l* and *l*, including zero**

   This quantum number describes the orientation of the orbital in space

Table 6.2 Relationship among Values of n, l, and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16



$n = 1$ shell has one orbital
$n = 2$ shell has two subshells composed of four orbitals
$n = 3$ shell has three subshells composed of nine orbitals

1. The shell with principal quantum number n consists of exactly n subshells.
2. Each subshell consists of a specific number of orbitals.
3. The total number of orbitals in a shell is n^2, where n is the principal quantum number of the shell.

EXAMPLE

(a) Without referring to Table 6.2, predict the number of subshells in the fourth shell, that is, for $n = 4$.

(b) Give the label for each of these subshells.

(c) How many orbitals are in each of these subshells?

(a) There are four subshells in the fourth shell, corresponding to the four possible values of l (0, 1, 2, and 3). These subshells are labeled 4s, 4p, 4d, and 4f.

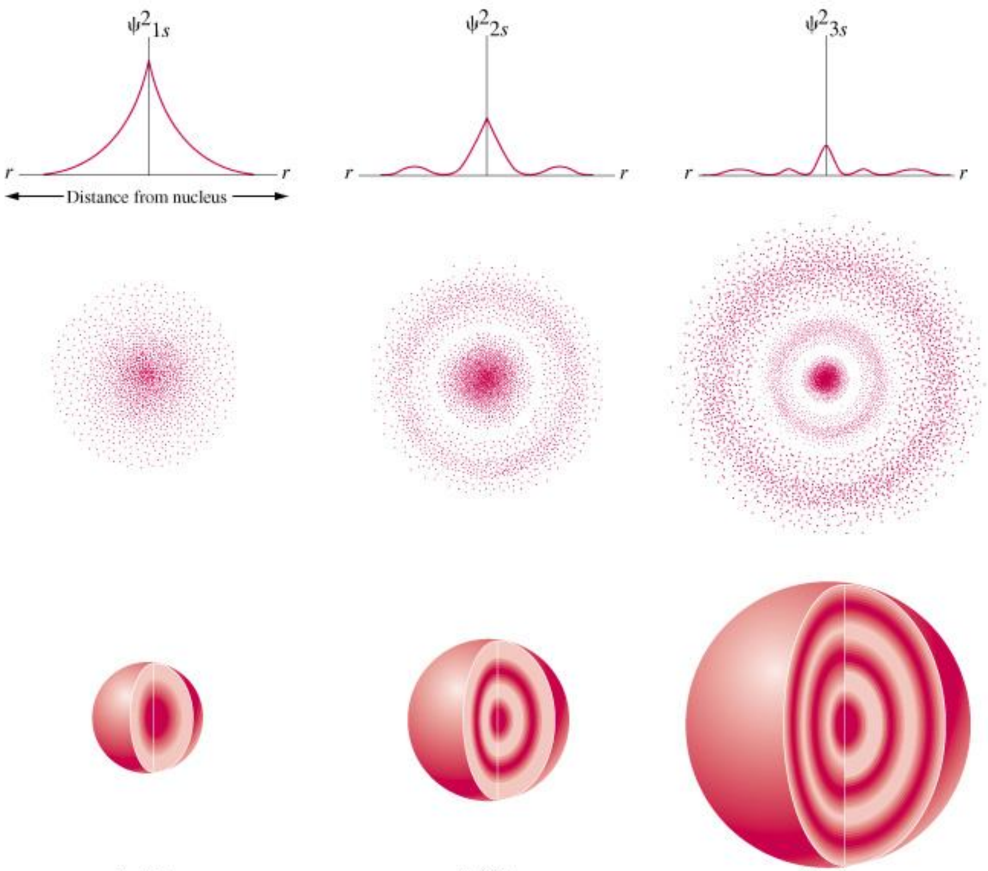
(b) The number given in the designation of a subshell is the principal quantum number, n;

The letter designates the value of the angular momentum quantum number, l: for $l = 0$, s; for $l = 1$, p; for $l = 2$, d; for $l = 3$, f.

(c) There is one 4s orbital (when $l = 0$, there is only one possible value of ml: 0). There are three 4p orbitals (when $l = 1$, there are three possible values of ml: 1, 0, -1). There are five 4d orbitals (when $l = 2$, there are five allowed values of ml: 2, 1, 0, -1, -2). There are seven 4f orbitals (when $l = 3$, there are seven permitted values of ml: 3, 2, 1, 0, -1, -2, -3).

