CHAPTER 4

Arrangement of Electrons in Atoms

The emission of light is fundamentally related to the behavior of electrons.

SECTION 4-1

The Development of a New Atomic Model

OBJECTIVES

- Explain the mathematical relationship among the speed, wavelength, and frequency of electromagnetic radiation.
- Discuss the dual wave-particle nature of light.
- Discuss the significance of the photoelectric effect and the line-emission spectrum of hydrogen to the development of the atomic model.
- Describe the Bohr model of the hydrogen atom.

The Rutherford model of the atom was an improvement over previous models, but it was incomplete. It did not explain where the atom's negatively charged electrons are located in the space surrounding its positively charged nucleus. After all, it was well known that oppositely charged particles attract each other. So what prevented the negative electrons from being drawn into the positive nucleus?

In the early twentieth century, a new atomic model evolved as a result of investigations into the absorption and emission of light by matter. The studies revealed an intimate relationship between light and an atom's electrons. This new understanding led directly to a revolutionary view of the nature of energy, matter, and atomic structure.

Properties of Light

Before 1900, scientists thought light behaved solely as a wave. This belief changed when it was later discovered that light also has particle-like characteristics. Still, many of light's properties can be described in terms of waves. A quick review of these wavelike properties will help you understand the basic theory of light as it existed at the beginning of the twentieth century.

The Wave Description of Light

Visible light is a kind of **electromagnetic radiation,** *which is a form of energy that exhibits wavelike behavior as it travels through space.* Other kinds of electromagnetic radiation include X rays, ultraviolet and infrared light, microwaves, and radio waves. *Together, all the forms of electromagnetic radiation form the* **electromagnetic spectrum.** The electromagnetic spectrum is represented in Figure 4-1 on page 92. All forms of electromagnetic radiation move at a constant speed of about 3.0×10^8 meters per second (m/s) through a vacuum and at slightly slower speeds through matter. Because air is mostly space, the value of 3.0×10^8 m/s is also light's approximate speed through air.

The significant feature of wave motion is its repetitive nature, which can be characterized by the measurable properties of wavelength and frequency. **Wavelength** (λ) *is the distance between corresponding points on adjacent waves.* Depending on the particular form of electromagnetic radiation, the unit for wavelength is the meter, centimeter, or nanome-

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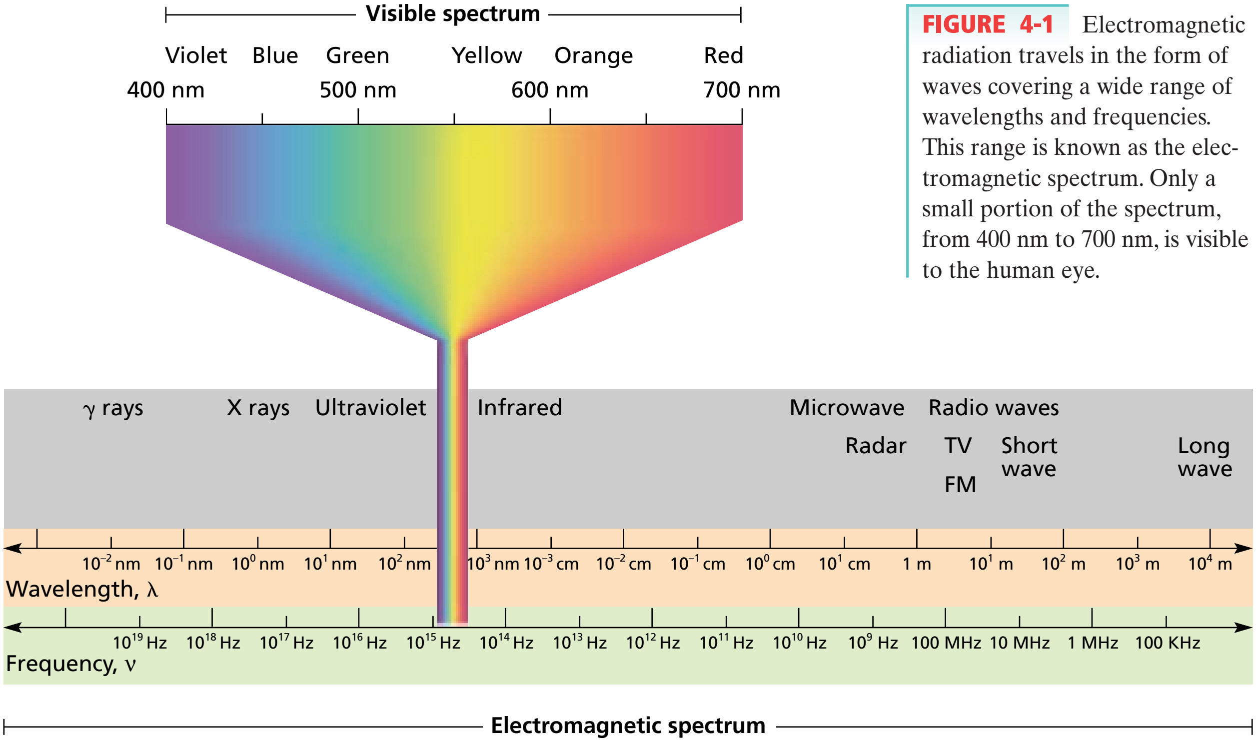

FIGURE 4-1 Electromagnetic radiation travels in the form of waves covering a wide range of wavelengths and frequencies. This range is known as the electromagnetic spectrum. Only a small portion of the spectrum, from 400 nm to 700 nm, is visible to the human eye.

ter (1 nm = 1×10^{-9} m), as shown in Figure 4-1. **Frequency** (ν) *is defined as the number of waves that pass a given point in a specific time, usually one second.* Frequency is expressed in waves/second. One wave/second is called a hertz (Hz), named for Heinrich Hertz, who was a pioneer in the study of electromagnetic radiation. Figure 4-2 illustrates the properties of wavelength and frequency for a familiar kind of wave, a wave on the surface of water. The wavelength in Figure 4-2(a) has a longer wavelength and a lower frequency than the wave in Figure 4-2(b).

