## Chapter 6.  Electronic Structure of Atoms

### 6.1 The Wave Nature of Light

The **electronic structure** of an atom refers to the arrangement of electrons.

Visible light is a form of **electromagnetic radiation** or radiant energy that carries energy through space.

Electromagnetic radiation is characterized by its wave nature.

All waves have a characteristic **wavelength,** $\lambda$ (lambda), and amplitude, A.
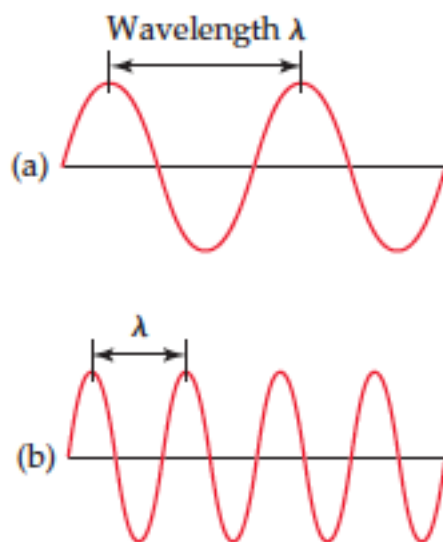
The **frequency**, $\nu$ (nu), of a wave is the number of cycles which pass a point in one second.

The units of  are Hertz ( $1 \text{ Hz} = 1 \text{ s}^{-1}$)

The speed of a wave is given by its wavelength ($\lambda$) multiplied by its frequency ($\nu$).

For light, speed, $c = \lambda \, \nu$

The shorter the wavelength, the higher the frequency.



Electromagnetic radiation moves through a vacuum with a speed of approximately $3.00 \times 10^{-8}$ m/s,  the speed of light .

Electromagnetic waves have characteristic wavelength and frequencies.

The electromagnetic spectrum is a display of the various types of electromagnetic radiation arranged in order of increasing wavelength.

Example: visible radiation has wavelength between 400 nm (violet) and 750 nm (red).

## 6.2 Quantized Energy and Photons

Some phenomena can't explain using a wave model of light:
    Blackbody radiation: emission of light from hot objects.
    The photoelectric effect: emission of electrons from metal surfaces on which light shines.
    Emission spectra: emission of light from electronically excited gas atoms.

**Hot Objects and the Quantization of Energy**
    Heated solids emit radiation (black body radiation)
        The wavelength distribution depends on the temperature (i.e., 'red hot' objects are cooler than 'white hot' object).
    Planck investigated black body radiation
        He proposed that energy can only be absorbed or released from atoms in certain amounts.
        These amounts are called quanta.
A **quantum** is the smallest amount of energy that can be emitted or absorbed as electromagnetic radiation
    The relationship between energy and frequency is
        $E = h\,\nu$
    Where $h$ is **Planck's constant** ($6.63 \times 10^{-34}$ J.s).



Potential energy of person walking up steps increases in stepwise, quantized manner

Potential energy of person walking up ramp increases in uniform, continuous manner

**The Photoelectric Effect and Photons**
The photoelectric effect provides evidence for the particle nature of light and quantization.
Einstein assumed that light traveled in energy packets called **photons**.
      The energy of one photon, $E = h\nu$
Light shining on the surface of a metal can cause electrons to be ejected from the metal.
      The electrons will only be ejected if the photons have sufficient energy
            Below the threshold frequency no electrons are ejected.
            Above the threshold frequency, the excess energy appears as the kinetic energy of the electrons.
Light has wave-like AND particle-like properties.


## 6.3 Line and the Bohr Model

**Line spectra**
      Radiation composed of only one wavelength is called monochromatic
      Radiation that spans a whole array of different wavelengths is called continuous.
      When radiation from a light source such as light bulb is separated into its different wavelength components, a **spectrum** is produced.
            White light can be separated into **continuous spectrum** of colors (e.g, rainbow)
      Not all radiation is continuous
            A gas placed in a partially evacuated tube and subjected to a high voltage produces single colors of light.
            The spectrum that we see contains radiation of only specific wavelengths; this is called a **line spectrum.**

**Bohr's Model**
Rutherford assumed the electrons orbited the nucleus analogous to planets around the sun.
      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 $E = h\nu$

The energy is gained or last as a photon.

