

Chapter Outline

- 7.1** From Classical Physics to Quantum Theory
- 7.2** The Photoelectric Effect
- 7.3** Bohr's Theory of the Hydrogen Atom
- 7.4** The Dual Nature of the Electron
- 7.5** Quantum Mechanics
- 7.6** Quantum Numbers
- 7.7** Atomic Orbitals
- 7.8** Electron Configuration
- 7.9** The Building-Up Principle

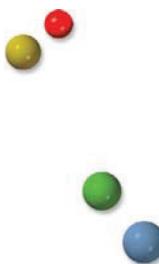
A Look Ahead

- We begin by discussing the transition from classical physics to quantum theory. In particular, we become familiar with properties of waves and electromagnetic radiation and Planck's formulation of the quantum theory. (7.1)
- Einstein's explanation of the photoelectric effect is another step toward the development of the quantum theory. To explain experimental observations, Einstein suggested that light behaves like a bundle of particles called photons. (7.2)
- We then study Bohr's theory for the emission spectrum of the hydrogen atom. In particular, Bohr postulated that the energies of an electron in the atom are quantized and transitions from higher levels to lower ones account for the emission lines. (7.3)
- Some of the mysteries of Bohr's theory are explained by de Broglie who suggested that electrons can behave like waves. (7.4)
- We see that the early ideas of quantum theory led to a new era in physics called quantum mechanics. The Heisenberg uncertainty principle sets the limits for measurement of quantum mechanical systems. The Schrödinger wave equation describes the behavior of electrons in atoms and molecules. (7.5)
- We learn that there are four quantum numbers to describe an electron in an atom and the characteristics of orbitals in which the electrons reside. (7.6 and 7.7)
- Electron configuration enables us to keep track of the distribution of electrons in an atom and understand its magnetic properties. (7.8)
- Finally, we apply the rules in writing electron configurations to the entire periodic table. In particular, we group elements according to their valence electron configurations. (7.9)

Quantum theory enables us to predict and understand the critical role that electrons play in chemistry. In one sense, studying atoms amounts to asking the following questions:

1. How many electrons are present in a particular atom?
2. What energies do individual electrons possess?
3. Where in the atom can electrons be found?

The answers to these questions have a direct relationship to the behavior of all substances in chemical reactions, and the story of the search for answers provides a fascinating backdrop for our discussion.



7.1 From Classical Physics to Quantum Theory

Early attempts by nineteenth-century physicists to understand atoms and molecules met with only limited success. By assuming that molecules behave like rebounding balls, physicists were able to predict and explain some macroscopic phenomena, such as the pressure exerted by a gas. However, this model did not account for the stability of molecules; that is, it could not explain the forces that hold atoms together. It took a long time to realize—and an even longer time to accept—that the properties of atoms and molecules are *not* governed by the same physical laws as larger objects.

The new era in physics started in 1900 with a young German physicist named Max Planck.[†] While analyzing the data on radiation emitted by solids heated to various temperatures, Planck discovered that atoms and molecules emit energy only in certain discrete quantities, or *quanta*. Physicists had always assumed that energy is continuous and that any amount of energy could be released in a radiation process. Planck's *quantum theory* turned physics upside down. Indeed, the flurry of research that ensued altered our concept of nature forever.

Properties of Waves



Figure 7.1 Ocean water waves.

To understand Planck's quantum theory, we must first know something about the nature of waves. A *wave* can be thought of as a *vibrating disturbance by which energy is transmitted*. The fundamental properties of a wave are illustrated by a familiar type—water waves. (Figure 7.1). The regular variation of the peaks and troughs enable us to sense the propagation of the waves.

Waves are characterized by their length and height and by the number of waves that pass through a certain point in one second (Figure 7.2). **Wavelength λ** (lambda) is the distance between identical points on successive waves. The **frequency ν** (nu) is the number of waves that pass through a particular point in 1 second. **Amplitude** is the vertical distance from the midline of a wave to the peak or trough.

[†]Max Karl Ernst Ludwig Planck (1858–1947). German physicist. Planck received the Nobel Prize in Physics in 1918 for his quantum theory. He also made significant contributions in thermodynamics and other areas of physics.

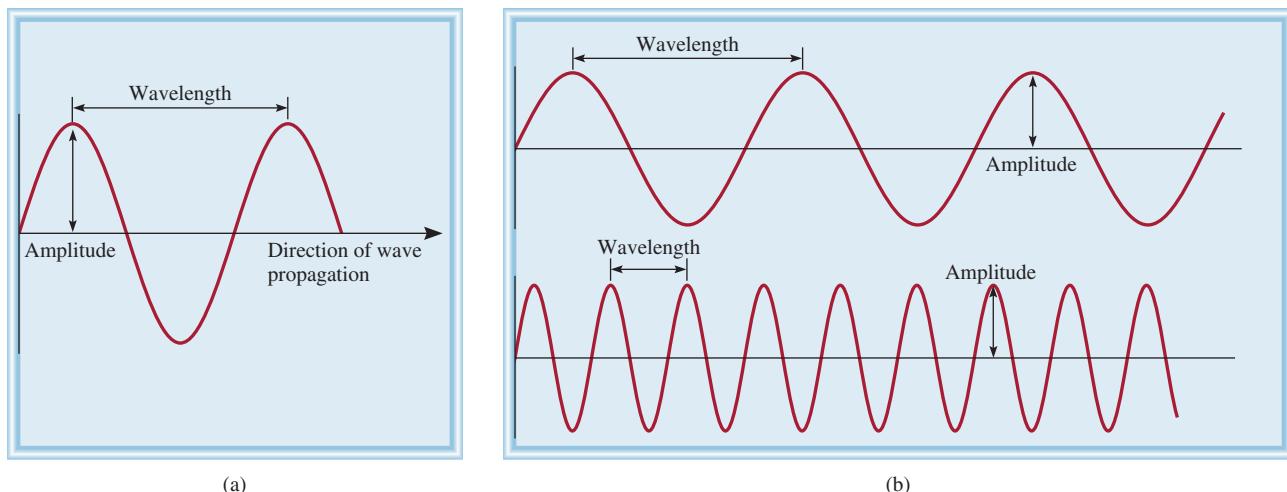


Figure 7.2 (a) Wavelength and amplitude. (b) Two waves having different wavelengths and frequencies. The wavelength of the top wave is three times that of the lower wave, but its frequency is only one-third that of the lower wave. Both waves have the same speed and amplitude.

Another important property of waves is their speed, which depends on the type of wave and the nature of the medium through which the wave is traveling (for example, air, water, or a vacuum). The speed (u) of a wave is the product of its wavelength and its frequency:

$$u = \lambda\nu \quad (7.1)$$

The inherent “sensibility” of Equation (7.1) becomes apparent if we analyze the physical dimensions involved in the three terms. The wavelength (λ) expresses the length of a wave, or distance/wave. The frequency (ν) indicates the number of these waves that pass any reference point per unit of time, or waves/time. Thus, the product of these terms results in dimensions of distance/time, which is speed:

$$\frac{\text{distance}}{\text{time}} = \frac{\text{distance}}{\text{wave}} \times \frac{\text{waves}}{\text{time}}$$

Wavelength is usually expressed in units of meters, centimeters, or nanometers, and frequency is measured in hertz (Hz), where

$$1 \text{ Hz} = 1 \text{ cycle/s}$$

The word “cycle” may be left out and the frequency expressed as, for example, 25/s or 25 s^{-1} (read as “25 per second”).

Electromagnetic Radiation

There are many kinds of waves, such as water waves, sound waves, and light waves. In 1873 James Clerk Maxwell proposed that visible light consists of electromagnetic waves. According to Maxwell’s theory, an *electromagnetic wave has an electric field component and a magnetic field component*. These two components have the same wavelength and frequency, and hence the same speed, but they travel in mutually perpendicular planes (Figure 7.3). The significance of Maxwell’s theory is that it provides a mathematical description of the general behavior of light. In particular, his model accurately describes how energy in the form of radiation can be propagated through space as vibrating electric and magnetic fields. *Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves.*

Sound waves and water waves are not electromagnetic waves, but X rays and radio waves are.

Electromagnetic waves travel 3.00×10^8 meters per second (rounded off), or 186,000 miles per second in a vacuum. This speed differs from one medium to another, but not enough to distort our calculations significantly. By convention, we use the symbol c for the speed of electromagnetic waves, or as it is more commonly called, the *speed of light*. The wavelength of electromagnetic waves is usually given in nanometers (nm).

A more accurate value for the speed of light is given on the inside back cover of the book.

EXAMPLE 7.1

The wavelength of the green light from a traffic signal is centered at 522 nm. What is the frequency of this radiation?

Strategy We are given the wavelength of an electromagnetic wave and asked to calculate its frequency. Rearranging Equation (7.1) and replacing u with c (the speed of light) gives

$$\nu = \frac{c}{\lambda}$$

(Continued)

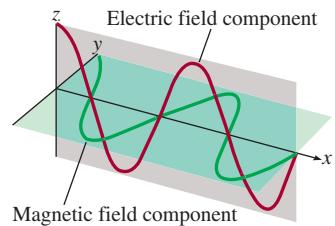


Figure 7.3 The electric field and magnetic field components of an electromagnetic wave. These two components have the same wavelength, frequency, and amplitude, but they vibrate in two mutually perpendicular planes.

Solution Because the speed of light is given in meters per second, it is convenient to first convert wavelength to meters. Recall that $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ (see Table 1.3). We write

$$\begin{aligned}\lambda &= 522 \text{ nm} \times \frac{1 \times 10^{-9} \text{ m}}{1 \text{ nm}} = 522 \times 10^{-9} \text{ m} \\ &= 5.22 \times 10^{-7} \text{ m}\end{aligned}$$

Substituting in the wavelength and the speed of light ($3.00 \times 10^8 \text{ m/s}$), the frequency is

$$\begin{aligned}\nu &= \frac{3.00 \times 10^8 \text{ m/s}}{5.22 \times 10^{-7} \text{ m}} \\ &= 5.75 \times 10^{14} \text{ s}^{-1} \text{, or } 5.75 \times 10^{14} \text{ Hz}\end{aligned}$$

Check The answer shows that 5.75×10^{14} waves pass a fixed point every second. This very high frequency is in accordance with the very high speed of light.

Figure 7.4 shows various types of electromagnetic radiation, which differ from one another in wavelength and frequency. The long radio waves are emitted by large antennas, such as those used by broadcasting stations. The shorter, visible light waves