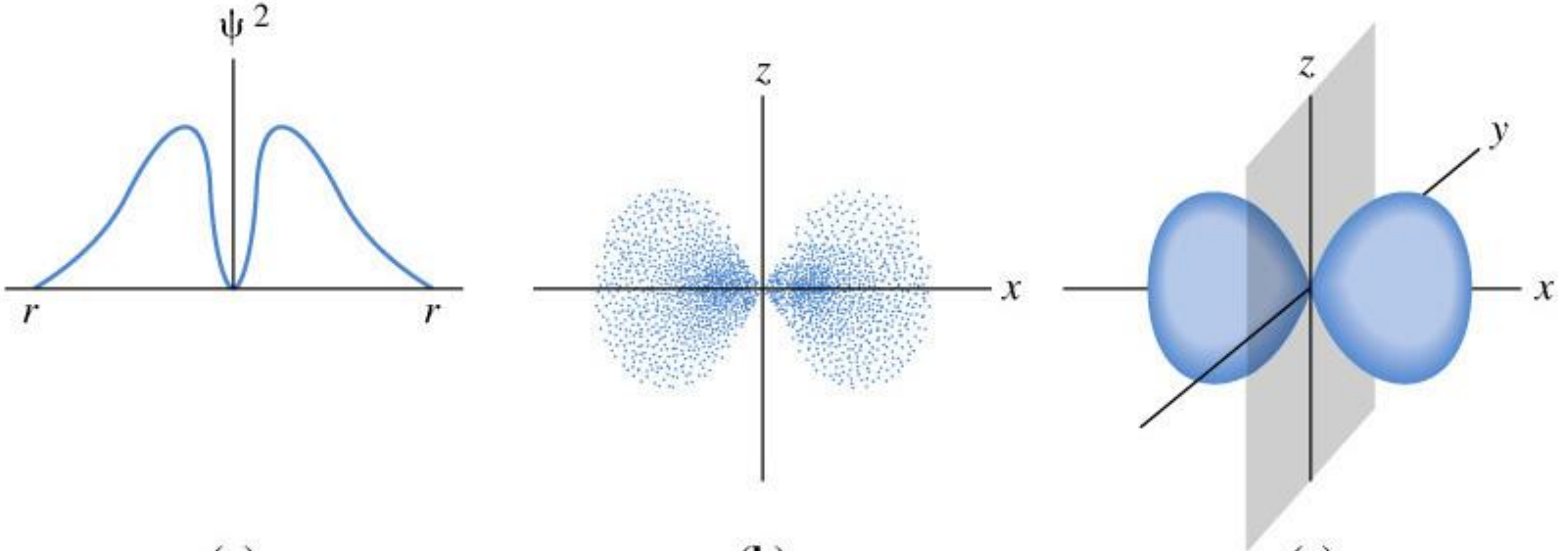
6.6 | Representations of Orbitals

s orbitals



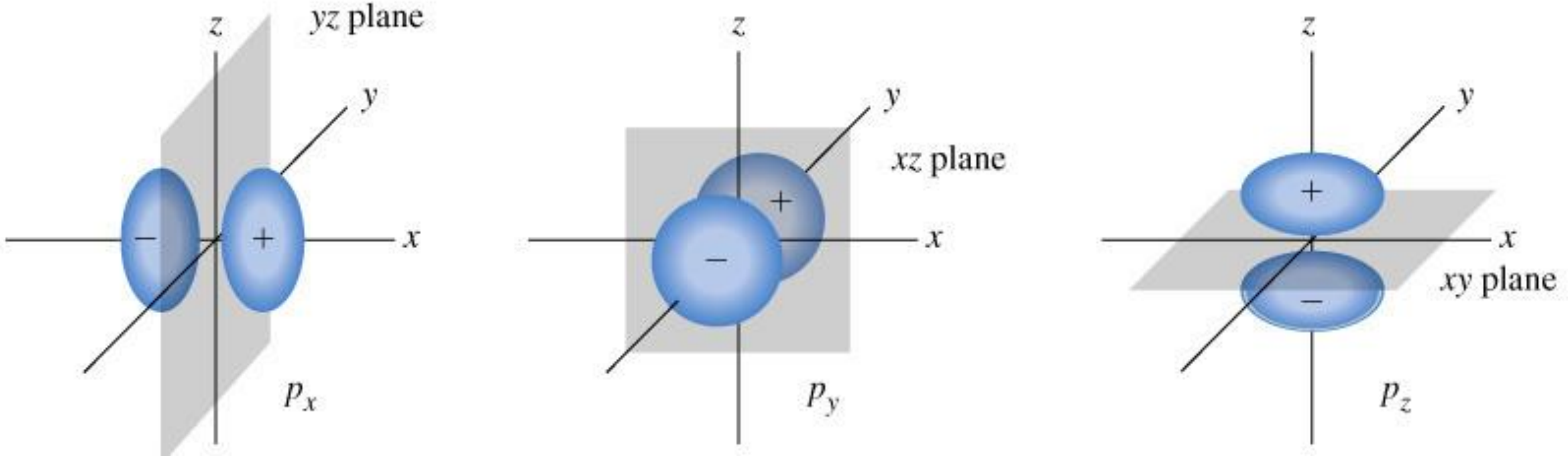