**The Energy States of the Hydrogen Atom**
Colors from exited gases arise because electrons move between energy states in the atom.

Since the energy states are quantized, the light emitted from excited atoms must be quantized and appear as line spectra.
Bohr showed mathematically that:

$E_n = - R_H (1/n^2)$

Where n is the principal quantum number (i.e., $n = 1, 2, 3,........$) and $R_H$ is the Rydberg constant $= 2.8 \times 10^{-18}$ J.

The first orbit in the Bohr model has $n = 1$ and is closest of the nucleus.
The furthest orbit in the Bohr model has $n$ and correspond to $E = 0$.
Electrons in the Bohr model can only move between orbits by absorbing and emitting energy in quanta ($E = h$ ).
   The **ground state** = the lowest energy state
   An electron in a higher energy state is said to be in **excited state**.
The amount of energy absorbed or emitted on moving between states is given by

$E = E_f - E_i = h ) = R_H \ 1/n^2_i + 1/n^2_f \}$

When $n_i > n_f$ energy is emitted and when $n_f > n_i$ energy is absorbed.

**Limitation of the Bohr Model**
The Bohr Model has several limitations;
   It cannot explain the spectra of atoms other than hydrogen.
   Electrons do not move about the nucleus in circular orbits.

However the model introduces two important ideas:
   The energy of an electron is quantized; electrons exist only in certain energy levels described by the quantum numbers.
   Energy gain or loss is involved in moving an electron from on energy level to another.
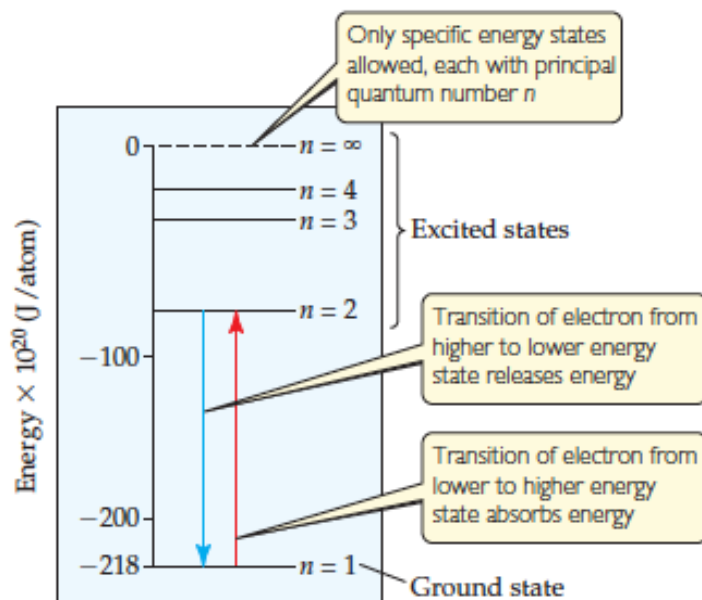
## 6.4 The Wave Behavior of Matter

Knowing that light has a particle nature, it seems reasonable to ask whether matter has a wave nature.
The question was answered by Louis deBroglie.
Using Einstein's and Planck's equations. DeBroglie derived:

$$= h/m$$

The **momentum**, $m$, is a particle property, whereas is a wave property.
      **Matter waves** is the term used to describe the wave characteristics of material particles.
      Therefore, in one equation deBroglie summarized the concepts of waves and particles as they apply to low-mass, high-speed objects.

**The Uncertainty Principle**
**Heisenberg's uncertainty principle**; We cannot determine the exact position, direction of motion and speed of subatomic particles simultaneously.
For electrons: we cannot determine their momentum and position simultaneously.