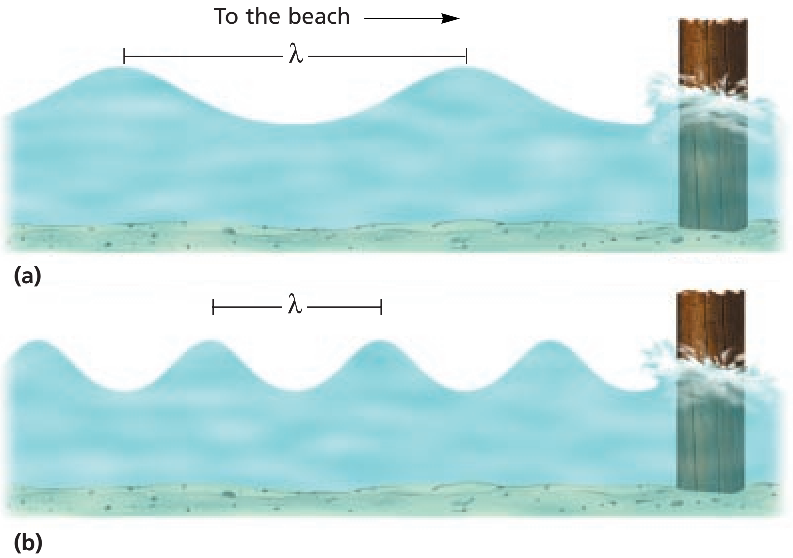

FIGURE 4-2 The distance between any two corresponding points on one of these water waves, such as from crest to crest, is the wave's wavelength, λ. We can measure the wave's frequency, ν, by observing how often the water level rises and falls at a given point, such as at the post.

Frequency and wavelength are mathematically related to each other. For electromagnetic radiation, this relationship is written as follows.

$$c = \lambda\nu$$

In the equation, c is the speed of light, λ is the wavelength of the electromagnetic wave, and ν is the frequency of the electromagnetic wave. Because c is the same for all electromagnetic radiation, the product $\lambda\nu$ is a constant. Consequently, we know that λ is inversely proportional to ν. In other words, as the wavelength of light decreases, its frequency increases, and vice versa.

The Photoelectric Effect

In the early 1900s, scientists conducted two experiments involving interactions of light and matter that could not be explained by the wave theory of light. One experiment involved a phenomenon known as the photoelectric effect. *The* **photoelectric effect** *refers to the emission of electrons from a metal when light shines on the metal,* as illustrated in Figure 4-3.

The mystery of the photoelectric effect involved the frequency of the light striking the metal. For a given metal, no electrons were emitted if the light's frequency was below a certain minimum—regardless of how long the light was shone. Light was known to be a form of energy, capable of knocking loose an electron from a metal. But the wave theory of light predicted that light of any frequency could supply enough energy to eject an electron. Scientists couldn't explain why the light had to be of a minimum frequency in order for the photoelectric effect to occur.

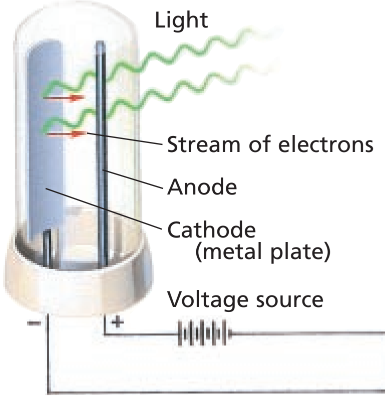

FIGURE 4-3 The photoelectric effect: electromagnetic radiation strikes the surface of the metal, ejecting electrons from the metal and creating an electric current.

The Particle Description of Light

The explanation of the photoelectric effect dates back to 1900, when German physicist Max Planck was studying the emission of light by hot objects. He proposed that a hot object does not emit electromagnetic energy continuously, as would be expected if the energy emitted were in the form of waves. Instead, Planck suggested that the object emits energy in small, specific amounts called quanta. *A* **quantum** *is the minimum quantity of energy that can be lost or gained by an atom*. Planck proposed the following relationship between a quantum of energy and the frequency of radiation.

$$E = h\nu$$

In the equation, E is the energy, in joules, of a quantum of radiation, ν is the frequency of the radiation emitted, and h is a fundamental physical constant now known as Planck's constant; $h = 6.626 \times 10^{-34}$ J•s.

In 1905, Albert Einstein expanded on Planck's theory by introducing the radical idea that electromagnetic radiation has a dual wave-particle nature. While light exhibits many wavelike properties, it can also be

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thought of as a stream of particles. Each particle of light carries a quantum of energy. Einstein called these particles photons. *A* **photon** *is a particle of electromagnetic radiation having zero mass and carrying a quantum of energy.* The energy of a particular photon depends on the frequency of the radiation.

$$E_{photon} = h\nu$$

Einstein explained the photoelectric effect by proposing that electromagnetic radiation is absorbed by matter only in whole numbers of photons. In order for an electron to be ejected from a metal surface, the electron must be struck by a single photon possessing at least the minimum energy required to knock the electron loose. According to the equation $E_{photon} = h\nu$, this minimum energy corresponds to a minimum frequency. If a photon's frequency is below the minimum, then the electron remains bound to the metal surface. Electrons in different metals are bound more or less tightly, so different metals require different minimum frequencies to exhibit the photoelectric effect.