(a) 1*s** (b)** 2*s** (c)** 3*s*

p Orbitals

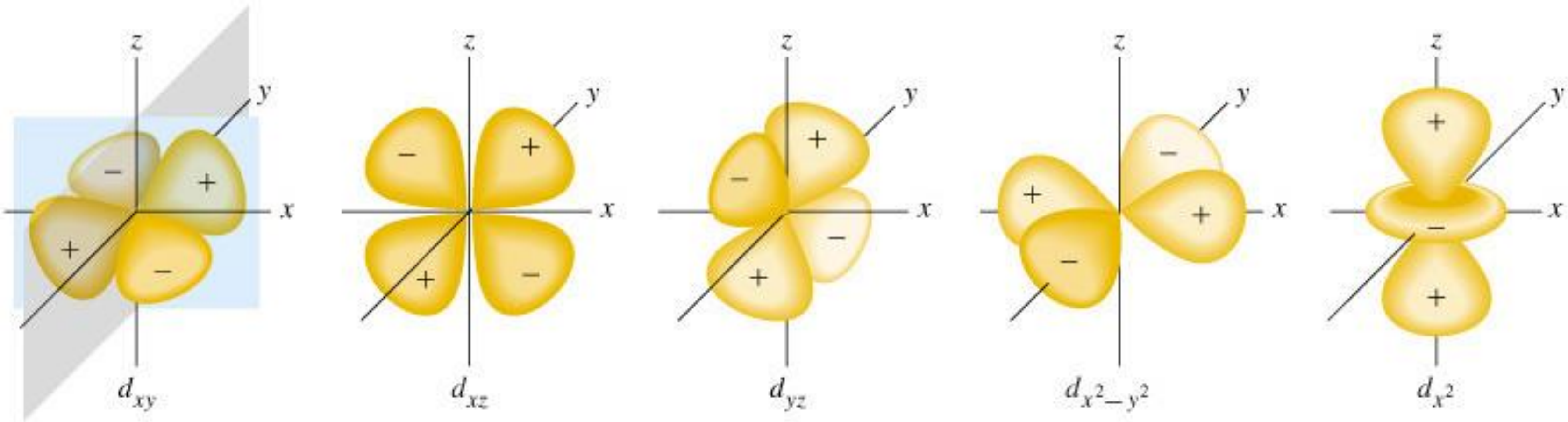


(a) (b) (c)