## 6.5     Quantum mechanics and Atomic Orbitals

Schrodinger proposed an equation containing both wave and particle terms
Solving the equation leads to **wave functions**, .
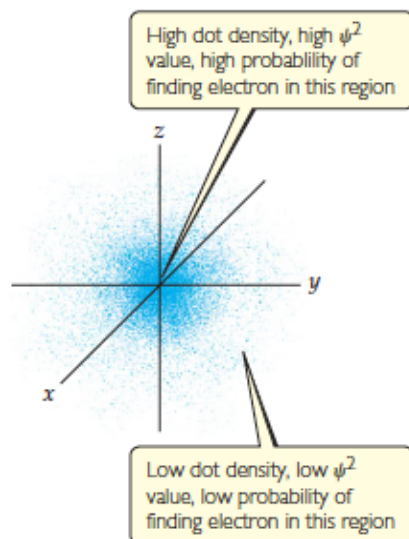The wave function gives the shape of the electron's orbital.
      The square of wave function, $\psi^2$, gives the probability of finding the electron.
      That is, $\psi^2$ gives the electron density for the atom
            $\psi^2$ is called the **probability density**.
**Electron density** is another way of expressing probability
      A region of high electron density is none where there is a high probability of finding an electron.



High dot density, high $\psi^2$ value, high probablility of finding electron in this region

Low dot density, low $\psi^2$ value, low probability of finding electron in this region

**Orbitals and Quantum Numbers**
If we solve the Schrodinger equation, we get wave functions and energies for the wave functions. We call   **orbitals**.
Schrodinger's equation requires three quantum numbers:
*Principal quantum number, n.* this is the same as Bohr's n.
    As *n* becomes larger, the atom becomes larger and the electron is further from the nucleus.
*Azimuthal quantum number, l.*  this quantum number depends on the value of *n*.
    The values of *l* begins at 0 and increase to $n - 1$.
    We usually use letters for *l* (*s, p, d*, and *f* for l = 0, 1, 2, and 3).  Usually we refer to the *s, p, d*, and *f* orbitals.
    This quantum number defines the shape of the orbital.
*Magnetic quantum number*, $m_l$.
    This quantum number depends on *l*.
    The magnetic quantum number has integer values between $-l$ and $+l$.
      The magnetic quantum number gives the three-dimensional orientation of each orbital.
A collection of orbitals with the same value if *n* is called **electron shell**.
    A set of orbitals with the same *n* and *l* is called **subshell**.
      Each subshell is designated by a number and a letter.
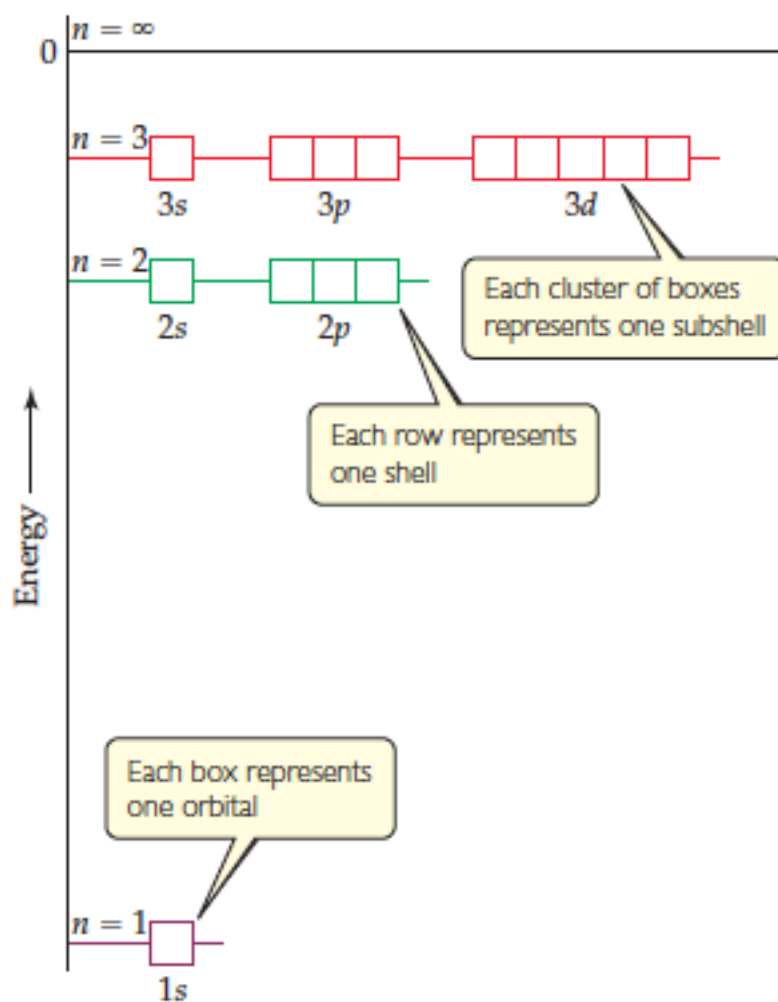      For example, 3*p* orbitals have $n = 3$ and $l = 1$.
Orbitals can be ranked in terms of energy to yield an Aufbau diagram
    Note that this Aufbau diagram is for a single electron system.
As n increases note that the spacing between energy levels becomes smaller.