The Hydrogen-Atom Line-Emission Spectrum

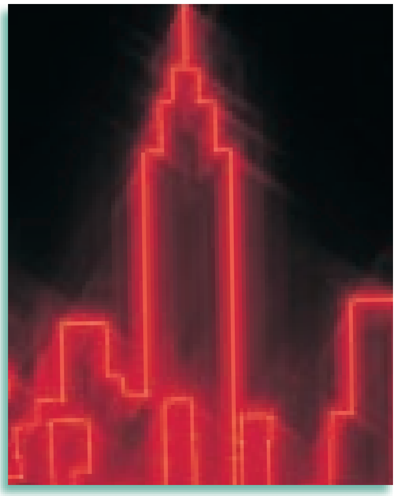
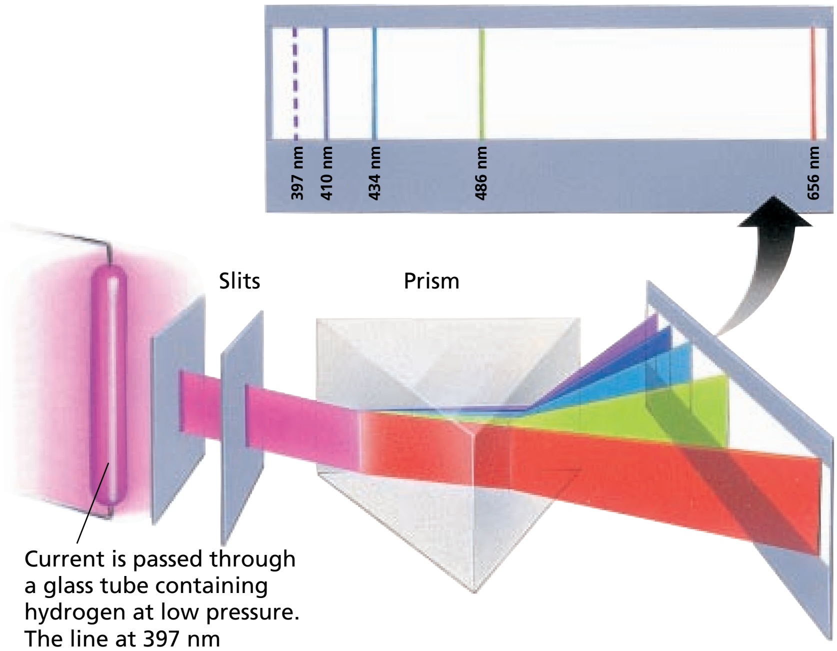


FIGURE 4-4 Excited neon atoms emit light when falling back to the ground state or to a lower-energy excited state.

When current is passed through a gas at low pressure, the potential energy of some of the gas atoms increases. *The lowest energy state of an atom is its* **ground state.** *A state in which an atom has a higher potential energy than it has in its ground state is an* **excited state.** When an excited atom returns to its ground state, it gives off the energy it gained in the form of electromagnetic radiation. The production of colored light in neon signs, as shown in Figure 4-4, is a familiar example of this process.

When investigators passed electric current through a vacuum tube containing hydrogen gas at low pressure, they observed the emission of a characteristic pinkish glow. *When a narrow beam of the emitted light was shined through a prism, it was separated into a series of specific frequencies (and therefore specific wavelengths, $\lambda = c/\nu$) of visible light.* The bands of light were part of what is known as hydrogen's **line-emission spectrum.** The production of hydrogen's line-emission spectrum is illustrated in Figure 4-5. Additional series of lines were discovered in the ultraviolet and infrared regions of hydrogen's line-emission spectrum. The wavelengths of some of the spectral series are shown in Figure 4-6. They are known as the Lyman, Balmer, and Paschen series, after their discoverers.

Classical theory predicted that the hydrogen atoms would be excited by whatever amount of energy was added to them. Scientists had thus expected to observe *the emission of a continuous range of frequencies of electromagnetic radiation,* that is, a **continuous spectrum.** Why had the hydrogen atoms given off only specific frequencies of light? Attempts to explain this observation led to an entirely new theory of the atom called *quantum theory.*



Current is passed through
a glass tube containing
hydrogen at low pressure.
The line at 397 nm
is in the ultraviolet and is
not visible to the human eye.

FIGURE 4-5 Excited hydrogen atoms emit a pinkish glow. When the visible portion of the emitted light is passed through a prism, it is separated into specific wavelengths that are part of hydrogen's line-emission spectrum. The line at 397 nm is in the ultraviolet and is not visible to the human eye.

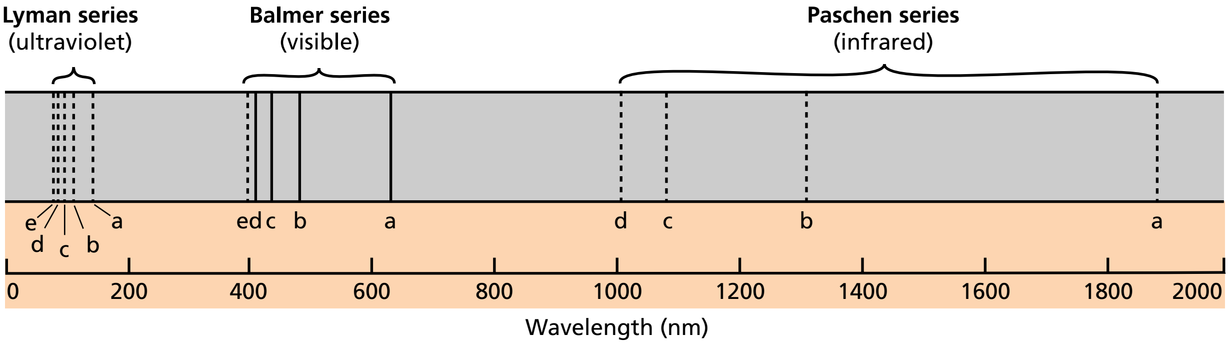


FIGURE 4-6 A series of specific wavelengths of emitted light makes up hydrogen's line-emission spectrum. The letters below the lines label hydrogen's various energy-level transitions. Niels Bohr's model of the hydrogen atom provided an explanation for these transitions.

Whenever an excited hydrogen atom falls back from an excited state to its ground state or to a lower-energy excited state, it emits a photon of radiation. The energy of this photon ($E_{photon} = h\nu$) is equal to the difference in energy between the atom's initial state and its final state, as illustrated in Figure 4-7. The fact that hydrogen atoms emit only specific frequencies of light indicated that the energy differences between the atoms' energy states were fixed. This suggested that the electron of a hydrogen atom exists only in very specific energy states.

In the late nineteenth century, a mathematical relationship that related the various wavelengths of hydrogen's line-emission spectrum was discovered. The challenge facing scientists was to provide a model of the hydrogen atom that accounted for this relationship.

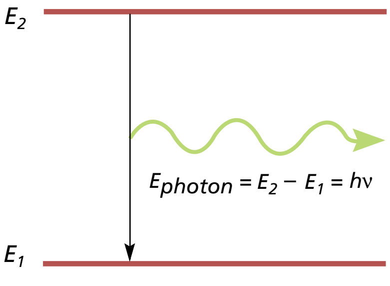


FIGURE 4-7 When an excited atom with energy E_2 falls back to energy E_1, it releases a photon that has energy $E_2 - E_1 = E_{photon} = h\nu$.