p Orbitals



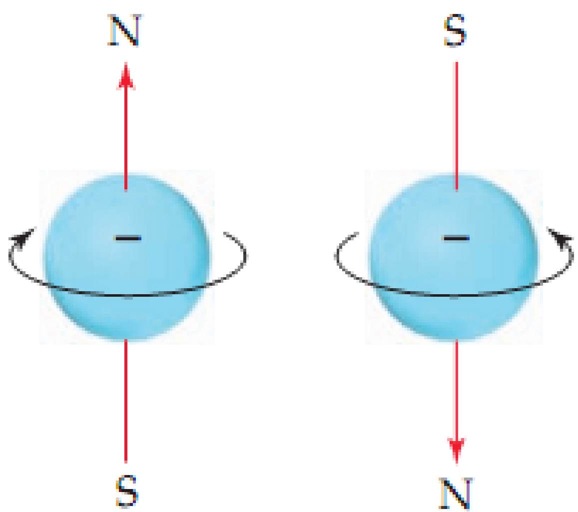
d Orbitals



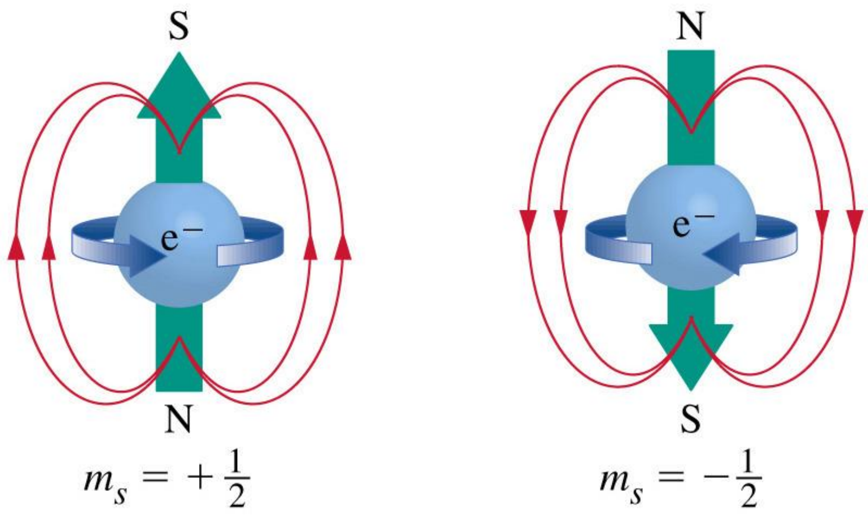
6.7 Multi-Electron Atoms

When scientists studied the line spectra of many-electron atoms in great detail, they noticed a very puzzling feature: Lines that were originally thought to be single were actually closely spaced pairs. This meant, in essence, that there were twice as many energy levels as there were "supposed" to be.

➔ Electrons have an intrinsic property, called electron spin, that causes each electron to behave as if it were a tiny sphere spinning on its own axis



New quantum number



The fourth quantum number: m_s spin magnetic quantum number

The Pauli exclusion principle: *No two electrons in an atom can have the same set of four quantum numbers n, l, m_l, and m_s*

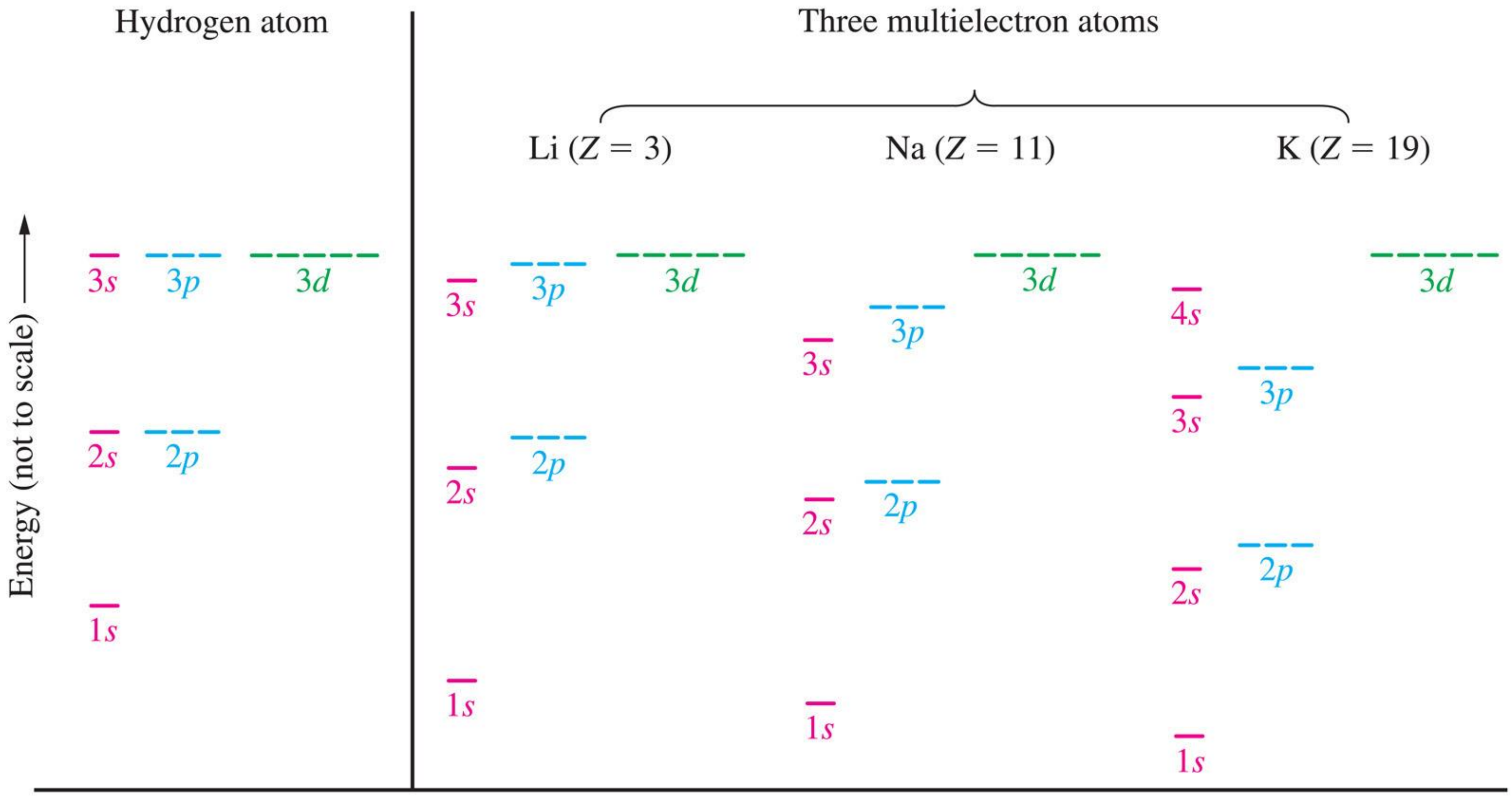
Thus, if we want to put more than one electron in an orbital and satisfy the Pauli exclusion principle, our only choice is to assign different m_s values to the electrons.