**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 | 1s | 0 | 1 | 1 |
| 2 | 0 | 2s | 0 | 1 | |
| | 1 | 2p | 1, 0, −1 | 3 | 4 |
| 3 | 0 | 3s | 0 | 1 | |
| | 1 | 3p | 1, 0, −1 | 3 | |
| | 2 | 3d | 2, 1, 0, −1, −2 | 5 | 9 |
| 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 | 16 |

$n = \infty$

0 ————————————————————————

$n = 3$

3s   3p   3d

Each cluster of boxes represents one subshell

$n = 2$

2s   2p

Each row represents one shell

Energy ⟶

Each box represents one orbital

$n = 1$

1s

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

## 6.6    Representation of Orbitals
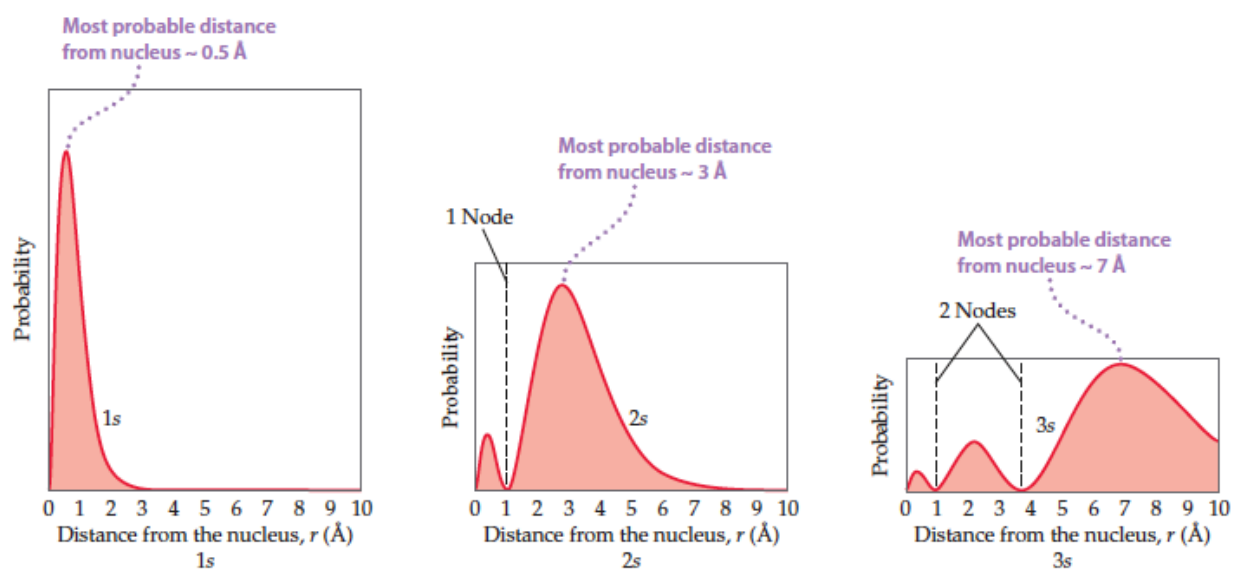
**The *s* Orbitals**

All *s* orbitals are spherical

As n increases, the *s* orbitals get larger

As n increases, the number of nodes increases

> A **node** is a region in space where the probability of finding an electron is zero.