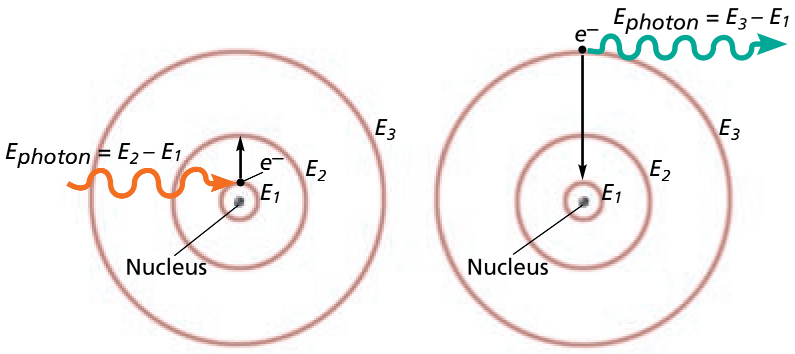
Bohr Model of the Hydrogen Atom

The puzzle of the hydrogen-atom spectrum was solved in 1913 by the Danish physicist Niels Bohr. He proposed a model of the hydrogen atom that linked the atom's electron with photon emission. According to the model, the electron can circle the nucleus only in allowed paths, or *orbits*. When the electron is in one of these orbits, the atom has a definite, fixed energy. The electron, and therefore the hydrogen atom, is in its lowest energy state when it is in the orbit closest to the nucleus. This orbit is separated from the nucleus by a large empty space where the electron cannot exist. The energy of the electron is higher when it is in orbits that are successively farther from the nucleus.

The electron orbits or atomic energy levels in Bohr's model can be compared to the rungs of a ladder. When you are standing on a ladder, your feet are on one rung or another. The amount of potential energy that you possess corresponds to standing on the first rung, the second rung, and so forth. Your energy cannot correspond to standing between two rungs because you cannot stand in midair. In the same way, an electron can be in one orbit or another, but not in between.

How does Bohr's model of the hydrogen atom explain the observed spectral lines? While in an orbit, the electron can neither gain nor lose energy. It can, however, move to a higher energy orbit by gaining an amount of energy equal to the difference in energy between the higher-energy orbit and the initial lower-energy orbit. When a hydrogen atom is in an excited state, its electron is in a higher-energy orbit. When the atom falls back from the excited state, the electron drops down to a lower-energy orbit. In the process, a photon is emitted that has an energy equal to the energy difference between the initial higher-energy orbit and the final lower-energy orbit. Absorption and emission of radiation according to the Bohr model of the hydrogen atom are illustrated in Figure 4-8. The energy of each emitted photon corresponds to a particular frequency of emitted radiation, $E_{photon} = h\nu$.

Based on the wavelengths of hydrogen's line-emission spectrum, Bohr calculated the energies that an electron would have in the allowed energy levels for the hydrogen atom. He then used these values to show



(a) Absorption **(b)** Emission

FIGURE 4-8 (a) Absorption and (b) emission of a photon by a hydrogen atom according to Bohr's model. The frequencies of light that can be absorbed and emitted are restricted because the electron can only be in orbits corresponding to the energies E_1, E_2, E_3, and so forth.

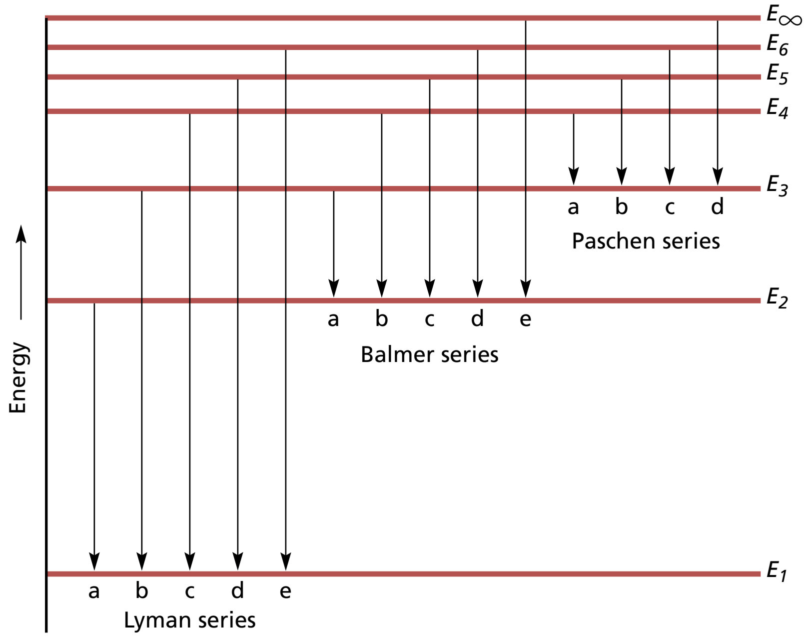


FIGURE 4-9 This electron energy-level diagram for hydrogen shows the energy transitions for the Lyman, Balmer, and Paschen spectral series. Bohr's model of the atom accounted mathematically for the energy of each of the transitions shown.

mathematically how the various spectral series of hydrogen were produced. The Lyman spectral series, for example, was shown to be the result of electrons dropping from various higher-energy levels to the ground-state energy level.

Bohr's calculated values agreed with the experimentally observed values for the lines in each series. The origins of several of the series of lines in hydrogen's line-emission spectrum are shown in Figure 4-9.

The success of Bohr's model of the hydrogen atom in explaining observed spectral lines led many scientists to conclude that a similar model could be applied to all atoms. It was soon recognized, however, that Bohr's approach did not explain the spectra of atoms with more than one electron. Nor did Bohr's theory explain the chemical behavior of atoms.

SECTION REVIEW

1. What was the major shortcoming of Rutherford's model of the atom?

2. Write and label the equation that relates the speed, wavelength, and frequency of electromagnetic radiation.

3. Define the following:
a. electromagnetic radiation b. wavelength
c. frequency d. quantum e. photon

4. What is meant by the dual wave-particle nature of light?

5. Describe the Bohr model of the hydrogen atom.

SECTION 4-2

The Quantum Model of the Atom

OBJECTIVES

- Discuss Louis de Broglie's role in the development of the quantum model of the atom.
- Compare and contrast the Bohr model and the quantum model of the atom.
- Explain how the Heisenberg uncertainty principle and the Schrödinger wave equation led to the idea of atomic orbitals.
- List the four quantum numbers, and describe their significance.
- Relate the number of sublevels corresponding to each of an atom's main energy levels, the number of orbitals per sublevel, and the number of orbitals per main energy level.