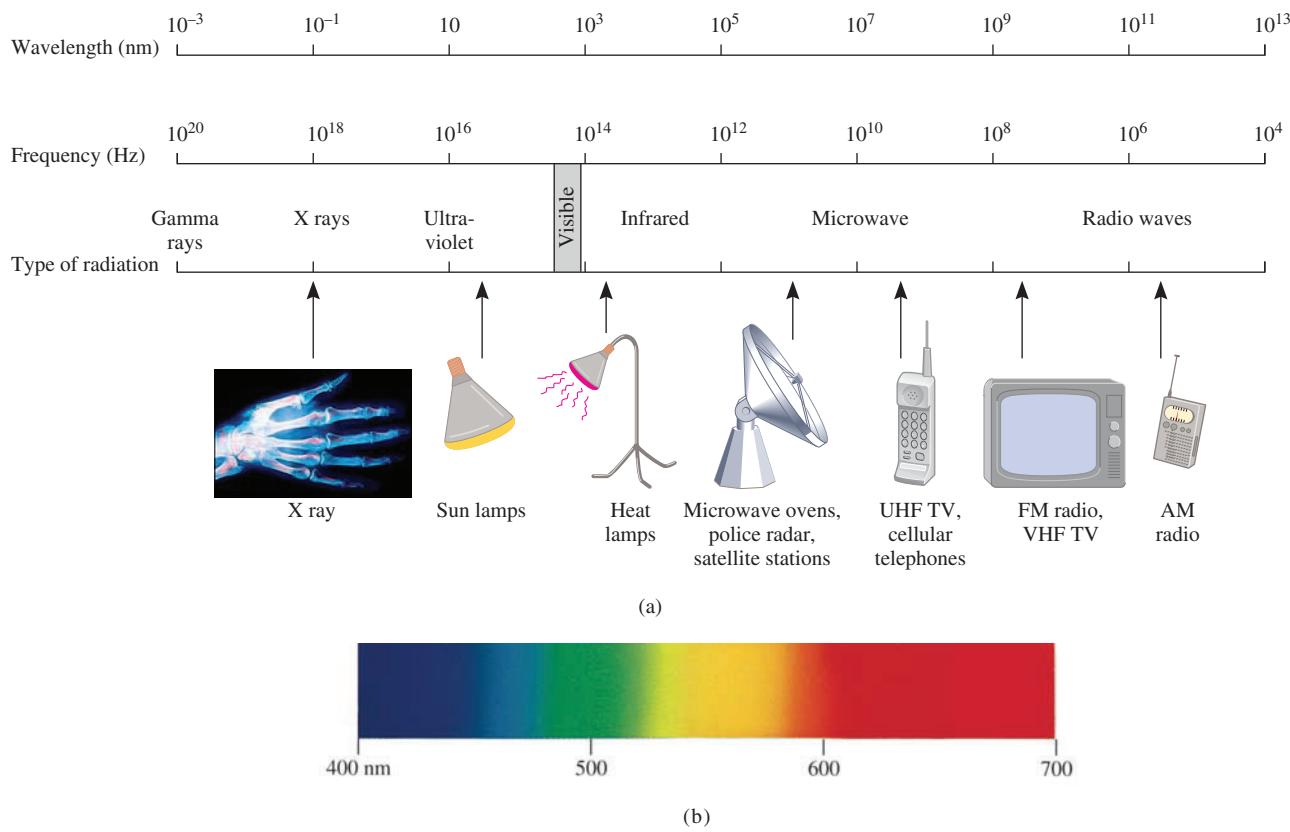


Figure 7.4 (a) Types of electromagnetic radiation. Gamma rays have the shortest wavelength and highest frequency; radio waves have the longest wavelength and the lowest frequency. Each type of radiation is spread over a specific range of wavelengths (and frequencies). (b) Visible light ranges from a wavelength of 400 nm (violet) to 700 nm (red).

are produced by the motions of electrons within atoms and molecules. The shortest waves, which also have the highest frequency, are associated with γ (gamma) rays, which result from changes within the nucleus of the atom (see Chapter 2). As we will see shortly, the higher the frequency, the more energetic the radiation. Thus, ultraviolet radiation, X rays, and γ rays are high-energy radiation.

Planck's Quantum Theory

When solids are heated, they emit electromagnetic radiation over a wide range of wavelengths. The dull red glow of an electric heater and the bright white light of a tungsten lightbulb are examples of radiation from heated solids.

Measurements taken in the latter part of the nineteenth century showed that the amount of radiant energy emitted by an object at a certain temperature depends on its wavelength. Attempts to account for this dependence in terms of established wave theory and thermodynamic laws were only partially successful. One theory explained short-wavelength dependence but failed to account for the longer wavelengths. Another theory accounted for the longer wavelengths but failed for short wavelengths. It seemed that something fundamental was missing from the laws of classical physics.

Planck solved the problem with an assumption that departed drastically from accepted concepts. Classical physics assumed that atoms and molecules could emit (or absorb) any arbitrary amount of radiant energy. Planck said that atoms and molecules could emit (or absorb) energy only in discrete quantities, like small packages or bundles. Planck gave the name **quantum** to the *smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation*. The energy E of a single quantum of energy is given by

$$E = h\nu \quad (7.2)$$

where h is called *Planck's constant* and ν is the frequency of radiation. The value of Planck's constant is $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$. Because $\nu = c/\lambda$, Equation (7.2) can also be expressed as

$$E = h\frac{c}{\lambda} \quad (7.3)$$

According to quantum theory, energy is always emitted in integral multiples of $h\nu$; for example, $h\nu$, $2 h\nu$, $3 h\nu$, . . . , but never, for example, $1.67 h\nu$ or $4.98 h\nu$. At the time Planck presented his theory, he could not explain why energies should be fixed or quantized in this manner. Starting with this hypothesis, however, he had no trouble correlating the experimental data for emission by solids over the *entire* range of wavelengths; they all supported the quantum theory.

The idea that energy should be quantized or “bundled” may seem strange, but the concept of quantization has many analogies. For example, an electric charge is also quantized; there can be only whole-number multiples of e , the charge of one electron. Matter itself is quantized, for the numbers of electrons, protons, and neutrons and the numbers of atoms in a sample of matter must also be integers. Our money system is based on a “quantum” of value called a penny. Even processes in living systems involve quantized phenomena. The eggs laid by hens are quantized, and a pregnant cat gives birth to an integral number of kittens, not to one-half or three-quarters of a kitten.

The failure in the short-wavelength region is called the *ultraviolet catastrophe*.

7.2 The Photoelectric Effect

In 1905, only five years after Planck presented his quantum theory, Albert Einstein[†] used the theory to solve another mystery in physics, the **photoelectric effect**, a phenomenon in which *electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency*, called *the threshold frequency* (Figure 7.5). The number of electrons ejected was proportional to the intensity (or brightness) of the light, but the energies of the ejected electrons were not. Below the threshold frequency no electrons were ejected no matter how intense the light.

The photoelectric effect could not be explained by the wave theory of light. Einstein, however, made an extraordinary assumption. He suggested that a beam of light is really a stream of particles. These *particles of light* are now called **photons**. Using Planck's quantum theory of radiation as a starting point, Einstein deduced that each photon must possess energy E , given by the equation

$$E = h\nu$$

where ν is the frequency of light.

EXAMPLE 7.2

Calculate the energy (in joules) of (a) a photon with a wavelength of 5.00×10^4 nm (infrared region) and (b) a photon with a wavelength of 5.00×10^{-2} nm (X ray region).

Strategy In both (a) and (b) we are given the wavelength of a photon and asked to calculate its energy. We need to use Equation (7.3) to calculate the energy. Planck's constant is given in the text and also on the back inside cover.

Solution (a) From Equation (7.3),

$$\begin{aligned} E &= h\frac{c}{\lambda} \\ &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(5.00 \times 10^4 \text{ nm}) \frac{1 \times 10^{-9} \text{ m}}{1 \text{ nm}}} \\ &= 3.98 \times 10^{-21} \text{ J} \end{aligned}$$

This is the energy of a single photon with a 5.00×10^4 nm wavelength.

(b) Following the same procedure as in (a), we can show that the energy of the photon that has a wavelength of 5.00×10^{-2} nm is 3.98×10^{-15} J.

The equation for the energy of the photon has the same form as Equation (7.2) because, as we will see shortly, electromagnetic radiation is emitted as well as absorbed in the form of photons.

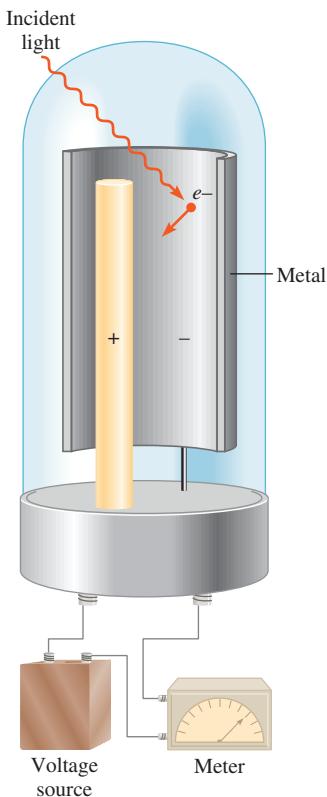


Figure 7.5 An apparatus for studying the photoelectric effect. Light of a certain frequency falls on a clean metal surface. Ejected electrons are attracted toward the positive electrode. The flow of electrons is registered by a detecting meter. Light meters used in cameras are based on photoelectric effect.

(Continued)

[†]Albert Einstein (1879–1955). German-born American physicist. Regarded by many as one of the two greatest physicists the world has known (the other is Isaac Newton). The three papers (on special relativity, Brownian motion, and the photoelectric effect) that he published in 1905 while employed as a technical assistant in the Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

Check Because the energy of a photon increases with decreasing wavelength, we see that an “X-ray” photon is 1×10^6 , or a million times, more energetic than an “infrared” photon.

Practice Exercise The energy of a photon is 5.87×10^{-20} J. What is its wavelength (in nanometers)?

Similar problem: 7.15.



Electrons are held in a metal by attractive forces, and so removing them from the metal requires light of a sufficiently high frequency (which corresponds to sufficiently high energy) to break them free. Shining a beam of light onto a metal surface can be thought of as shooting a beam of particles—photons—at the metal atoms. If the frequency of photons is such that $h\nu$ is exactly equal to the energy that binds the electrons in the metal, then the light will have just enough energy to knock the electrons loose. If we use light of a higher frequency, then not only will the electrons be knocked loose, but they will also acquire some kinetic energy. T

Now consider two beams of light having the same frequency (which is greater than the threshold frequency) but different intensities. The more intense beam of light consists of a larger number of photons; consequently, it ejects more electrons from the metal’s surface than the weaker beam of light. Thus, the more intense the light, the greater the number of electrons emitted by the target metal; the higher the frequency of the light, the greater the kinetic energy of the ejected electrons.

Einstein's theory of light posed a dilemma for scientists. On the one hand, it explains the photoelectric effect satisfactorily. On the other hand, the particle theory of light is not consistent with the known wave behavior of light. The only way to resolve the dilemma is to accept the idea that light possesses *both* particlelike and wavelike properties. Depending on the experiment, light behaves either as a wave or as a stream of particles. This concept, called particle-wave duality, was totally alien to the way physicists had thought about matter and radiation, and it took a long time for them to accept it. We will see in Section 7.4 that a dual nature (particles and waves) is not unique to light but is characteristic of all matter, including electrons.

7.3 Bohr's Theory of the Hydrogen Atom

Einstein's work paved the way for the solution of yet another nineteenth-century "mystery" in physics: the emission spectra of atoms.

Emission Spectra

Ever since the seventeenth century, when Newton showed that sunlight is composed of various color components that can be recombined to produce white light, chemists and physicists have studied the characteristics of **emission spectra**, that is, *either continuous or line spectra of radiation emitted by substances*. The emission spectrum of a substance can be seen by energizing a sample of material either with thermal energy or with some other form of energy (such as a high-voltage electrical discharge). A "red-hot" or "white-hot" iron bar freshly removed from a high-temperature source produces a characteristic glow. This visible glow is the portion of its emission spectrum that is

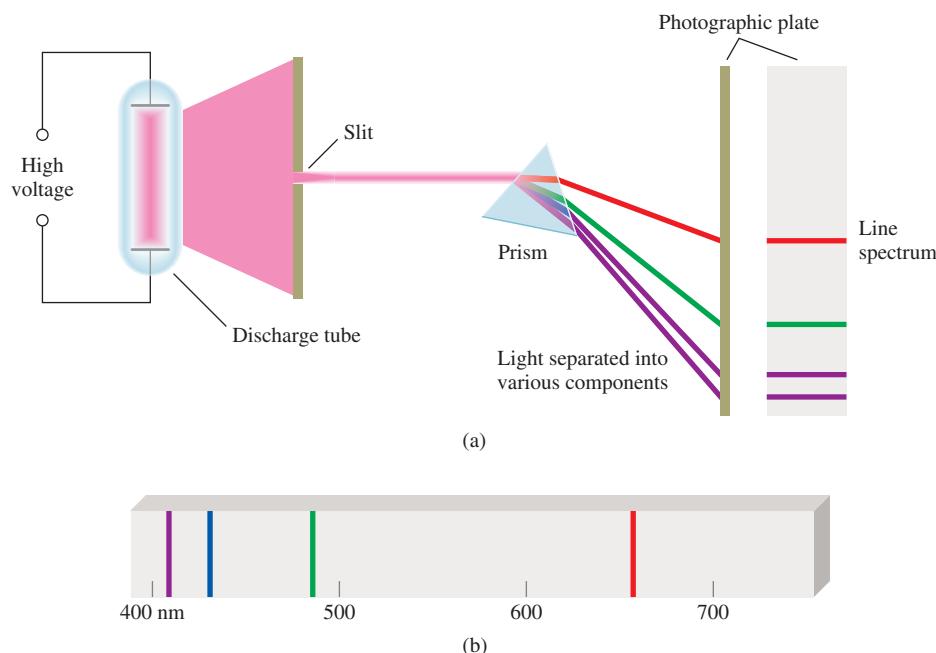


Figure 7.6 (a) An experimental arrangement for studying the emission spectra of atoms and molecules. The gas under study is in a discharge tube containing two electrodes. As electrons flow from the negative electrode to the positive electrode, they collide with the gas. This collision process eventually leads to the emission of light by the atoms (or molecules). The emitted light is separated into its components by a prism. Each component color is focused at a definite position, according to its wavelength, and forms a colored image of the slit on the photographic plate. The colored images are called spectral lines. (b) The line emission spectrum of hydrogen atoms.