> > $\psi^2 = 0$ at a node
>
> For an *s* orbital the number of nodes is given by *n*-1.

Radial probability distributions for the 1s, 2s, and 3s orbitals of hydrogen. These graphs of the radial probability function plot probability of finding the electron as a function of distance from the nucleus. As n increases, the most likely distance at which to find the electron (the highest peak) moves farther from the nucleus.
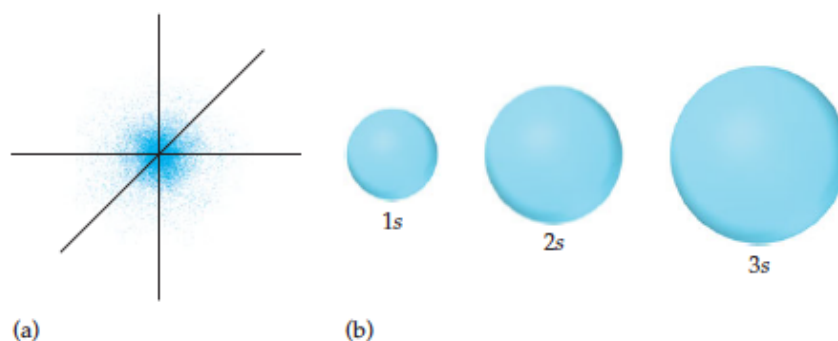
Each sphere is centered on the atom's nucleus and encloses the volume in which there is a 90% probability of finding the electron.

**The *p* Orbitals**

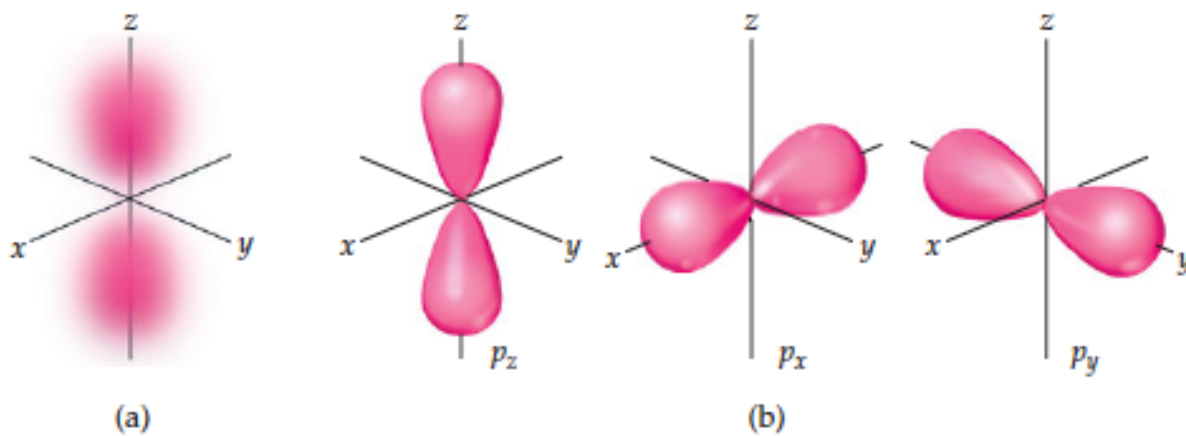There are three *p* orbitals, *px, py,* and *pz.*

      The three *p* orbitals lie along the *x-, y-,* and *z*-axes of a Cartesian system

      The letters correspond to allowed values of $m_l$ of $-1$, 0 and $+1$.