To the scientists of the early twentieth century, Bohr's model of the hydrogen atom contradicted common sense. Why did hydrogen's electron exist around the nucleus only in certain allowed orbits with definite energies? Why couldn't the electron exist in a limitless number of orbits with slightly different energies? To explain why atomic energy states are quantized, scientists had to change the way they viewed the nature of the electron.

Electrons as Waves

The investigations into the photoelectric effect and hydrogen atomic emission revealed that light could behave as both a wave and a particle. Could electrons have a dual wave-particle nature as well? In 1924, the French scientist Louis de Broglie asked himself this very question. And the answer that he proposed led to a revolution in our basic understanding of matter.

De Broglie pointed out that in many ways the behavior of Bohr's quantized electron orbits was similar to the known behavior of waves. For example, scientists at the time knew that any wave confined to a space can have only certain frequencies. De Broglie suggested that electrons be considered waves confined to the space around an atomic nucleus. It followed that the electron waves could exist only at specific frequencies. And according to the relationship $E = h\nu$, these frequencies corresponded to specific energies—the quantized energies of Bohr's orbits.

Other aspects of de Broglie's hypothesis that electrons have wave-like properties were soon confirmed by experiments. Investigators demonstrated that electrons, like light waves, can be bent, or diffracted. *Diffraction* refers to the bending of a wave as it passes by the edge of an object, such as the edge of an atom in a crystal. Diffraction experiments and other investigations also showed that electron beams, like waves, can interfere with each other. *Interference* occurs when waves overlap (see the Quick Lab on page 100). This overlapping results in a reduction of energy in some areas and an increase of energy in others. The effects of diffraction and interference can be seen in Figure 4-10.

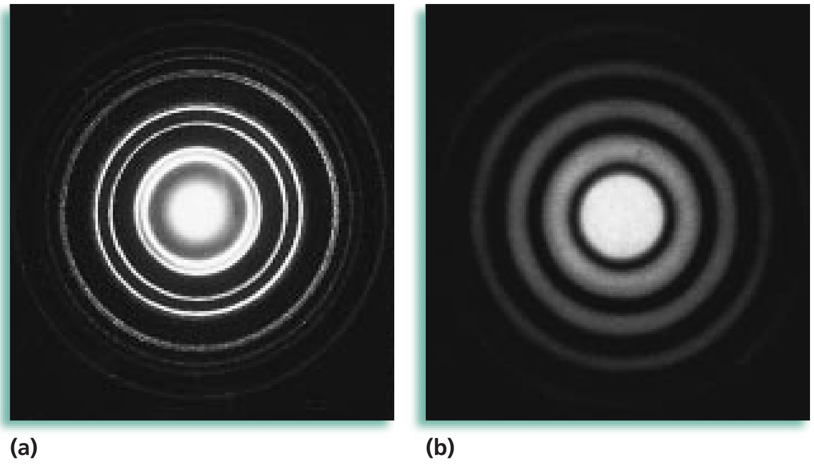

(a) (b)

FIGURE 4-10 Diffraction patterns produced by (a) a beam of electrons passed through a crystal and (b) a beam of visible light passed through a tiny aperture. Each pattern shows the results of bent waves that have interfered with each other. The bright areas correspond to areas of increased energy, while the dark areas correspond to areas of decreased energy.

The Heisenberg Uncertainty Principle

The idea of electrons having a dual wave-particle nature troubled scientists. If electrons are both particles and waves, then where are they in the atom? To answer this question, it is important to consider a proposal first made in 1927 by the German theoretical physicist Werner Heisenberg.

Heisenberg's idea involved the detection of electrons. Electrons are detected by their interaction with photons. Because photons have about the same energy as electrons, any attempt to locate a specific electron with a photon knocks the electron off its course. As a result, there is always a basic uncertainty in trying to locate an electron (or any other particle). *The* **Heisenberg uncertainty principle** *states that it is impossible to determine simultaneously both the position and velocity of an electron or any other particle*. Although it was difficult for scientists to accept this fact at the time, it has proven to be one of the fundamental principles of our present understanding of light and matter.

The Schrödinger Wave Equation

In 1926, the Austrian physicist Erwin Schrödinger used the hypothesis that electrons have a dual wave-particle nature to develop an equation that treated electrons in atoms as waves. Unlike Bohr's theory, which assumed quantization as a fact, quantization of electron energies was a natural outcome of Schrödinger's equation. Only waves of specific energies, and therefore frequencies, provided solutions to the equation. Together with the Heisenberg uncertainty principle, the Schrödinger wave equation laid the foundation for modern quantum theory. **Quantum theory** *describes mathematically the wave properties of electrons and other very small particles.*

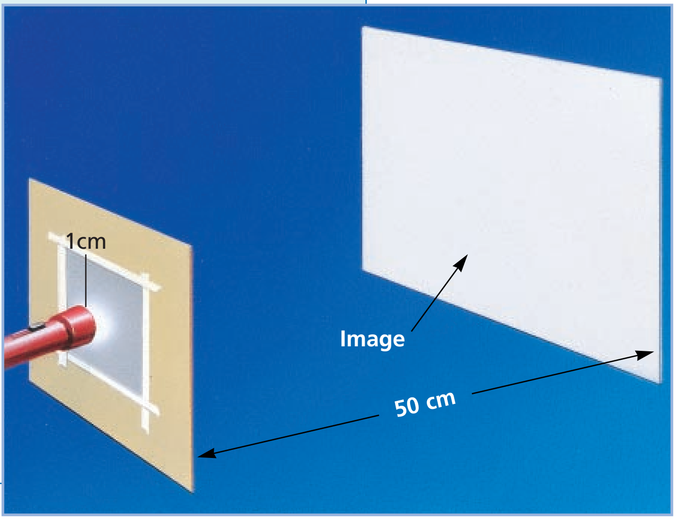
Quick LAB

The Wave Nature of Light: Interference

Wear Safety Goggles and an Apron.