An orbital can hold a maximum of two electrons and they must have opposite spins

6-8 Electron Configurations

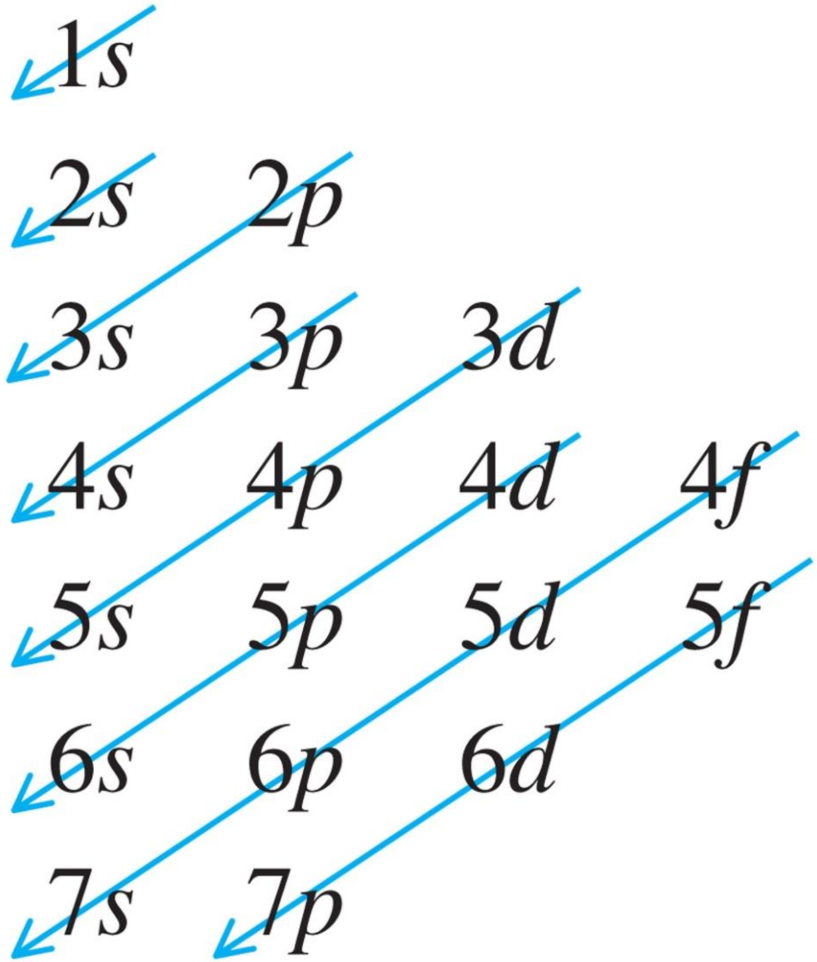
- Aufbau process.
  - Build up and minimize energy.
- Pauli exclusion principle.
  - No two electrons can have all four quantum numbers alike.
- Hund’s rule.
  - Degenerate orbitals are occupied singly first.