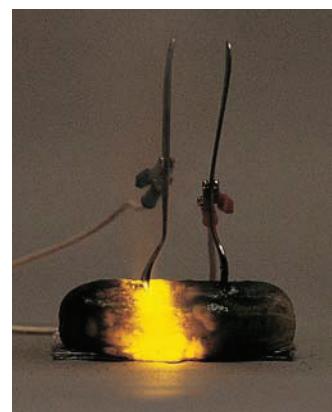
sensed by eye. The warmth of the same iron bar represents another portion of its emission spectrum—the infrared region. A feature common to the emission spectra of the sun and of a heated solid is that both are continuous; that is, all wavelengths of visible light are represented in the spectra (see the visible region in Figure 7.4).

The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelengths from red to violet; rather, the atoms produce bright lines in different parts of the visible spectrum. These **line spectra** are the light emission only at specific wavelengths. Figure 7.6 is a schematic diagram of a discharge tube that is used to study emission spectra, and Figure 7.7 on p. 284 shows the color emitted by hydrogen atoms in a discharge tube.

Every element has a unique emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms, much as fingerprints are used to identify people. When the lines of the emission spectrum of a known element exactly match the lines of the emission spectrum of an unknown sample, the identity of the sample is established. Although the utility of this procedure was recognized some time ago in chemical analysis, the origin of these lines was unknown until early in the twentieth century. Figure 7.8 shows the emission spectra of several elements.

Emission Spectrum of the Hydrogen Atom

In 1913, not too long after Planck's and Einstein's discoveries, a theoretical explanation of the emission spectrum of the hydrogen atom was presented by the Danish physicist Niels Bohr.[†] Bohr's treatment is very complex and is no longer considered to be correct in all its details. Thus, we will concentrate only on his important assumptions and final results, which do account for the spectral lines.



When a high voltage is applied between the forks, some of the sodium ions in the pickle are converted to sodium atoms in an excited state. These atoms emit the characteristic yellow light as they relax to the ground state.

[†]Niels Henrik David Bohr (1885–1962). Danish physicist. One of the founders of modern physics, he received the Nobel Prize in Physics in 1922 for his theory explaining the spectrum of the hydrogen atom.

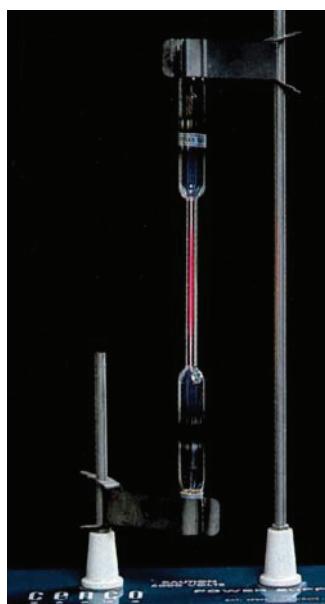


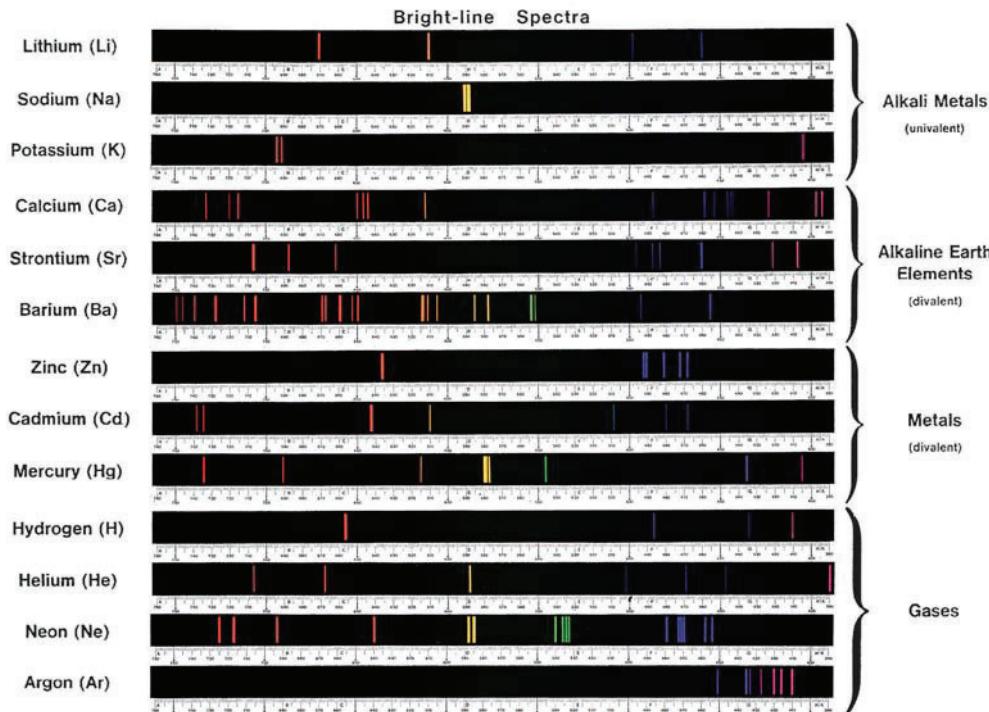
Figure 7.7 Color emitted by hydrogen atoms in a discharge tube. The color observed results from the combination of the colors emitted in the visible spectrum.

When Bohr first tackled this problem, physicists already knew that the atom contains electrons and protons. They thought of an atom as an entity in which electrons whirled around the nucleus in circular orbits at high velocities. This was an appealing model because it resembled the motions of the planets around the sun. In the hydrogen atom, it was believed that the electrostatic attraction between the positive “solar” proton and the negative “planetary” electron pulls the electron inward and that this force is balanced exactly by the outward acceleration due to the circular motion of the electron.

According to the laws of classical physics, however, an electron moving in an orbit of a hydrogen atom would experience an acceleration toward the nucleus by radiating away energy in the form of electromagnetic waves. Thus, such an electron would quickly spiral into the nucleus and annihilate itself with the proton. To explain why this does not happen, Bohr postulated that the electron is allowed to occupy only certain orbits of specific energies. In other words, the energies of the electron are quantized. An electron in any of the allowed orbits will not spiral into the nucleus and therefore will not radiate energy. Bohr attributed the emission of radiation by an energized hydrogen atom to the electron dropping from a higher-energy allowed orbit to a lower one and emitting a quantum of energy (a photon) in the form of light (Figure 7.9).

[†]Johannes Robert Rydberg (1854–1919). Swedish physicist. Rydberg's major contribution to physics was his study of the line spectra of many elements.

Figure 7.8 The emission spectra of various elements.



The **ground state**, or the **ground level**, which refers to *the lowest energy state of a system* (which is an atom in our discussion). The sta-

bility of the electron diminishes for $n = 2, 3, \dots$. Each of these levels is called an **excited state**, or **excited level**, which is *higher in energy than the ground state*. A hydrogen electron for which n is greater than 1 is said to be in an excited state. The radius of each circular orbit in Bohr's model depends on n^2 . Thus, as n increases from 1 to 2 to 3, the orbit radius increases very rapidly. The higher the excited state, the farther away the electron is from the nucleus (and the less tightly it is held by the nucleus).

Bohr's theory enables us to explain the line spectrum of the hydrogen atom. Radiant energy absorbed by the atom causes the electron to move from a lower-energy state (characterized by a smaller n value) to a higher-energy state (characterized by a larger n value). Conversely, radiant energy (in the form of a photon) is emitted when the electron moves from a higher-energy state to a lower-energy state. The quantized movement of the electron from one energy state to another is analogous to the movement of a tennis ball either up or down a set of stairs (Figure 7.10). The ball can be on any of several steps but never between steps. The journey from a lower step to a higher one is an energy-requiring process, whereas movement from a higher step to a lower step is an energy-releasing process. The quantity of energy involved in either type of change is determined by the distance between the beginning and ending steps. Similarly, the amount of energy needed to move an electron in the Bohr atom depends on the difference in energy levels between the initial and final states.

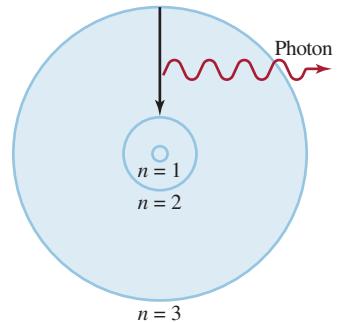


Figure 7.9 The emission process in an excited hydrogen atom, according to Bohr's theory. An electron originally in a higher-energy orbit ($n = 3$) falls back to a lower-energy orbit ($n = 2$). As a result, a photon with energy $h\nu$ is given off. The value of $h\nu$ is equal to the difference in energies of the two orbits occupied by the electron in the emission process. For simplicity, only three orbits are shown.

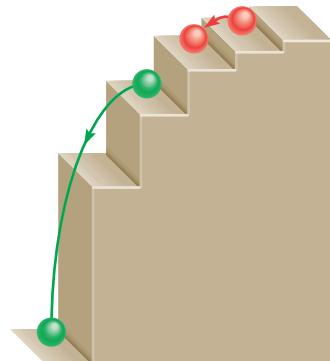


Figure 7.10 A mechanical analogy for the emission processes. The ball can rest on any step but not between steps.

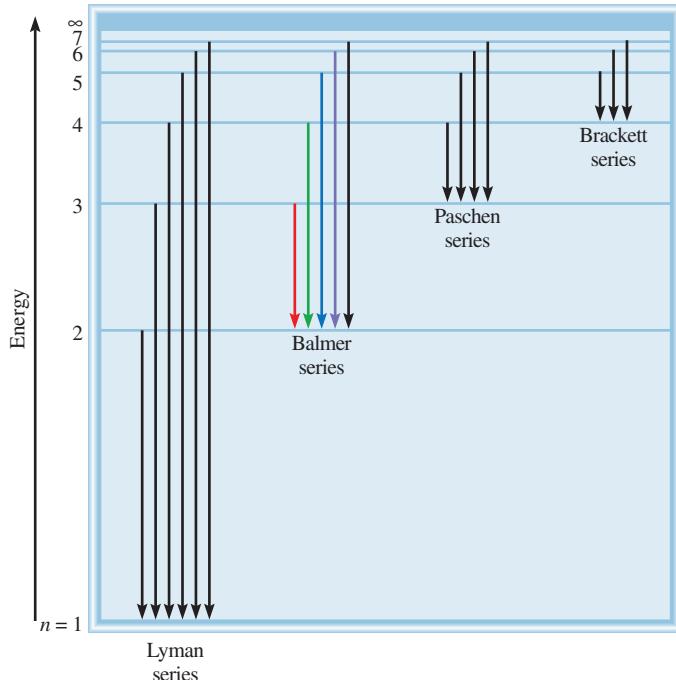
TABLE 7.1 The Various Series in Atomic Hydrogen Emission Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared

When we study a large number of hydrogen atoms, we observe all possible transitions and hence the corresponding spectral lines. The brightness of a spectral line depends on how many photons of the same wavelength are emitted.