Materials

- scissors
- manila folders
- thumbtack
- masking tape
- aluminum foil
- white poster board or cardboard
- flashlight



Question

Does light show the wave property of interference when a beam of light is projected through a pinhole onto a screen?

Procedure

Record all your observations.

1. To make the pinhole screen, cut a 20 cm × 20 cm square from a manila folder. In the center of the square, cut a 2 cm square hole. Cut a 7 cm × 7 cm square of aluminum foil. Using a thumbtack, make a pinhole in the center of the foil square. Tape the aluminum foil over the 2 cm square hole, making sure the pinhole is centered as shown in the diagram.
2. Use white poster board to make a projection screen 35 cm × 35 cm.
3. In a dark room, center the light beam from a flashlight on the pinhole. Hold the flashlight about 1 cm from the pinhole. The pinhole screen should be about 50 cm from the projection screen, as shown in the diagram. Adjust the distance to form a sharp image on the projection screen.

Discussion

1. Did you observe interference patterns on the screen?
2. As a result of your observations, what do you conclude about the nature of light?

Solutions to the Schrödinger wave equation are known as wave functions. Based on the Heisenberg uncertainty principle, the early developers of quantum theory determined that wave functions give only the *probability* of finding an electron at a given place around the nucleus. Thus, electrons do not travel around the nucleus in neat orbits, as Bohr had postulated. Instead, they exist in certain regions called orbitals. *An* **orbital** *is a three-dimensional region around the nucleus that indicates the probable location of an electron.*

Figure 4-11 illustrates two ways of picturing one type of atomic orbital. As you will see later in this section, atomic orbitals have different shapes and sizes.

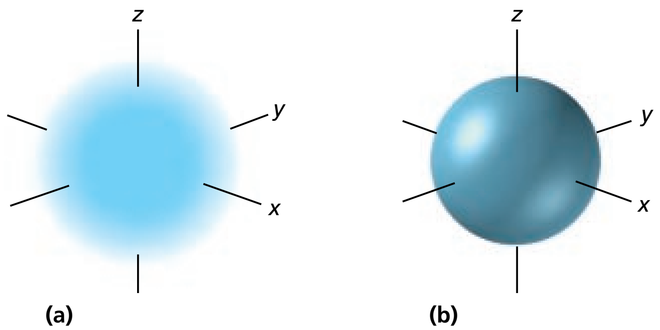


FIGURE 4-11 Two ways of showing a simple atomic orbital are presented. In (a) the probability of finding the electron is proportional to the density of the cloud. Shown in (b) is a surface within which the electron can be found a certain percentage of the time, in this case 90%.

Atomic Orbitals and Quantum Numbers

In the Bohr atomic model, electrons of increasing energy occupy orbits farther and farther from the nucleus. According to the Schrödinger equation, electrons in atomic orbitals also have quantized energies. An electron's energy level is not the only characteristic of an orbital that is indicated by solving the Schrödinger equation.

In order to completely describe orbitals, scientists use quantum numbers. **Quantum numbers** *specify the properties of atomic orbitals and the properties of electrons in orbitals*. The first three quantum numbers result from solutions to the Schrödinger equation. They indicate the main energy level, the shape, and the orientation of an orbital. The fourth, the spin quantum number, describes a fundamental state of the electron that occupies the orbital. As you read the following descriptions of the quantum numbers, refer to the appropriate columns in Table 4-2 on page 104.

Principal Quantum Number

The **principal quantum number,** *symbolized by n, indicates the main energy level occupied by the electron.* Values of n are positive integers only—1, 2, 3, and so on. As n increases, the electron's energy and its average distance from the nucleus increase (see Figure 4-12). For example, an electron for which $n = 1$ occupies the first, or lowest, main energy level and is located closest to the nucleus. As you will see, more than one electron can have the same n value. These electrons are sometimes said to be in the same electron *shell.* The total number of orbitals that exist in a given shell, or main energy level, is equal to n^2.

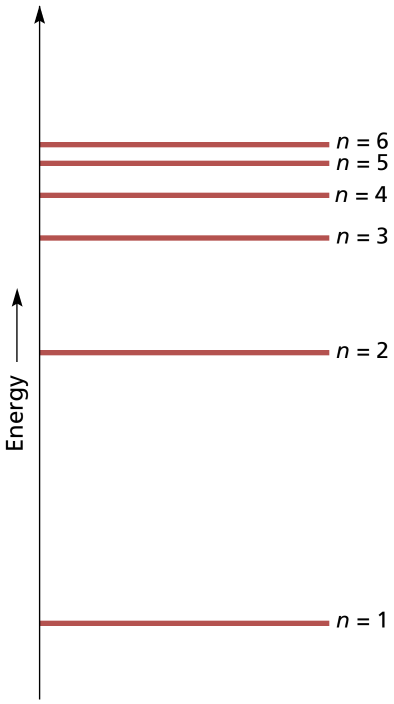


FIGURE 4-12 The main energy levels of an atom are represented by the principal quantum number, n.

Angular Momentum Quantum Number

Except at the first main energy level, orbitals of different shapes—known as *sublevels*—exist for a given value of n. *The* **angular momentum quantum number,** *symbolized by l, indicates the shape of the orbital.* For a specific main energy level, the number of orbital shapes possible is equal to n. The values of l allowed are zero and all positive integers less

TABLE 4-1 ***Orbital Letter Designations According to Values of l***

l	Letter
0	*s*
1	*p*
2	*d*
3	*f*

than or equal to $n - 1$. For example, orbitals for which $n = 2$ can have one of two shapes corresponding to $l = 0$ and $l = 1$. Depending on its value of *l*, an orbital is assigned a letter, as shown in Table 4-1.