The orbitals are dumb-bell shaped; each has *two lobes.*

As *n* increases, the *p* orbitals get larger

All *p* orbitals have a node at the nucleus.



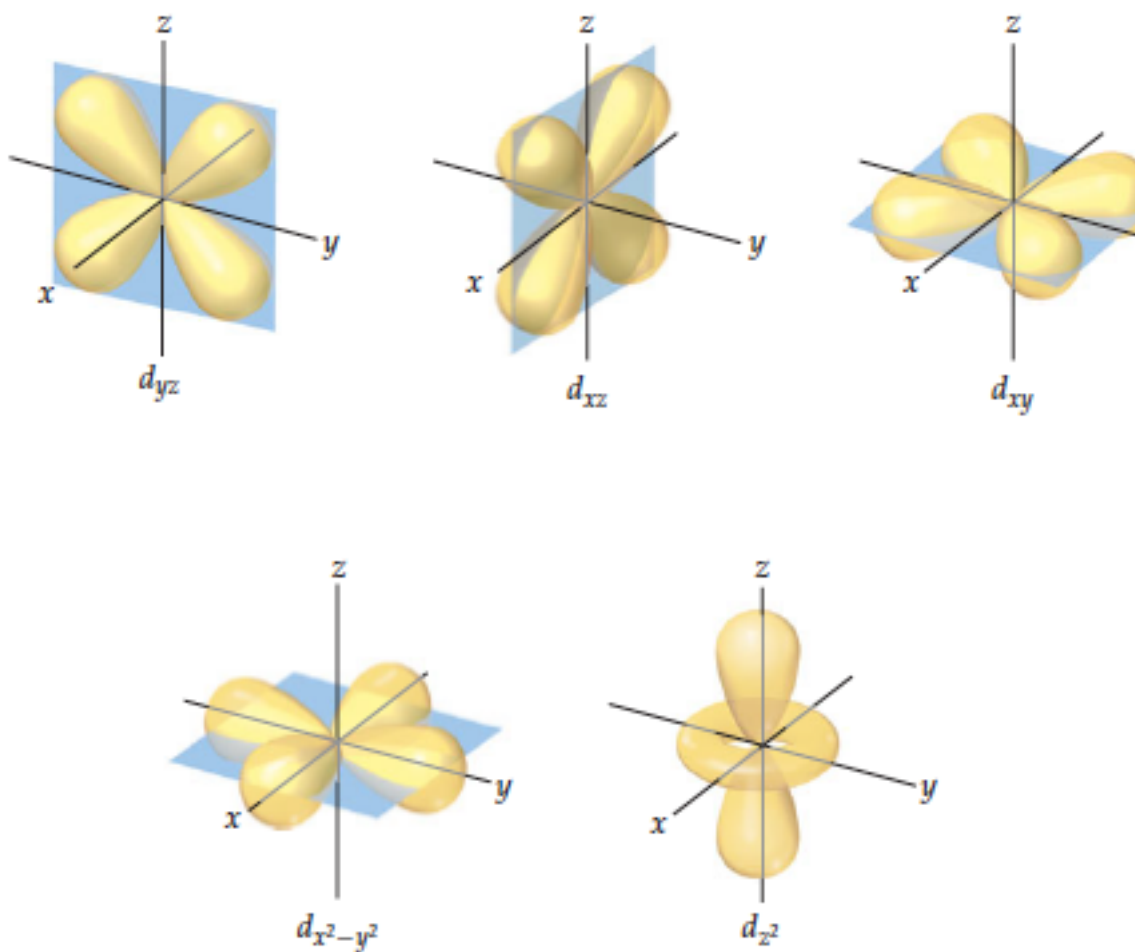(a)                (b)

**The *d* and *f* Orbitals**

There are five d and seven *f* orbitals.

       Three of the *d* orbitals lie in a plane bisecting the *x*-, *y*-, and *z*-axes.

       Two of the *d* orbitals lie in a plane aligned along the *x*-, *y*-, and *z*-axes.