The emission spectrum of hydrogen includes a wide range of wavelengths from the infrared to the ultraviolet. Table 7.1 lists the series of transitions in the hydrogen spectrum; they are named after their discoverers. The Balmer series was particularly easy to study because a number of its lines fall in the visible range. Figure 7.9 shows a single transition. However, it is more informative to express transitions as shown in Figure 7.11. Each horizontal line represents an allowed energy level for the electron in a hydrogen atom. The energy levels are labeled with their principal quantum numbers.

Figure 7.11 The energy levels in the hydrogen atom and the various emission series. Each energy level corresponds to the energy associated with an allowed energy state for an orbit, as postulated by Bohr and shown in Figure 7.9. The emission lines are labeled according to the scheme in Table 7.1.

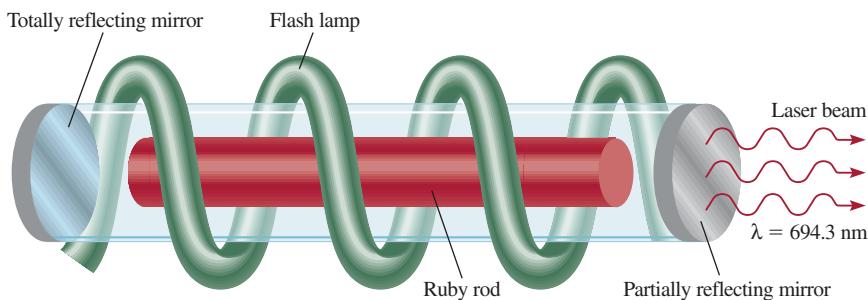


Laser—The Splendid Light

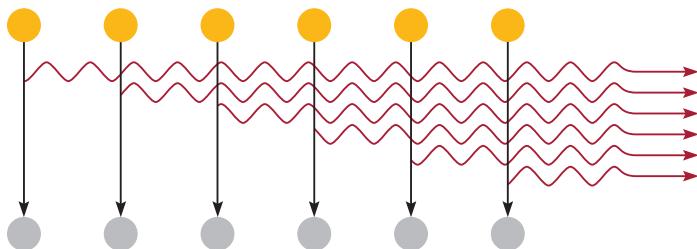
Laser is an acronym for light amplification by stimulated emission of radiation. It is a special type of emission that involves either atoms or molecules. Since the discovery of laser in 1960, it has been used in numerous systems designed to operate in the gas, liquid, and solid states. These systems emit

radiation with wavelengths ranging from infrared through visible and ultraviolet. The advent of laser has truly revolutionized science, medicine, and technology.

Ruby laser was the first known laser. Ruby is a deep-red mineral containing corundum, Al_2O_3 , in which some of the Al^{3+}



The emission of laser light from a ruby laser.



The stimulated emission of one photon by another photon in a cascade event that leads to the emission of laser light. The synchronization of the light waves produces an intensely penetrating laser beam.

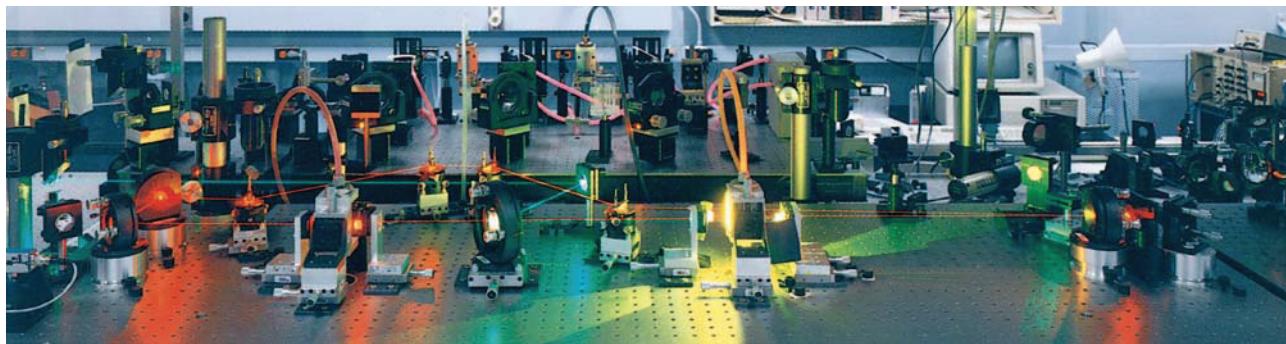
7.4 The Dual Nature of the Electron

Physicists were both mystified and intrigued by Bohr's theory. They questioned why the energies of the hydrogen electron are quantized. Or, phrasing the question in a more concrete way, Why is the electron in a Bohr atom restricted to orbiting the nucleus at certain fixed distances? For a decade no one, not even Bohr himself, had a logical explanation. In 1924 Louis de Broglie[†] provided a solution to this puzzle. De Broglie reasoned that if light waves can behave like a stream of particles (photons), then perhaps particles such as electrons can possess wave properties. According to de Broglie, an electron bound to the nucleus behaves like a *standing wave*. Standing

[†]Louis Victor Pierre Raymond Duc de Broglie (1892–1977). French physicist. Member of an old and noble family in France, he held the title of a prince. In his doctoral dissertation, he proposed that matter and radiation have the properties of both wave and particle. For this work, de Broglie was awarded the Nobel Prize in Physics in 1929.

ions have been replaced by Cr^{3+} ions. A flashlamp is used to excite the chromium atoms to a higher energy level. The excited atoms are unstable, so at a given instant some of them will return to the ground state by emitting a photon in the red region of the spectrum. The photon bounces back and forth many times between mirrors at opposite ends of the laser tube. This photon can stimulate the emission of photons of exactly the same wavelength from other excited chromium atoms; these photons in turn can stimulate the emission of more photons, and so on. Because the light waves are *in phase*—that is, their maxima and minima coincide—the photons enhance one another, increasing their power with each passage between the mirrors. One of the mirrors is only partially reflecting, so that when the light reaches a certain intensity it emerges from the mirror as a laser beam. Depending on the mode of operation, the laser light may be emitted in pulses (as in the ruby laser case) or in continuous waves.

Laser light is characterized by three properties: It is intense, it has precisely known wavelength and hence energy, and it is coherent. By *coherent* we mean that the light waves are all in phase. The applications of lasers are quite numerous. Their high intensity and ease of focus make them suitable for doing eye surgery, for drilling holes in metals and welding, and for carrying out nuclear fusion. The fact that they are highly directional and have precisely known wavelengths makes them very useful for telecommunications. Lasers are also used in isotope separation, in holography (three-dimensional photography), in compact disc players, and in supermarket scanners. Lasers have played an important role in the spectroscopic investigation of molecular properties and of many chemical and biological processes. Laser lights are increasingly being used to probe the details of chemical reactions (see Chapter 13).



State-of-the-art lasers used in the research laboratory of Dr. A. H. Zewail at the California Institute of Technology.

waves can be generated by plucking, say, a guitar string (Figure 7.12). The waves are described as standing, or stationary, because they do not travel along the string. Some points on the string, called **nodes**, do not move at all; that is, *the amplitude of the wave at these points is zero*. There is a node at each end, and there may be nodes between the ends. The greater the frequency of vibration, the shorter the wavelength of the standing wave and the greater the number of nodes. As Figure 7.12 shows, there can be only certain wavelengths in any of the allowed motions of the string.

De Broglie argued that if an electron does behave like a standing wave in the hydrogen atom, the length of the wave must fit the circumference of the orbit exactly

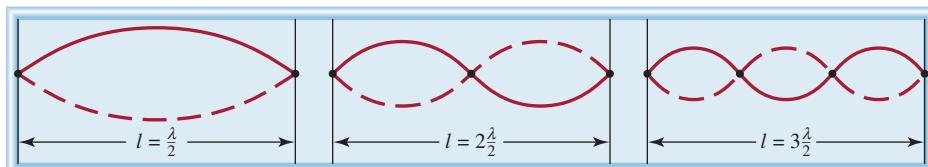
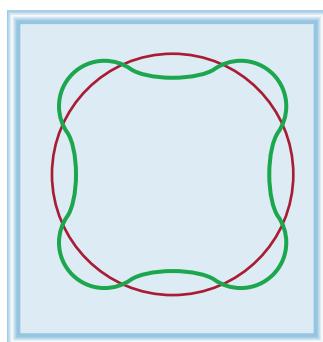
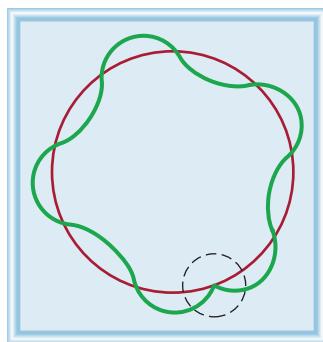


Figure 7.12 The standing waves generated by plucking a guitar string. Each dot represents a node. The length of the string (l) must be equal to a whole number times one-half the wavelength ($\lambda/2$).

(Figure 7.13). Otherwise the wave would partially cancel itself on each successive orbit. Eventually the amplitude of the wave would be reduced to zero, and the wave would not exist.



(a)



(b)

Figure 7.13 (a) The circumference of the orbit is equal to an integral number of wavelengths. This is an allowed orbit. (b) The circumference of the orbit is not equal to an integral number of wavelengths. As a result, the electron wave does not close in on itself. This is a nonallowed orbit.

7.5 Quantum Mechanics

The spectacular success of Bohr's theory was followed by a series of disappointments. Bohr's approach did not account for the emission spectra of atoms containing more than one electron, such as atoms of helium and lithium. Nor did it explain why extra lines appear in the hydrogen emission spectrum when a magnetic field is applied. Another problem arose with the discovery that electrons are wavelike: How can the "position" of a wave be specified? We cannot define the precise location of a wave because a wave extends in space.

To describe the problem of trying to locate a subatomic particle that behaves like a wave, Werner Heisenberg[†] formulated what is now known as the **Heisenberg uncertainty principle**: *it is impossible to know simultaneously both the momentum p (defined as mass times velocity) and the position of a particle with certainty.*

In reality, Bohr's theory accounted for the observed emission spectra of He^+ and Li^{2+} ions, as well as that of hydrogen. However, all three systems have one feature in common—each contains a single electron. Thus, the Bohr model worked successfully only for the hydrogen atom and for "hydrogenlike ions."

Applying the Heisenberg uncertainty principle to the hydrogen atom, we see that in reality the electron does not orbit the nucleus in a well-defined path, as Bohr thought. If it did, we could determine precisely both the position of the electron (from its location on a particular orbit) and its momentum (from its kinetic energy) at the same time, a violation of the uncertainty principle.

To be sure, Bohr made a significant contribution to our understanding of atoms, and his suggestion that the energy of an electron in an atom is quantized remains unchallenged. But his theory did not provide a complete description of electronic behavior in atoms. In 1926 the Austrian physicist Erwin Schrödinger,[‡] using a complicated mathematical technique, formulated an equation that describes the behavior and energies of submicroscopic particles in general, an equation analogous to Newton's laws of motion for macroscopic objects. The *Schrödinger equation* requires advanced calculus to solve, and we will not discuss it here. It is important to know, however, that the equation incorporates both particle behavior, in terms of mass m , and wave behavior, in terms of a *wave function ψ* (psi), which depends on the location in space of the system (such as an electron in an atom). The wave function itself has no direct physical meaning. However, the probability of finding the electron in a certain region in space is proportional to the square of

[†]Werner Karl Heisenberg (1901–1976). German physicist. One of the founders of modern quantum theory, Heisenberg received the Nobel Prize in Physics in 1932.

[‡]Erwin Schrödinger (1887–1961). Austrian physicist. Schrödinger formulated wave mechanics, which laid the foundation for modern quantum theory. He received the Nobel Prize in Physics in 1933.



Figure 7.15 A representation of the electron density distribution surrounding the nucleus in the hydrogen atom. It shows a high probability of finding the electron closer to the nucleus.

Although the helium atom has only two electrons, in quantum mechanics it is regarded as a many-electron atom.

the wave function, ψ^2 . The idea of relating ψ^2 to probability stemmed from a wave theory analogy. According to wave theory, the intensity of light is proportional to the square of the amplitude of the wave, or ψ^2 . The most likely place to find a photon is where the intensity is greatest, that is, where the value of ψ^2 is greatest. A similar argument associates ψ^2 with the likelihood of finding an electron in regions surrounding the nucleus.