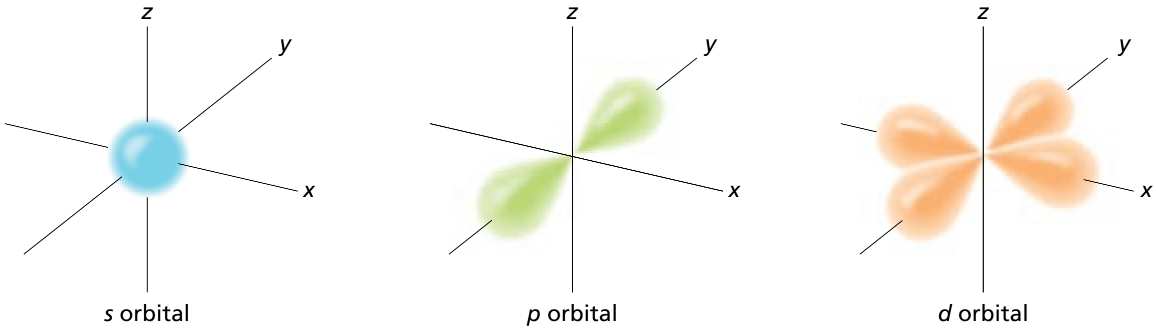
As shown in Figure 4-13, *s* orbitals are spherical, *p* orbitals have dumbbell shapes, and *d* orbitals are more complex. (The *f* orbital shapes are too complex to discuss here.) In the first energy level, $n = 1$, there is only one sublevel possible—an *s* orbital. As mentioned, the second energy level, $n = 2$, has two sublevels—the *s* and *p* orbitals. The third energy level, $n = 3$, has three sublevels—the *s*, *p*, and *d* orbitals. The fourth energy level, $n = 4$, has four sublevels—the *s*, *p*, *d*, and *f* orbitals. In an *n*th main energy level, there are *n* sublevels.

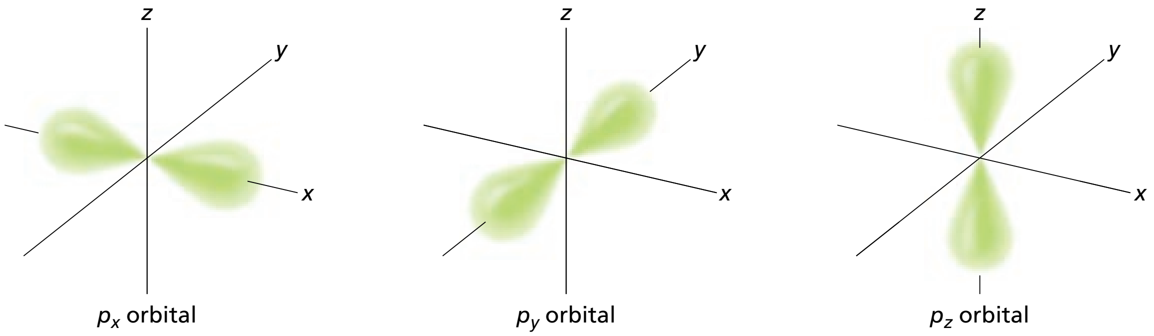
Each atomic orbital is designated by the principal quantum number followed by the letter of the sublevel. For example, the 1*s* sublevel is the *s* orbital in the first main energy level, while the 2*p* sublevel is the set of *p* orbitals in the second main energy level. On the other hand, a 4*d* orbital is part of the *d* sublevel in the fourth main energy level. How would you designate the *p* sublevel in the third main energy level? How many other sublevels are in the same main energy level with this one?

Magnetic Quantum Number

Atomic orbitals can have the same shape but different orientations around the nucleus. *The* **magnetic quantum number,** *symbolized by m, indicates the orientation of an orbital around the nucleus.* Here we describe the orbital orientations that correspond to various values of *m*. Because an *s* orbital is spherical and is centered around the nucleus, it has only one possible orientation. This orientation corresponds to a

FIGURE 4-13 The orbitals *s*, *p*, and *d* have different shapes. Each of the orbitals shown occupies a different region of space around the nucleus.



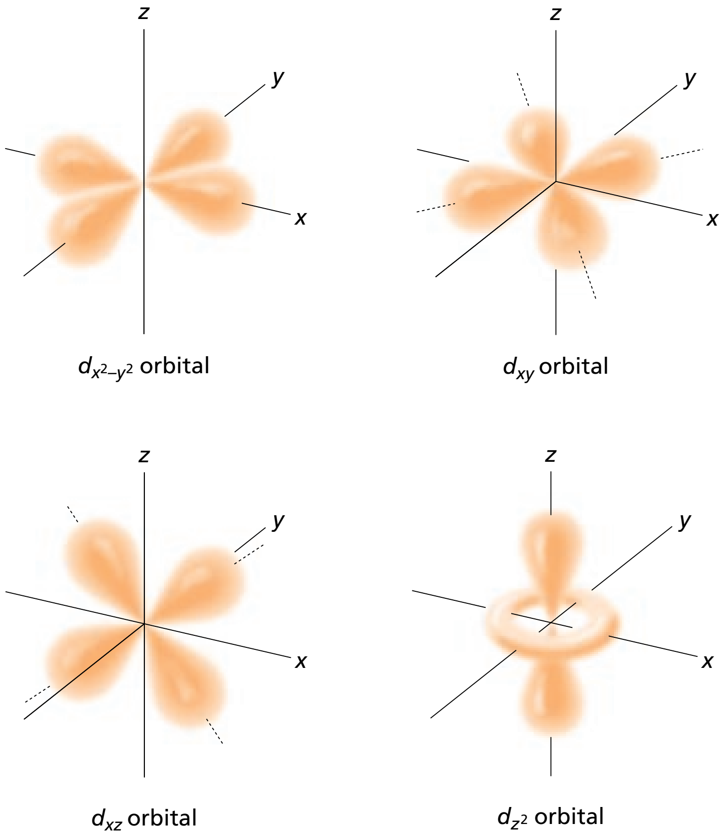


p_x orbital p_y orbital p_z orbital

FIGURE 4-14 The subscripts *x, y,* and *z* indicate the three different orientations of *p* orbitals. The intersection of the *x, y,* and *z* axes indicates the location of the center of the nucleus.

magnetic quantum number of $m = 0$. There is therefore only one *s* orbital in each *s* sublevel. As shown in Figure 4-14, the lobes of a *p* orbital can extend along the *x, y,* or *z* axis of a three-dimensional coordinate system. There are therefore three *p* orbitals in each *p* sublevel, which are designated as p_x, p_y, and p_z orbitals. The three *p* orbitals occupy different regions of space and correspond, in no particular order, to values of $m = -1$, $m = 0$, and $m = +1$.