Orbital Energies

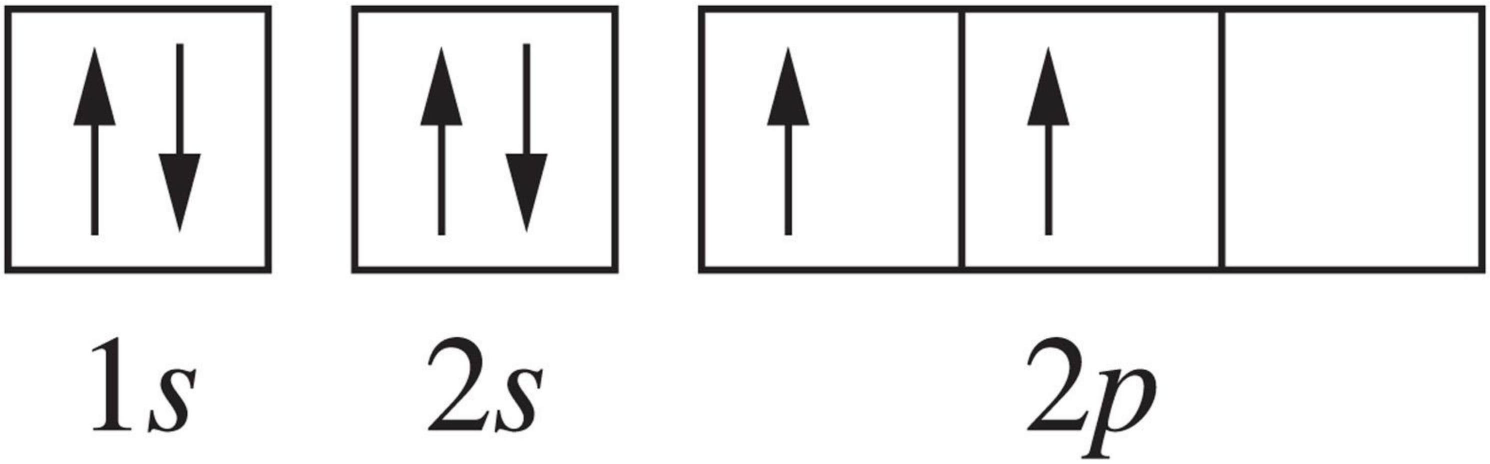


Degenerate orbitals: orbitals that have same energy

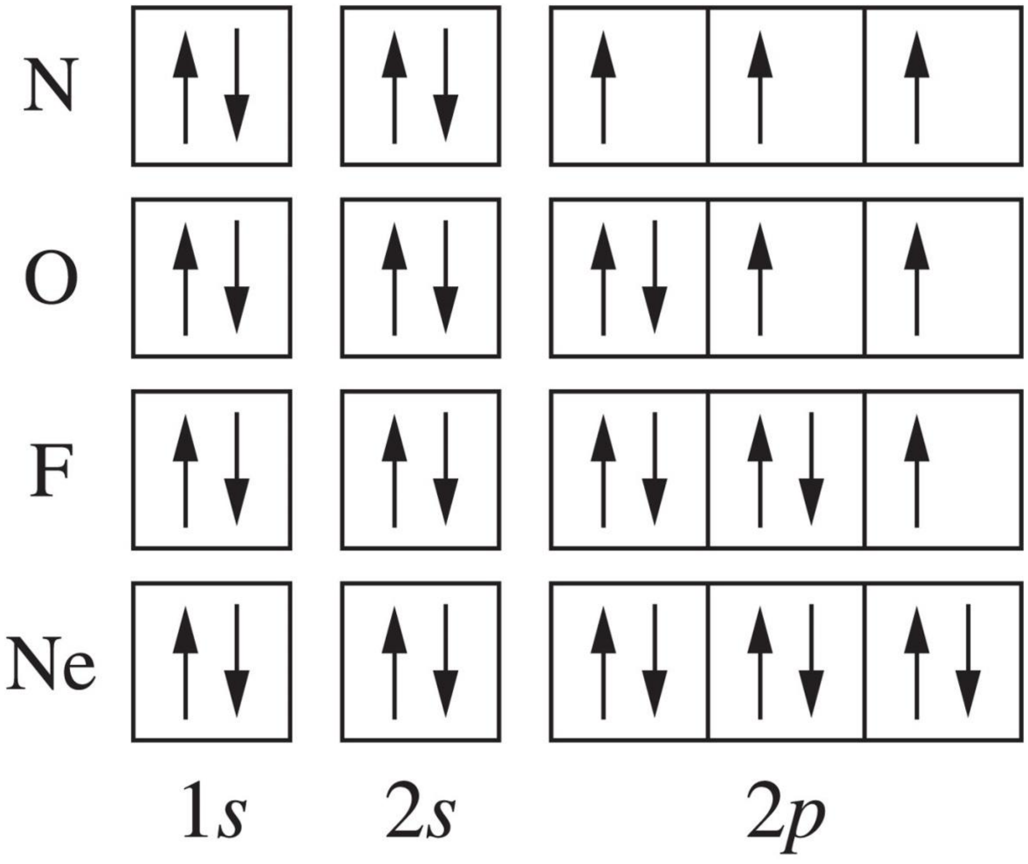
Orbital Filling



Aufbau Process and Hunds Rule



Filling p Orbitals



Filling the d Orbitals

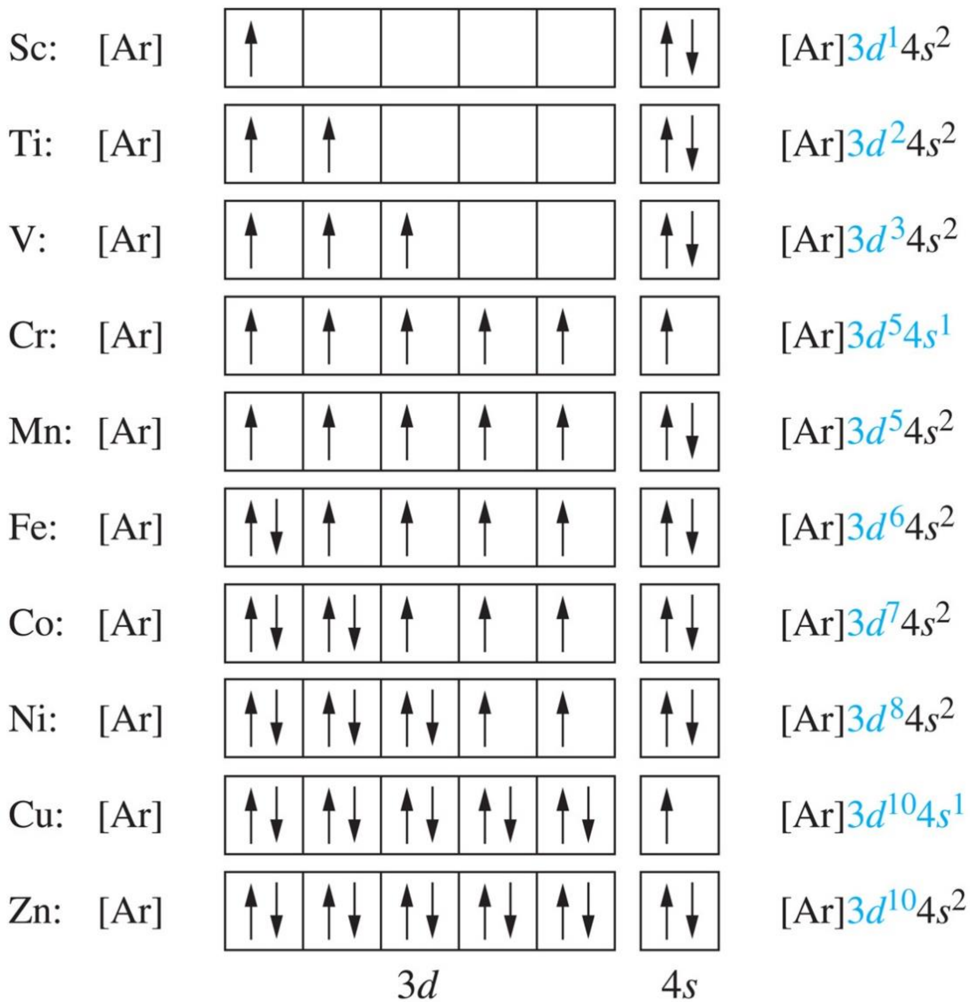