Schrödinger's equation began a new era in physics and chemistry, for it launched a new field, *quantum mechanics* (also called *wave mechanics*). We now refer to the developments in quantum theory from 1913—the time Bohr presented his analysis for the hydrogen atom—to 1926 as “old quantum theory.”

The Quantum Mechanical Description of the Hydrogen Atom

The Schrödinger equation specifies the possible energy states the electron can occupy in a hydrogen atom and identifies the corresponding wave functions (ψ). These energy states and wave functions are characterized by a set of quantum numbers (to be discussed shortly), with which we can construct a comprehensive model of the hydrogen atom.

Although quantum mechanics tells us that we cannot pinpoint an electron in an atom, it does define the region where the electron might be at a given time. The concept of *electron density* gives the probability that an electron will be found in a particular region of an atom. The square of the wave function, ψ^2 , defines the distribution of electron density in three-dimensional space around the nucleus. Regions of high electron density represent a high probability of locating the electron, whereas the opposite holds for regions of low electron density (Figure 7.15).

To distinguish the quantum mechanical description of an atom from Bohr's model, we speak of an atomic orbital, rather than an orbit. An *atomic orbital* can be thought of as the wave function of an electron in an atom. When we say that an electron is in a certain orbital, we mean that the distribution of the electron density or the probability of locating the electron in space is described by the square of the wave function associated with that orbital. An atomic orbital, therefore, has a characteristic energy, as well as a characteristic distribution of electron density.

The Schrödinger equation works nicely for the simple hydrogen atom with its one proton and one electron, but it turns out that it cannot be solved exactly for any atom containing more than one electron! Fortunately, chemists and physicists have learned to get around this kind of difficulty by approximation. For example, although the behavior of electrons in *many-electron atoms* (that is, atoms containing two or more electrons) is not the same as in the hydrogen atom, we assume that the difference is probably not too great. Thus, we can use the energies and wave functions obtained from the hydrogen atom as good approximations of the behavior of electrons in more complex atoms. In fact, this approach provides fairly reliable descriptions of electronic behavior in many-electron atoms.

7.6 Quantum Numbers

In quantum mechanics, three *quantum numbers* are required to describe the distribution of electrons in hydrogen and other atoms. These numbers are derived from the mathematical solution of the Schrödinger equation for the hydrogen atom. They are called the *principal quantum number*, the *angular momentum quantum number*, and the *magnetic quantum number*. These quantum numbers will be used to describe

atomic orbitals and to label electrons that reside in them. A fourth quantum number—the *spin quantum number*—describes the behavior of a specific electron and completes the description of electrons in atoms.

The Principal Quantum Number (n)

The principal quantum number (n) can have integral values 1, 2, 3, and so forth; it corresponds to the quantum number in Equation (7.5). In a hydrogen atom, the value of n determines the energy of an orbital. As we will see shortly, this is not the case for a many-electron atom. The principal quantum number also relates to the average distance of the electron from the nucleus in a particular orbital. The larger n is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital.

The Angular Momentum Quantum Number (ℓ)

The angular momentum quantum number (ℓ) tells us the “shape” of the orbitals (see Section 7.7). The values of ℓ depend on the value of the principal quantum number, n . For a given value of n , ℓ has possible integral values from 0 to $(n - 1)$. If $n = 1$, there is only one possible value of ℓ ; that is, $\ell = n - 1 = 1 - 1 = 0$. If $n = 2$, there are two values of ℓ , given by 0 and 1. If $n = 3$, there are three values of ℓ , given by 0, 1, and 2. The value of ℓ is generally designated by the letters s, p, d, \dots as follows:

ℓ	0	1	2	3	4	5
Name of orbital	s	p	d	f	g	h

Thus, if $\ell = 0$, we have an s orbital; if $\ell = 1$, we have a p orbital; and so on.

The unusual sequence of letters (s, p , and d) has a historical origin. Physicists who studied atomic emission spectra tried to correlate the observed spectral lines with the particular energy states involved in the transitions. They noted that some of the lines were sharp; some were rather spread out, or *diffuse*; and some were very strong and hence referred to as *principal* lines. Subsequently, the initial letters of each adjective were assigned to those energy states. However, after the letter d and starting with the letter f (for *fundamental*), the orbital designations follow alphabetical order.

A collection of orbitals with the same value of n is frequently called a shell. One or more orbitals with the same n and ℓ values are referred to as a subshell. For example, the shell with $n = 2$ is composed of two subshells, $\ell = 0$ and 1 (the allowed values for $n = 2$). These subshells are called the $2s$ and $2p$ subshells where 2 denotes the value of n , and s and p denote the values of ℓ .

The value of ℓ is fixed based on the type of the orbital.

Remember that the “2” in $2s$ refers to the value of n , and the “s” symbolizes the value of ℓ .

The Magnetic Quantum Number (m_ℓ)

The magnetic quantum number (m_ℓ) describes the orientation of the orbital in space (to be discussed in Section 7.7). Within a subshell, the value of m_ℓ depends on the value of the angular momentum quantum number, ℓ . For a certain value of ℓ , there are $(2\ell + 1)$ integral values of m_ℓ as follows:

$$-\ell, (-\ell + 1), \dots, 0, \dots, (+\ell - 1), +\ell$$

If $\ell = 0$, then $m_\ell = 0$. If $\ell = 1$, then there are $[(2 \times 1) + 1]$, or three values of m_ℓ , namely, $-1, 0$, and 1 . If $\ell = 2$, there are $[(2 \times 2) + 1]$, or five values of m_ℓ , namely,

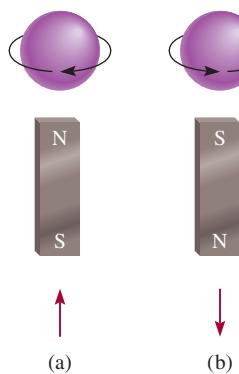


Figure 7.16 The (a) clockwise and (b) counterclockwise spins of an electron. The magnetic fields generated by these two spinning motions are analogous to those from the two magnets. The upward and downward arrows are used to denote the direction of spin.

In their experiment, Stern and Gerlach used silver atoms, which contain just one unpaired electron. To illustrate the principle, we can assume that hydrogen atoms are used in the study.

$-2, -1, 0, 1$, and 2 . The number of m_ℓ values indicates the number of orbitals in a subshell with a particular ℓ value.

To conclude our discussion of these three quantum numbers, let us consider a situation in which $n = 2$ and $\ell = 1$. The values of n and ℓ indicate that we have a $2p$ subshell, and in this subshell we have *three* $2p$ orbitals (because there are three values of m_ℓ , given by $-1, 0$, and 1).

The Electron Spin Quantum Number (m_s)

Experiments on the emission spectra of hydrogen and sodium atoms indicated that lines in the emission spectra could be split by the application of an external magnetic field. The only way physicists could explain these results was to assume that electrons act like tiny magnets. If electrons are thought of as spinning on their own axes, as Earth does, their magnetic properties can be accounted for. According to electromagnetic theory, a spinning charge generates a magnetic field, and it is this motion that causes an electron to behave like a magnet. Figure 7.16 shows the two possible spinning motions of an electron, one clockwise and the other counterclockwise. To take the electron spin into account, it is necessary to introduce a fourth quantum number, called the electron spin quantum number (m_s), which has a value of $+\frac{1}{2}$ or $-\frac{1}{2}$.

Conclusive proof of electron spin was provided by Otto Stern[†] and Walther Gerlach[‡] in 1924. Figure 7.17 shows the basic experimental arrangement. A beam of gaseous atoms generated in a hot furnace passes through a nonhomogeneous magnetic field. The interaction between an electron and the magnetic field causes the atom to be deflected from its straight-line path. Because the spinning motion is completely random, the electrons in half of the atoms will be spinning in one direction, and those atoms will be deflected in one way; the electrons in the other half of the atoms will be spinning in the opposite direction, and those atoms will be deflected in the other direction. Thus, two spots of equal intensity are observed on the detecting screen.

[†]Otto Stern (1888–1969). German physicist. He made important contributions to the study of magnetic properties of atoms and the kinetic theory of gases. Stern was awarded the Nobel Prize in Physics in 1943.

[‡]Walther Gerlach (1889–1979). German physicist. Gerlach's main area of research was in quantum theory.

Figure 7.17 Experimental arrangement for demonstrating the spinning motion of electrons. A beam of atoms is directed through a magnetic field. For example, when a hydrogen atom with a single electron passes through the field, it is deflected in one direction or the other, depending on the direction of the spin. In a stream consisting of many atoms, there will be equal distributions of the two kinds of spins, so that two spots of equal intensity are detected on the screen.

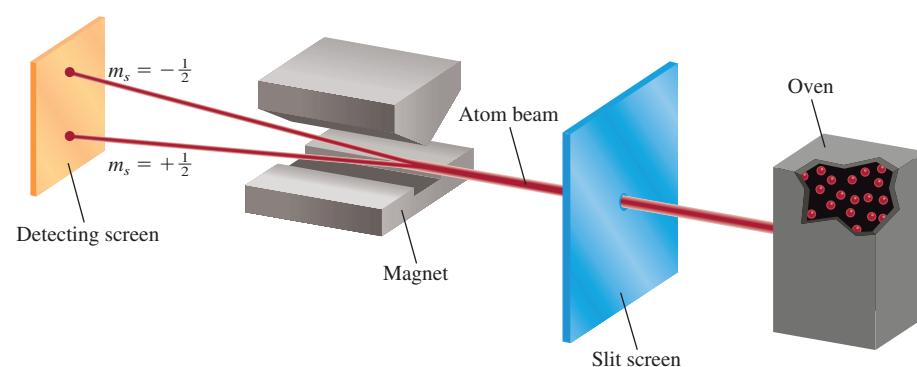


TABLE 7.2 Relation Between Quantum Numbers and Atomic Orbitals

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	$-1, 0, 1$	3	$2p_x, 2p_y, 2p_z$
3	0	0	1	$3s$
	1	$-1, 0, 1$	3	$3p_x, 3p_y, 3p_z$
	2	$-2, -1, 0, 1, 2$	5	$3d_{xy}, 3d_{yz}, 3d_{xz}, 3d_{x^2-y^2}, 3d_{z^2}$
:	:	:	:	:

An s subshell has one orbital, a p subshell has three orbitals, and a d subshell has five orbitals.

7.7 Atomic Orbitals

Table 7.2 shows the relation between quantum numbers and atomic orbitals. We see that when $\ell = 0$, $(2\ell + 1) = 1$ and there is only one value of m_ℓ , thus we have an s orbital. When $\ell = 1$, $(2\ell + 1) = 3$, so there are three values of m_ℓ or three p orbitals, labeled p_x , p_y , and p_z . When $\ell = 2$, $(2\ell + 1) = 5$ and there are five values of m_ℓ , and the corresponding five d orbitals are labeled with more elaborate subscripts. In the following sections we will consider the s , p , and d orbitals separately.

s Orbitals. One of the important questions we ask when studying the properties of atomic orbitals is, What are the shapes of the orbitals? Strictly speaking, an orbital does not have a well-defined shape because the wave function characterizing the orbital extends from the nucleus to infinity. In that sense, it is difficult to say what an orbital looks like. On the other hand, it is certainly convenient to think of orbitals as having specific shapes, particularly in discussing the formation of chemical bonds between atoms, as we will do in Chapters 9 and 10.

Although in principle an electron can be found anywhere, we know that most of the time it is quite close to the nucleus. Figure 7.18(a) shows the distribution of electron density in a hydrogen $1s$ orbital moving outward from the nucleus. As you

That the wave function for an orbital theoretically has no outer limit as one moves outward from the nucleus raises interesting philosophical questions regarding the sizes of atoms. Chemists have agreed on an operational definition of atomic size, as we will see in later chapters.