       Four of the *d* orbitals have four lobes each

       One *d* orbital has two lobes and a collar.



Contour representations of the five d orbitals.

## 6.7    Many-Electron Atoms

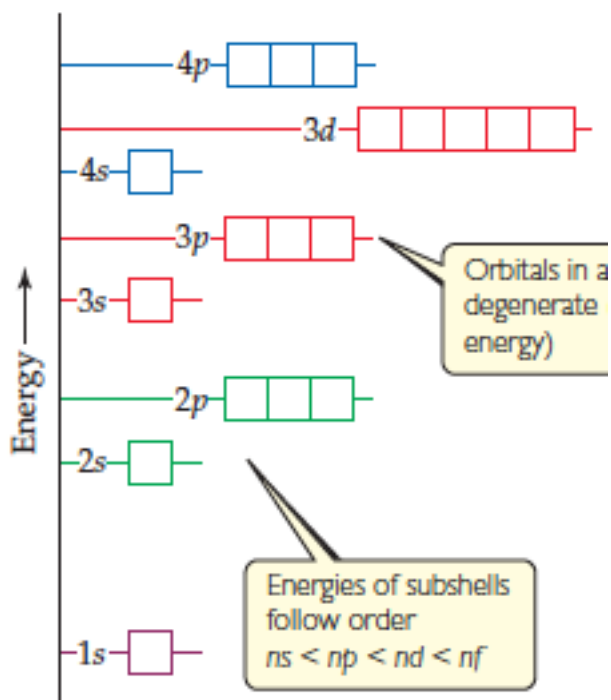**Orbitals and Their Energies**
In many-electron atom, for a given value of $n$,
        The energy of an orbital increases with increasing value of $l$.
Orbitals of the same energy are said to be **degenerate**
For  2, the s and p orbitals are no longer degenerate.
Therefore, the Aufbau digram looks slightly different for many-electron systems.

General energy ordering of orbitals for a many-electron atom.

**Electron Spin and the Pauli Exclusion Principle**
Line spectra of many-electron atoms show each line as a closely spaced pair of lines
Stern and Gerlach designed an experiment to determine why.

A beam of atoms was passed through a slit and into a magnetic field and the
atoms were then detected.

Two spots were found: one with the electrons spinning in one direction and one
with the electrons spinning in the opposite direction.
Since **electron spin** (electron as a tiny sphere spinning on its own axis) is quantized

We define $m_s$ = **spin magnetic quantum number** = 1/2.
**Pauli's exclusion principle** states that no two electrons can have the same set of 4
quantum numbers.

Therefore, two electrons in the same orbit must have opposite spins.
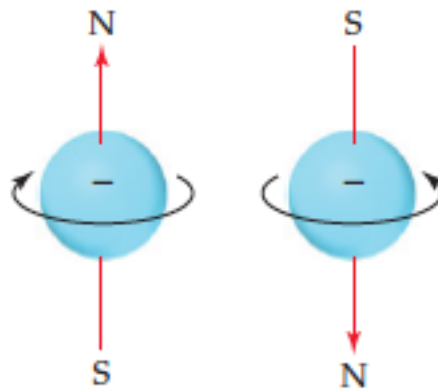


Electron spin. The electron behaves as if it were spinning about an axis, thereby generating a
magnetic field whose direction depends on the direction of spin. The two directions for the
magnetic field correspond to the two possible values for the spin quantum number, . $m_s$, +1/2,
-1/2

## 6.8    Electron Configurations

**Electron configurations** tell us how the electrons are distributed among the various orbitals of an atom.

The most stable configuration or ground state is that in which the electrons are in the lowest possible energy state.

When writing ground-state electronic configurations:

Electrons fill orbitals in order of increasing energy with no more than two electrons per orbital.

No two electrons can fill one orbital with the same spin (Pauli)

For degenerated orbitals, electrons fill each orbital singly before any orbital gets a second electron.

How do we show spin?