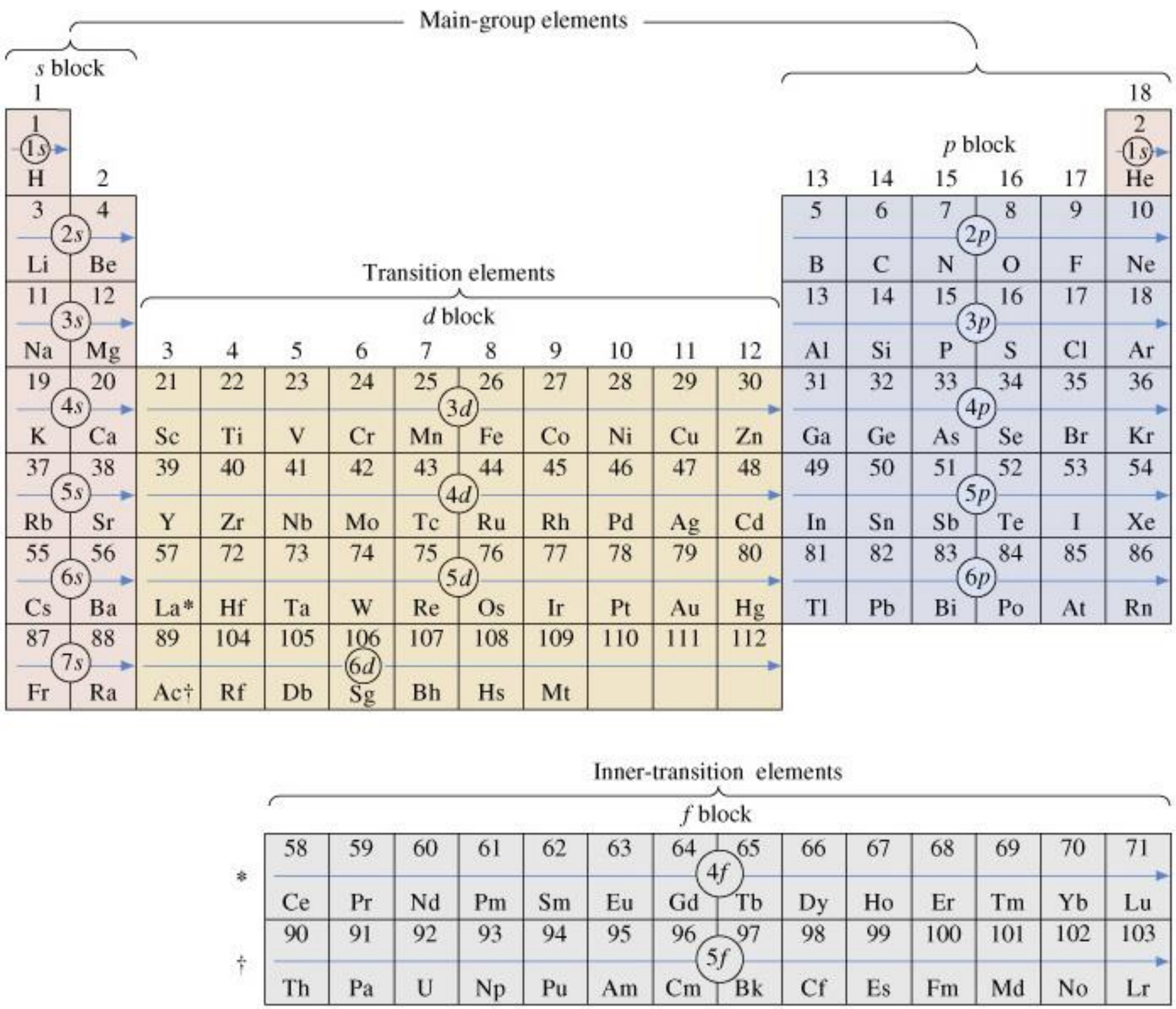


TABLE 8.2 Electron Configurations of Some Groups of Elements

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	$[Xe]4f^{14} 5d^{10} 6s^2 6p^6$

7-11 Electron Configurations and the Periodic Table



Homeworks

Excercises:

6.105

6.106

6.107

6.108

6.110

Chemistry

The Central Science

Fourteenth Edition in SI Units

Due date: May 13th, 2020

You will have a 20 minute quiz next week

What are allowed?

- A pen
- A periodic table
- An A4-sized sheet of hand written notes
- A calculator

No other devices are allowed!