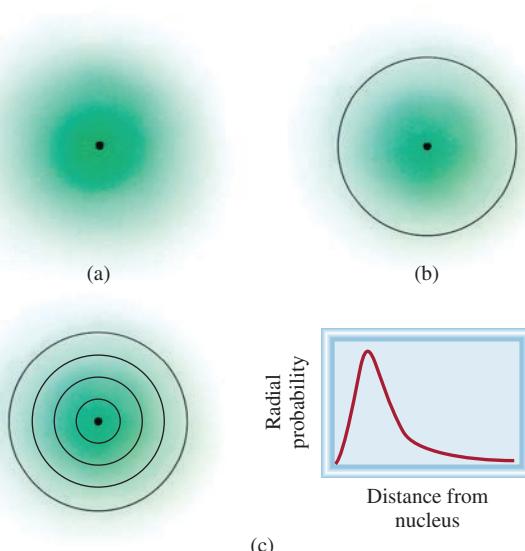


Figure 7.18 (a) Plot of electron density in the hydrogen $1s$ orbital as a function of the distance from the nucleus. The electron density falls off rapidly as the distance from the nucleus increases. (b) Boundary surface diagram of the hydrogen $1s$ orbital. (c) A more realistic way of viewing electron density distribution is to divide the $1s$ orbital into successive spherical thin shells. A plot of the probability of finding the electron in each shell, called radial probability, as a function of distance shows a maximum at 52.9 pm from the nucleus. Interestingly, this is equal to the radius of the innermost orbit in the Bohr model.

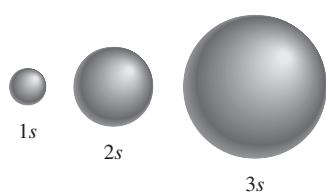


Figure 7.19 Boundary surface diagrams of the hydrogen 1s, 2s, and 3s orbitals. Each sphere contains about 90 percent of the total electron density. All s orbitals are spherical. Roughly speaking, the size of an orbital is proportional to n^2 , where n is the principal quantum number.

Orbitals that have the same energy are said to be degenerate orbitals.

can see, the electron density falls off rapidly as the distance from the nucleus increases. Roughly speaking, there is about a 90 percent probability of finding the electron within a sphere of radius 100 pm (1 pm = 1×10^{-12} m) surrounding the nucleus. Thus, we can represent the 1s orbital by drawing a **boundary surface diagram** that encloses about 90 percent of the total electron density in an orbital, as shown in Figure 7.18(b). A 1s orbital represented in this manner is merely a sphere.

Figure 7.19 shows boundary surface diagrams for the 1s, 2s, and 3s hydrogen atomic orbitals. All s orbitals are spherical in shape but differ in size, which increases as the principal quantum number increases. Although the details of electron density variation within each boundary surface are lost, there is no serious disadvantage. For us the most important features of atomic orbitals are their shapes and *relative* sizes, which are adequately represented by boundary surface diagrams.

p Orbitals. It should be clear that the *p* orbitals start with the principal quantum number $n = 2$. If $n = 1$, then the angular momentum quantum number ℓ can assume only the value of zero; therefore, there is only a 1s orbital. As we saw earlier, when $\ell = 1$, the magnetic quantum number m_ℓ can have values of $-1, 0, 1$. Starting with $n = 2$ and $\ell = 1$, we therefore have three 2p orbitals: $2p_x$, $2p_y$, and $2p_z$ (Figure 7.20). The letter subscripts indicate the axes along which the orbitals are oriented. These three *p* orbitals are identical in size, shape, and energy; they differ from one another only in orientation. Note, however, that there is no simple relation between the values of m_ℓ and the *x*, *y*, and *z* directions. For our purpose, you need only remember that because there are three possible values of m_ℓ , there are three *p* orbitals with different orientations.

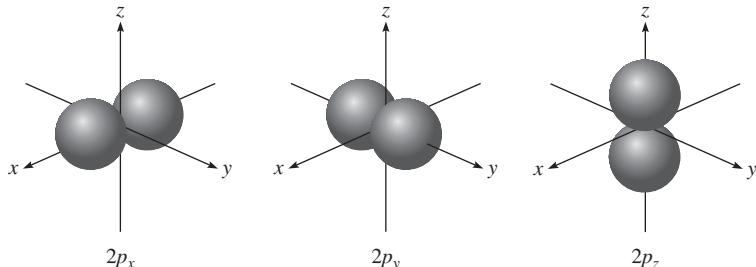
The boundary surface diagrams of *p* orbitals in Figure 7.20 show that each *p* orbital can be thought of as two lobes on opposite sides of the nucleus. Like *s* orbitals, *p* orbitals increase in size from $2p$ to $3p$ to $4p$ orbital and so on.

d Orbitals and Other Higher-Energy Orbitals. When $\ell = 2$, there are five values of m_ℓ , which correspond to five *d* orbitals. The lowest value of n for a *d* orbital is 3. Because ℓ can never be greater than $n - 1$, when $n = 3$ and $\ell = 2$, we have five 3d orbitals ($3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$, and $3d_{z^2}$), shown in Figure 7.21. As in the case of the *p* orbitals, the different orientations of the *d* orbitals correspond to the different values of m_ℓ , but again there is no direct correspondence between a given orientation and a particular m_ℓ value. All the 3d orbitals in an atom are identical in energy. The *d* orbitals for which n is greater than 3 ($4d$, $5d$, . . .) have similar shapes.

Orbitals having higher energy than *d* orbitals are labeled *f*, *g*, . . . and so on. The *f* orbitals are important in accounting for the behavior of elements with atomic numbers greater than 57, but their shapes are difficult to represent. In general chemistry, we are not concerned with orbitals having ℓ values greater than 3 (the *g* orbitals and beyond).

Examples 7.6 and 7.7 illustrate the labeling of orbitals with quantum numbers and the calculation of total number of orbitals associated with a given principal quantum number.

Figure 7.20 The boundary surface diagrams of the three 2p orbitals. These orbitals are identical in shape and energy, but their orientations are different. The *p* orbitals of higher principal quantum numbers have a similar shape.



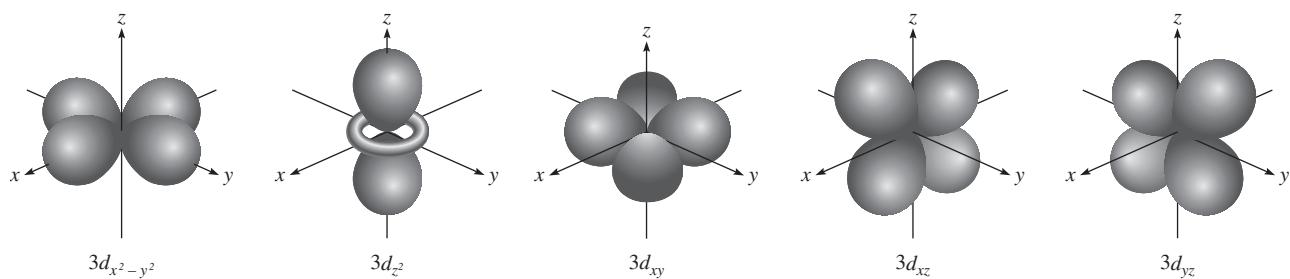


Figure 7.21 Boundary surface diagrams of the five 3d orbitals. Although the $3d_{z^2}$ orbital looks different, it is equivalent to the other four orbitals in all other respects. The d orbitals of higher principal quantum numbers have similar shapes.

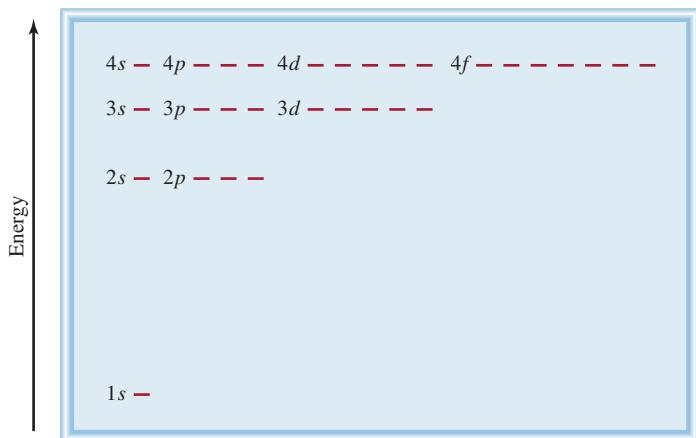
The Energies of Orbitals

Now that we have some understanding of the shapes and sizes of atomic orbitals, we are ready to inquire into their relative energies and look at how energy levels affect the actual arrangement of electrons in atoms.

According to Equation (7.5), the energy of an electron in a hydrogen atom is determined solely by its principal quantum number. Thus, the energies of hydrogen orbitals increase as follows (Figure 7.22):

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$$

Figure 7.22 Orbital energy levels in the hydrogen atom. Each short horizontal line represents one orbital. Orbitals with the same principal quantum number (n) all have the same energy.



Although the electron density distributions are different in the $2s$ and $2p$ orbitals, hydrogen's electron has the same energy whether it is in the $2s$ orbital or a $2p$ orbital. The $1s$ orbital in a hydrogen atom corresponds to the most stable condition, the ground state. An electron residing in this orbital is most strongly held by the nucleus because it is closest to the nucleus. An electron in the $2s$, $2p$, or higher orbitals in a hydrogen atom is in an excited state.

The energy picture is more complex for many-electron atoms than for hydrogen. The energy of an electron in such an atom depends on its angular momentum quantum number as well as on its principal quantum number (Figure 7.23). For many-electron atoms, the $3d$ energy level is very close to the $4s$ energy level. The total energy of an atom, however, depends not only on the sum of the orbital energies but also on the energy of repulsion between the electrons in these orbitals (each orbital can accommodate up to two electrons, as we will see in Section 7.8).

Electron Configuration

The four quantum numbers n , ℓ , m_ℓ , and m_s enable us to label completely an electron in any orbital in any atom. In a sense, we can regard the set of four quantum numbers as the “address” of an electron in an atom, somewhat in the same way that a street address, city, state, and postal ZIP code specify the address of an individual.

The hydrogen atom is a particularly simple system because it contains only one electron. The electron may reside in the 1s orbital (the ground state), or it may be found in some higher-energy orbital (an excited state). For many-electron atoms, however, we must know the ***electron configuration*** of the atom, that is, *how the electrons are distributed among the various atomic orbitals*, in order to understand electronic behavior. We will use the first 10 elements (hydrogen to neon) to illustrate the rules for writing electron configurations for atoms in the *ground state*. (Section 7.9 will describe how these rules can be applied to the remainder of the elements in the periodic table.) For this discussion, recall that the number of electrons in an atom is equal to its atomic number Z .

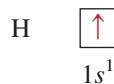
Figure 7.22 indicates that the electron in a ground-state hydrogen atom must be in the $1s$ orbital, so its electron configuration is $1s^1$:

denotes the number of electrons in the orbital or subshell

denotes the principal quantum number n

denotes the angular momentum quantum number ℓ

The electron configuration can also be represented by an *orbital diagram* that shows the spin of the electron (see Figure 7.16):

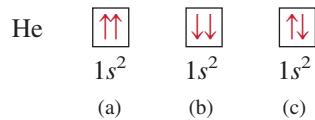


Remember that the direction of electron spin has no effect on the energy of the electron.

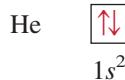
The upward arrow denotes one of the two possible spinning motions of the electron. (Alternatively, we could have represented the electron with a downward arrow.) The box represents an atomic orbital.

The Pauli Exclusion Principle

For many-electron atoms we use the **Pauli[†] exclusion principle** to determine electron configurations. This principle states that *no two electrons in an atom can have the same set of four quantum numbers*. If two electrons in an atom should have the same n , ℓ , and m_ℓ values (that is, these two electrons are in the *same* atomic orbital), then they must have different values of m_s . In other words, only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins. Consider the helium atom, which has two electrons. The three possible ways of placing two electrons in the $1s$ orbital are as follows:



Diagrams (a) and (b) are ruled out by the Pauli exclusion principle. In (a), both electrons have the same upward spin and would have the quantum numbers $(1, 0, 0, +\frac{1}{2})$; in (b), both electrons have downward spins and would have the quantum numbers $(1, 0, 0, -\frac{1}{2})$. Only the configuration in (c) is physically acceptable, because one electron has the quantum numbers $(1, 0, 0, +\frac{1}{2})$ and the other has $(1, 0, 0, -\frac{1}{2})$. Thus, the helium atom has the following configuration:



Electrons that have opposite spins are said to be paired. In helium, $m_s = +\frac{1}{2}$ for one electron; $m_s = -\frac{1}{2}$ for the other.