An arrow pointing upwards has $m_s = + 1/2$

An arrow pointing downward has $m_s = -1/2$

**Hund's Rule**

**Hund's rule:** for degenerated orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized

Thus electrons fill each orbital singly with their spin parallel before any orbital gets a second electron.

By placing electrons in different orbitals, electron-electron repulsion are minimized.

**TABLE 6.3  •  Electron Configurations of Several Lighter Elements**

| Element | Total Electrons | Orbital Diagram | | | | Electron Configuration |
|---------|-----------------|-----|-----|-----|-----|------------------------|
|         |                 | 1s  | 2s  | 2p  | 3s  |                        |
| Li      | 3               | ⇅   | ↑   |     |     | $1s^2 2s^1$            |
| Be      | 4               | ⇅   | ⇅   |     |     | $1s^2 2s^2$            |
| B       | 5               | ⇅   | ⇅   | ↑   |     | $1s^2 2s^2 2p^1$       |
| C       | 6               | ⇅   | ⇅   | ↑ ↑ |     | $1s^2 2s^2 2p^2$       |
| N       | 7               | ⇅   | ⇅   | ↑ ↑ ↑ |   | $1s^2 2s^2 2p^3$       |
| Ne      | 10              | ⇅   | ⇅   | ⇅ ⇅ ⇅ |   | $1s^2 2s^2 2p^6$       |
| Na      | 11              | ⇅   | ⇅   | ⇅ ⇅ ⇅ | ↑ | $1s^2 2s^2 2p^6 3s^1$  |

**Condensed Electron Configurations**

Electron configurations may be written using shorthand notation (*condensed electron configuration*):

Write **valence electrons** explicitly

**Valence electrons**: electrons in the outer shell.

These electrons are gained and lost in reactions.

Write **core electrons** corresponding to the filled noble gas in square brackets

Core electrons: electrons in the inner shells.

These are generally not involved in bonding.

Example:

P; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

But **Ne** is $1s^2\ 2s^2\ 2p^6$

Therefore, P: [**Ne**] $3s^2\ 3p^3$

**TABLE 6.4** •
**Electron Configurations
of Group 2A and 3A Elements**

**Group 2A**

| | |
|---|---|
| Be | $[He]2s^2$ |
| Mg | $[Ne]3s^2$ |
| Ca | $[Ar]4s^2$ |
| Sr | $[Kr]5s^2$ |
| Ba | $[Xe]6s^2$ |
| Ra | $[Rn]7s^2$ |

**Group 3A**

| | |
|---|---|
| B | $[He]2s^22p^1$ |
| Al | $[Ne]3s^23p^1$ |
| Ga | $[Ar]3d^{10}4s^24p^1$ |
| In | $[Kr]4d^{10}5s^25p^1$ |
| Tl | $[Xe]4f^{14}5d^{10}6s^26p^1$ |

**Transition Metals**
After Ar the d orbitals begin to fill
After the $3d$ orbitals are full the $4p$ orbitals begin to fill
The ten elements between Ti and Zn are called the **transition metals** or **transition elements**.
 The $4f$ orbitals begin to fill with Ce.
      Note:  the electron configuration of La is [Xe] $6s^2\ 5d^1\ 4f^0$
The $4f$ orbitals are filled for the elements Ce-Lu which are called **Lanthanide elements** (or *rare earth elements*)
The $5f$ orbitals are filled for the elements Th-Lr, which are called **actinide elements**.
      Most actinides are not found in nature.

**6.9      Electron Configuratios and the Periodic Table.**
The periodic table can be used as a guide for electron configurations.
The period number is the value of $n$.
Groups 1A and 2A have their $s$ orbitals being filled.
Groups 3A – 8A have their p orbitals being filled.
The $s$-block and $p$-block of the periodic table contain the representative or main-group elements
The lanthanides and actinides have their $f$ orbitals being filled
      The actinides and lathanide elements are collectively referred to as the **f-block** metals.
Note that the $3d$ orbitals fill after the $4s$ orbital.  Similarly, the $4f$ orbitals fill after the $5d$ orbitals.