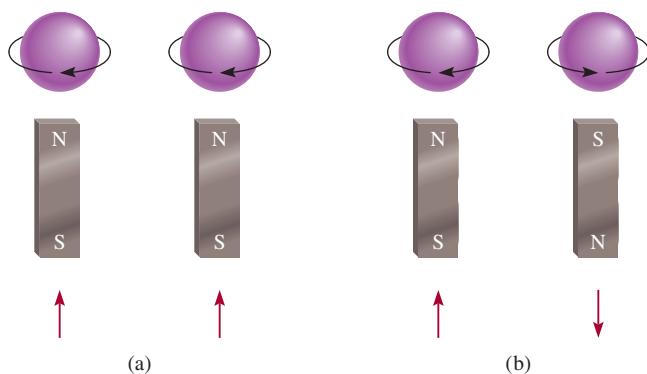
Note that $1s^2$ is read “one s two,” not “one s squared.”

Diamagnetism and Paramagnetism

The Pauli exclusion principle is one of the fundamental principles of quantum mechanics. It can be tested by a simple observation. If the two electrons in the $1s$ orbital of a helium atom had the same, or parallel, spins ($\uparrow\uparrow$ or $\downarrow\downarrow$), their net magnetic fields would reinforce each other [Figure 7.25(a)]. Such an arrangement would make the

[†]Wolfgang Pauli (1900–1958). Austrian physicist. One of the founders of quantum mechanics, Pauli was awarded the Nobel Prize in Physics in 1945.

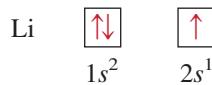
Figure 7.25 The (a) parallel and (b) antiparallel spins of two electrons. In (a) the two magnetic fields reinforce each other. In (b) the two magnetic fields cancel each other.



helium gas paramagnetic. **Paramagnetic** substances are those that *contain net unpaired spins and are attracted by a magnet*. On the other hand, if the electron spins are paired, or antiparallel to each other ($\uparrow\downarrow$ or $\downarrow\uparrow$), the magnetic effects cancel out [Figure 7.25(b)]. **Diamagnetic** substances *do not contain net unpaired spins and are slightly repelled by a magnet*.

Measurements of magnetic properties provide the most direct evidence for specific electron configurations of elements. Advances in instrument design during the last 30 years or so enable us to determine the number of unpaired electrons in an atom (Figure 7.26). By experiment we find that the helium atom in its ground state has no net magnetic field. Therefore, the two electrons in the $1s$ orbital must be paired in accord with the Pauli exclusion principle and the helium gas is diamagnetic. A useful rule to keep in mind is that any atom with an *odd* number of electrons will always contain one or more unpaired spins because we need an even number of electrons for complete pairing. On the other hand, atoms containing an even number of electrons may or may not contain unpaired spins. We will see the reason for this behavior shortly.

As another example, consider the lithium atom ($Z = 3$) which has three electrons. The third electron cannot go into the $1s$ orbital because it would inevitably have the same set of four quantum numbers as one of the first two electrons. Therefore, this electron “enters” the next (energetically) higher orbital, which is the $2s$ orbital (see Figure 7.23). The electron configuration of lithium is $1s^22s^1$, and its orbital diagram is



The lithium atom contains one unpaired electron and the lithium metal is therefore paramagnetic.

The Shielding Effect in Many-Electron Atoms

Experimentally we find that the $2s$ orbital lies at a lower energy level than the $2p$ orbital in a many-electron atom. Why? In comparing the electron configurations of $1s^22s^1$ and $1s^22p^1$, we note that, in both cases, the $1s$ orbital is filled with two electrons. Figure 7.27 shows the radial probability plots for the $1s$, $2s$, and $2p$ orbitals. Because the $2s$ and $2p$ orbitals are larger than the $1s$ orbital, an electron in either of these orbitals will spend more time away from the nucleus than an electron in the $1s$ orbital. Thus, we can speak of a $2s$ or $2p$ electron being partly “shielded” from the attractive force of the nucleus by the $1s$ electrons. The important consequence of the shielding effect is that it *reduces* the electrostatic attraction between the protons in the nucleus and the electron in the $2s$ or $2p$ orbital.

The manner in which the electron density varies as we move from the nucleus outward depends on the type of orbital. Although a $2s$ electron spends most of its time (on average) slightly farther from the nucleus than a $2p$ electron, the electron density near the nucleus is actually greater for the $2s$ electron (see the small maximum for the $2s$ orbital in Figure 7.27). For this reason, the $2s$ orbital is said to be more “penetrating” than the $2p$ orbital. Therefore, a $2s$ electron is less shielded by the $1s$ electrons and is more strongly held by the nucleus. In fact, for the same principal quantum number n , the penetrating power decreases as the angular momentum quantum number ℓ increases, or

$$s > p > d > f > \dots$$

Because the stability of an electron is determined by the strength of its attraction to the nucleus, it follows that a $2s$ electron will be lower in energy than a $2p$ electron.

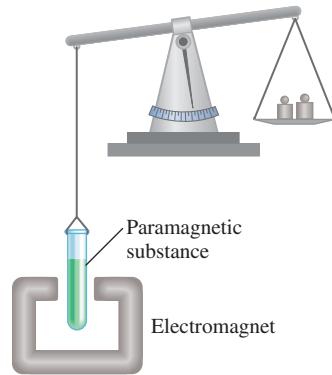


Figure 7.26 Initially the paramagnetic substance was weighed on a balance. When the electromagnet is turned on, the balance is offset because the sample tube is drawn into the magnetic field. Knowing the concentration and the additional mass needed to reestablish balance, it is possible to calculate the number of unpaired electrons in the sample.

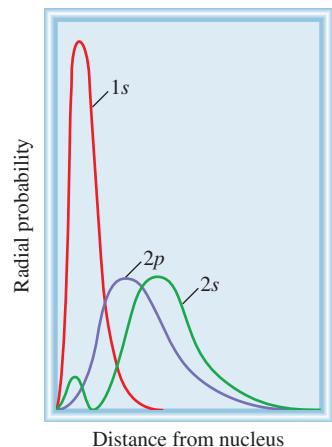
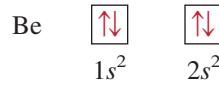


Figure 7.27 Radial probability plots (see Figure 7.18) for the $1s$, $2s$, and $2p$ orbitals. The $1s$ electrons effectively shield both the $2s$ and $2p$ electrons from the nucleus. The $2s$ orbital is more penetrating than the $2p$ orbital.

To put it another way, less energy is required to remove a $2p$ electron than a $2s$ electron because a $2p$ electron is not held quite as strongly by the nucleus. The hydrogen atom has only one electron and, therefore, is without such a shielding effect.

Continuing our discussion of atoms of the first 10 elements, we go next to beryllium ($Z = 4$). The ground-state electron configuration of beryllium is $1s^22s^2$, or



Beryllium is diamagnetic, as we would expect.

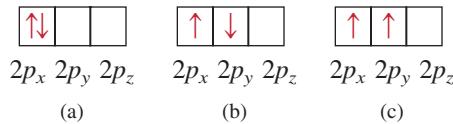
The electron configuration of boron ($Z = 5$) is $1s^22s^22p^1$, or



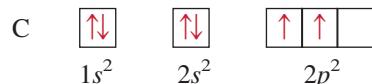
Note that the unpaired electron can be in the $2p_x$, $2p_y$, or $2p_z$ orbital. The choice is completely arbitrary because the three p orbitals are equivalent in energy. As the diagram shows, boron is paramagnetic.

Hund's Rule

The electron configuration of carbon ($Z = 6$) is $1s^22s^22p^2$. The following are different ways of distributing two electrons among three p orbitals:

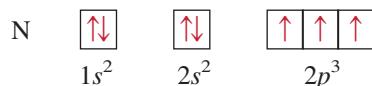


None of the three arrangements violates the Pauli exclusion principle, so we must determine which one will give the greatest stability. The answer is provided by **Hund's rule**,[†] which states that *the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins*. The arrangement shown in (c) satisfies this condition. In both (a) and (b) the two spins cancel each other. Thus, the orbital diagram for carbon is



Qualitatively, we can understand why (c) is preferred to (a). In (a), the two electrons are in the same $2p_x$ orbital, and their proximity results in a greater mutual repulsion than when they occupy two separate orbitals, say $2p_x$ and $2p_y$. The choice of (c) over (b) is more subtle but can be justified on theoretical grounds. The fact that carbon atoms contain two unpaired electrons is in accord with Hund's rule.

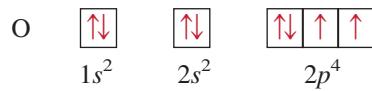
The electron configuration of nitrogen ($Z = 7$) is $1s^22s^22p^3$:



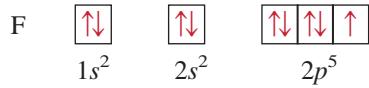
Again, Hund's rule dictates that all three $2p$ electrons have spins parallel to one another; the nitrogen atom contains three unpaired electrons.

[†]Frederick Hund (1896–1997). German physicist. Hund's work was mainly in quantum mechanics. He also helped to develop the molecular orbital theory of chemical bonding.

The electron configuration of oxygen ($Z = 8$) is $1s^22s^22p^4$. An oxygen atom has two unpaired electrons:

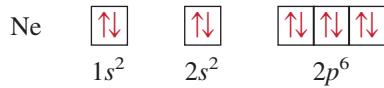


The electron configuration of fluorine ($Z = 9$) is $1s^22s^22p^5$. The nine electrons are arranged as follows:



The fluorine atom has one unpaired electron.

In neon ($Z = 10$), the $2p$ subshell is completely filled. The electron configuration of neon is $1s^22s^22p^6$, and *all* the electrons are paired, as follows:



The neon gas should be diamagnetic, and experimental observation bears out this prediction.

At this point let's summarize what our examination of the first ten elements has revealed about ground-state electron configurations and the properties of electrons in atoms:

1. No two electrons in the same atom can have the same four quantum numbers. This is the Pauli exclusion principle.
2. Each orbital can be occupied by a maximum of two electrons. They must have opposite spins, or different electron spin quantum numbers.
3. The most stable arrangement of electrons in a subshell is the one that has the greatest number of parallel spins. This is Hund's rule.

7.9 The Building-Up Principle

Here we will extend the rules used in writing electron configurations for the first 10 elements to the rest of the elements. This process is based on the Aufbau principle. The **Aufbau principle** dictates that *as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to the atomic orbitals*. Through this process we gain a detailed knowledge of the ground-state electron configurations of the elements. As we will see later, knowledge of electron configurations helps us to understand and predict the properties of the elements; it also explains why the periodic table works so well.

Table 7.3 gives the ground-state electron configurations of elements from H ($Z = 1$) through Rg ($Z = 111$). The electron configurations of all elements except hydrogen and helium are represented by a **noble gas core**, which shows in brackets the noble gas element that most nearly precedes the element being considered, followed by the symbol for the highest filled subshells in the outermost shells. Notice that the electron configurations of the highest filled subshells in the outermost shells for the elements sodium ($Z = 11$) through argon ($Z = 18$) follow a pattern similar to those of lithium ($Z = 3$) through neon ($Z = 10$).

As mentioned in Section 7.7, the $4s$ subshell is filled before the $3d$ subshell in a many-electron atom (see Figure 7.24). Thus, the electron configuration of potassium ($Z = 19$) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. Because $1s^2 2s^2 2p^6 3s^2 3p^6$ is the electron configuration of argon, we can simplify the electron configuration of potassium by writing $[Ar]4s^1$, where $[Ar]$ denotes the “argon core.” Similarly, we can write the electron configuration of calcium ($Z = 20$) as $[Ar]4s^2$. The placement of the outermost electron in the $4s$ orbital (rather than in the $3d$ orbital) of potassium is strongly supported by experimental evidence. The following comparison also suggests that this is the correct configuration. The chemistry of potassium is very similar to that of lithium and sodium, the first two alkali metals. The outermost electron of both lithium and sodium is in an s orbital (there is no ambiguity in assigning their electron configurations); therefore, we expect the last electron in potassium to occupy the $4s$ rather than the $3d$ orbital.

The German word “Aufbau” means “building up.”

1A	2A	3A	4A	5A	6A	7A	8A
						He	
						Ne	
						Ar	
						Kr	
						Xe	
						Rn	

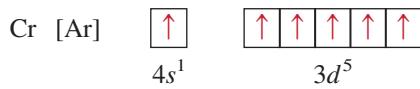
The noble gases.

TABLE 7.3 The Ground-State Electron Configurations of the Elements*

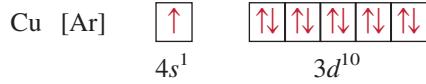
Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration
1	H	$1s^1$	38	Sr	$[Kr]5s^2$	75	Re	$[Xe]6s^24f^{14}5d^5$
2	He	$1s^2$	39	Y	$[Kr]5s^24d^1$	76	Os	$[Xe]6s^24f^{14}5d^6$
3	Li	$[He]2s^1$	40	Zr	$[Kr]5s^24d^2$	77	Ir	$[Xe]6s^24f^{14}5d^7$
4	Be	$[He]2s^2$	41	Nb	$[Kr]5s^14d^4$	78	Pt	$[Xe]6s^14f^{14}5d^9$
5	B	$[He]2s^22p^1$	42	Mo	$[Kr]5s^14d^5$	79	Au	$[Xe]6s^14f^{14}5d^{10}$
6	C	$[He]2s^22p^2$	43	Tc	$[Kr]5s^24d^5$	80	Hg	$[Xe]6s^24f^{14}5d^{10}$
7	N	$[He]2s^22p^3$	44	Ru	$[Kr]5s^14d^7$	81	Tl	$[Xe]6s^24f^{14}5d^{10}6p^1$
8	O	$[He]2s^22p^4$	45	Rh	$[Kr]5s^14d^8$	82	Pb	$[Xe]6s^24f^{14}5d^{10}6p^2$
9	F	$[He]2s^22p^5$	46	Pd	$[Kr]4d^{10}$	83	Bi	$[Xe]6s^24f^{14}5d^{10}6p^3$
10	Ne	$[He]2s^22p^6$	47	Ag	$[Kr]5s^14d^{10}$	84	Po	$[Xe]6s^24f^{14}5d^{10}6p^4$
11	Na	$[Ne]3s^1$	48	Cd	$[Kr]5s^24d^{10}$	85	At	$[Xe]6s^24f^{14}5d^{10}6p^5$
12	Mg	$[Ne]3s^2$	49	In	$[Kr]5s^24d^{10}5p^1$	86	Rn	$[Xe]6s^24f^{14}5d^{10}6p^6$
13	Al	$[Ne]3s^23p^1$	50	Sn	$[Kr]5s^24d^{10}5p^2$	87	Fr	$[Rn]7s^1$
14	Si	$[Ne]3s^23p^2$	51	Sb	$[Kr]5s^24d^{10}5p^3$	88	Ra	$[Rn]7s^2$
15	P	$[Ne]3s^23p^3$	52	Te	$[Kr]5s^24d^{10}5p^4$	89	Ac	$[Rn]7s^26d^1$
16	S	$[Ne]3s^23p^4$	53	I	$[Kr]5s^24d^{10}5p^5$	90	Th	$[Rn]7s^26d^2$
17	Cl	$[Ne]3s^23p^5$	54	Xe	$[Kr]5s^24d^{10}5p^6$	91	Pa	$[Rn]7s^25f^26d^1$
18	Ar	$[Ne]3s^23p^6$	55	Cs	$[Xe]6s^1$	92	U	$[Rn]7s^25f^36d^1$
19	K	$[Ar]4s^1$	56	Ba	$[Xe]6s^2$	93	Np	$[Rn]7s^25f^46d^1$
20	Ca	$[Ar]4s^2$	57	La	$[Xe]6s^25d^1$	94	Pu	$[Rn]7s^25f^6$
21	Sc	$[Ar]4s^23d^1$	58	Ce	$[Xe]6s^24f^{14}5d^1$	95	Am	$[Rn]7s^25f^7$
22	Ti	$[Ar]4s^23d^2$	59	Pr	$[Xe]6s^24f^3$	96	Cm	$[Rn]7s^25f^76d^1$
23	V	$[Ar]4s^23d^3$	60	Nd	$[Xe]6s^24f^4$	97	Bk	$[Rn]7s^25f^9$
24	Cr	$[Ar]4s^13d^5$	61	Pm	$[Xe]6s^24f^5$	98	Cf	$[Rn]7s^25f^{10}$
25	Mn	$[Ar]4s^23d^5$	62	Sm	$[Xe]6s^24f^6$	99	Es	$[Rn]7s^25f^{11}$
26	Fe	$[Ar]4s^23d^6$	63	Eu	$[Xe]6s^24f^7$	100	Fm	$[Rn]7s^25f^{12}$
27	Co	$[Ar]4s^23d^7$	64	Gd	$[Xe]6s^24f^75d^1$	101	Md	$[Rn]7s^25f^{13}$
28	Ni	$[Ar]4s^23d^8$	65	Tb	$[Xe]6s^24f^9$	102	No	$[Rn]7s^25f^{14}$
29	Cu	$[Ar]4s^13d^{10}$	66	Dy	$[Xe]6s^24f^{10}$	103	Lr	$[Rn]7s^25f^{14}6d^1$
30	Zn	$[Ar]4s^23d^{10}$	67	Ho	$[Xe]6s^24f^{11}$	104	Rf	$[Rn]7s^25f^{14}6d^2$
31	Ga	$[Ar]4s^23d^{10}4p^1$	68	Er	$[Xe]6s^24f^{12}$	105	Db	$[Rn]7s^25f^{14}6d^3$
32	Ge	$[Ar]4s^23d^{10}4p^2$	69	Tm	$[Xe]6s^24f^{13}$	106	Sg	$[Rn]7s^25f^{14}6d^4$
33	As	$[Ar]4s^23d^{10}4p^3$	70	Yb	$[Xe]6s^24f^{14}$	107	Bh	$[Rn]7s^25f^{14}6d^5$
34	Se	$[Ar]4s^23d^{10}4p^4$	71	Lu	$[Xe]6s^24f^{14}5d^1$	108	Hs	$[Rn]7s^25f^{14}6d^6$
35	Br	$[Ar]4s^23d^{10}4p^5$	72	Hf	$[Xe]6s^24f^{14}5d^2$	109	Mt	$[Rn]7s^25f^{14}6d^7$
36	Kr	$[Ar]4s^23d^{10}4p^6$	73	Ta	$[Xe]6s^24f^{14}5d^3$	110	Ds	$[Rn]7s^25f^{14}6d^8$
37	Rb	$[Kr]5s^1$	74	W	$[Xe]6s^24f^{14}5d^4$	111	Rg	$[Rn]7s^25f^{14}6d^9$

*The symbol [He] is called the helium core and represents $1s^2$. [Ne] is called the neon core and represents $1s^22s^22p^6$. [Ar] is called the argon core and represents $[Ne]3s^23p^6$. [Kr] is called the krypton core and represents $[Ar]4s^23d^{10}4p^6$. [Xe] is called the xenon core and represents $[Kr]5s^24d^{10}5p^6$. [Rn] is called the radon core and represents $[Xe]6s^24f^{14}5d^{10}6p^6$.

The elements from scandium ($Z = 21$) to copper ($Z = 29$) are transition metals. **Transition metals** either have incompletely filled d subshells or readily give rise to cations that have incompletely filled d subshells. Consider the first transition metal series, from scandium through copper. In this series additional electrons are placed in the $3d$ orbitals, according to Hund's rule. However, there are two irregularities. The electron configuration of chromium ($Z = 24$) is $[\text{Ar}]4s^13d^5$ and not $[\text{Ar}]4s^23d^4$, as we might expect. A similar break in the pattern is observed for copper, whose electron configuration is $[\text{Ar}]4s^13d^{10}$ rather than $[\text{Ar}]4s^23d^9$. The reason for these irregularities is that a slightly greater stability is associated with the half-filled ($3d^5$) and completely filled ($3d^{10}$) subshells. Electrons in the same subshell (in this case, the d orbitals) have equal energy but different spatial distributions. Consequently, their shielding of one another is relatively small, and the electrons are more strongly attracted by the nucleus when they have the $3d^5$ configuration. According to Hund's rule, the orbital diagram for Cr is

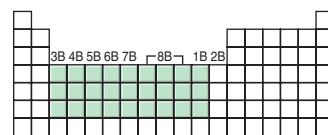


Thus, Cr has a total of six unpaired electrons. The orbital diagram for copper is



For elements Zn ($Z = 30$) through Kr ($Z = 36$), the $4s$ and $4p$ subshells fill in a straight-forward manner. With rubidium ($Z = 37$), electrons begin to enter the $n = 5$ energy level.

The electron configurations in the second transition metal series [yttrium ($Z = 39$) to silver ($Z = 47$)] are also irregular, but we will not be concerned with the details here.

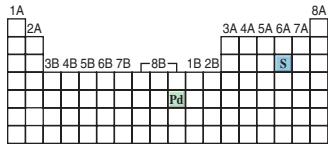


The transition metals.

The Cr and Cu exceptions are not part of AP Chemistry. However many colleges require students to know of these exceptions.

Figure 7.28 Classification of groups of elements in the periodic table according to the type of subshell being filled with electrons.

1s		1s
2s		2p
3s		3p
4s	3d	4p
5s	4d	5p
6s	5d	6p
7s	6d	7p
		4f
		5f



EXAMPLE 7.11

Write the ground-state electron configurations for (a) sulfur (S) and (b) palladium (Pd), which is diamagnetic.

(a) Strategy How many electrons are in the S ($Z = 16$) atom? We start with $n = 1$ and proceed to fill orbitals in the order shown in Figure 7.24. For each value of ℓ , we assign the possible values of m_ℓ . We can place electrons in the orbitals according to the Pauli exclusion principle and Hund's rule and then write the electron configuration. The task is simplified if we use the noble-gas core preceding S for the inner electrons.

Solution Sulfur has 16 electrons. The noble-gas core in this case is [Ne]. (Ne is the noble gas in the period preceding sulfur.) [Ne] represents $1s^2 2s^2 2p^6$. This leaves us 6 electrons to fill the $3s$ subshell and partially fill the $3p$ subshell. Thus, the electron configuration of S is $1s^2 2s^2 2p^6 3s^2 3p^4$ or [Ne] $3s^2 3p^4$.

(b) Strategy We use the same approach as that in (a). What does it mean to say that Pd is a diamagnetic element?

Solution Palladium has 46 electrons. The noble-gas core in this case is [Kr]. (Kr is the noble gas in the period preceding palladium.) [Kr] represents

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$$

The remaining 10 electrons are distributed among the $4d$ and $5s$ orbitals. The three choices are (1) $4d^{10}$, (2) $4d^9 5s^1$, and (3) $4d^8 5s^2$. Because palladium is diamagnetic, all the electrons are paired and its electron configuration must be

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10}$$

or simply [Kr] $4d^{10}$. The configurations in (2) and (3) both represent paramagnetic

elements. **Check** To confirm the answer, write the orbital diagrams for (1), (2), and (3).

Key Equations

$$u = \lambda\nu$$

(7.1)

Relating speed of a wave to its wavelength and frequency.

$$E = h\nu$$

(7.2)

Relating energy of a quantum (and of a photon) to the frequency.

$$E = h\frac{c}{\lambda}$$

(7.3)

Relating energy of a quantum (and of a photon) to the wavelength.

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

(7.8)

Energy of a photon absorbed or emitted as the electron undergoes a transition from the n_i level to the n_f level.Relating wavelength of a particle to its mass m and velocity u .