There are five different *d* orbitals in each *d* sublevel (see Figure 4-15). The five different orientations, including one with a different shape, correspond to values of $m = -2$, $m = -1$, $m = 0$, $m = +1$, and $m = +2$. There are seven different *f* orbitals in each *f* sublevel.



$d_{x^2-y^2}$ orbital d_{xy} orbital d_{yz} orbital

d_{xz} orbital d_{z^2} orbital

FIGURE 4-15 The five different orientations of the *d* orbitals. Four have the same shape but different orientations. The fifth has a different shape and a different orientation than the others. Each orbital occupies a different region of space.

TABLE 4-2 *Quantum Number Relationships in Atomic Structure*

Principal quantum number: main energy level (*n*)	Sublevels in main energy level (*n* sublevels)	Number of orbitals per sublevel	Number of orbitals per main energy level (n^2)	Number of electrons per sublevel	Number of electrons per main energy level ($2n^2$)
1	*s*	1	1	2	2
2	*s* *p*	1 3	4	2 6	8
3	*s* *p* *d*	1 3 5	9	2 6 10	18
4	*s* *p* *d* *f*	1 3 5 7	16	2 6 10 14	32

As you can see in Table 4-2, the total number of orbitals at a main energy level increases with the value of *n*. In fact, the number of orbitals at each main energy level equals the square of the principal quantum number, n^2. What is the total number of orbitals in the third energy level? Specify each of the sublevels using the three quantum numbers you've learned so far.

Spin Quantum Number

Like Earth, an electron in an orbital can be thought of as spinning on an internal axis. It spins in one of two possible directions, or states. As it spins, it creates a magnetic field. To account for the magnetic properties of the electron, theoreticians of the early twentieth century created the spin quantum number. *The* **spin quantum number** *has only two possible values—*($+\frac{1}{2}$, $-\frac{1}{2}$)*—which indicate the two fundamental spin states of an electron in an orbital.* A single orbital can hold a maximum of two electrons, which must have opposite spins.

SECTION REVIEW

1. Define the following:
a. main energy levels
b. quantum numbers

2. a. List the four quantum numbers.
b. What general information about atomic orbitals is provided by the quantum numbers?

3. Describe briefly what specific information is given by each of the four quantum numbers.

Electron Configurations

SECTION 4-3

OBJECTIVES

- List the total number of electrons needed to fully occupy each main energy level.
- State the Aufbau principle, the Pauli exclusion principle, and Hund's rule.
- Describe the electron configurations for the atoms of any element using orbital notation, electron-configuration notation, and, when appropriate, noble-gas notation.

The quantum model of the atom improves on the Bohr model because it describes the arrangements of electrons in atoms other than hydrogen. *The arrangement of electrons in an atom is known as the atom's* **electron configuration.** Because atoms of different elements have different numbers of electrons, a distinct electron configuration exists for the atoms of each element. Like all systems in nature, electrons in atoms tend to assume arrangements that have the lowest possible energies. The lowest-energy arrangement of the electrons for each element is called the element's *ground-state electron configuration.* A few simple rules, combined with the quantum number relationships discussed in Section 4-2, allow us to determine these ground-state electron configurations.

Rules Governing Electron Configurations

To build up electron configurations for the ground state of any particular atom, first the energy levels of the orbitals are determined. Then electrons are added to the orbitals one by one according to three basic rules. (Remember that real atoms are not built up by adding protons and electrons one at a time.)

The first rule shows the order in which electrons occupy orbitals. According to the **Aufbau principle,** *an electron occupies the lowest-energy orbital that can receive it.* Figure 4-16 shows the atomic orbitals in order of increasing energy. The orbital with the lowest energy is the 1*s* orbital. In a ground-state hydrogen atom, the electron is in this orbital. The 2*s* orbital is the next highest in energy, then the 2*p* orbitals. Beginning with the third main energy level, $n = 3$, the energies of the sublevels in different main energy levels begin to overlap.

Note in the figure, for example, that the 4*s* sublevel is lower in energy than the 3*d* sublevel. Therefore, the 4*s* orbital is filled before any electrons enter the 3*d* orbitals. (Less energy is required for two electrons to pair up in the 4*s* orbital than for a single electron to

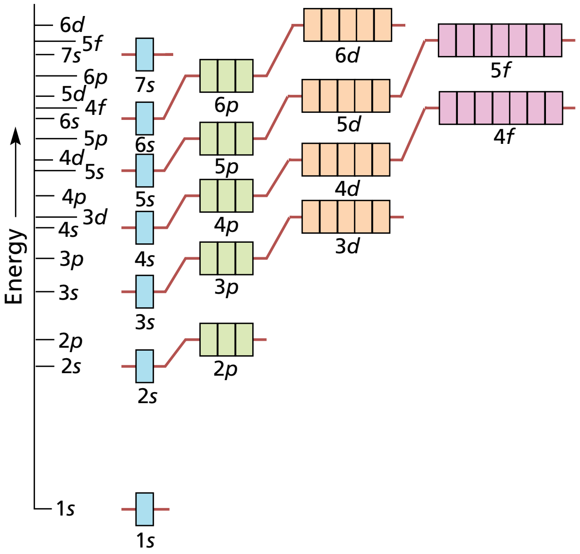


FIGURE 4-16 The order of increasing energy for atomic sublevels is shown on the vertical axis. Each individual box represents an orbital.

occupy a 3*d* orbital.) Once the 3*d* orbitals are fully occupied, which sublevel will be occupied next?

The second rule reflects the importance of the spin quantum number. According to the **Pauli exclusion principle,** *no two electrons in the same atom can have the same set of four quantum numbers.* The principal, angular momentum, and magnetic quantum numbers specify the energy, shape, and orientation of an orbital. The two values of the spin quantum number allow two electrons of opposite spins to occupy the orbital (see Figure 4-17).

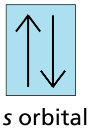


FIGURE 4-17 According to the Pauli exclusion principle, an orbital can hold two electrons of opposite spin. In this electron configuration of a helium atom, each arrow represents one of the atom's two electrons. The direction of the arrow indicates the electron's spin.

The third rule requires placing as many unpaired electrons as possible in separate orbitals in the same sublevel. In this way, electron-electron repulsion is minimized so that the electron arrangements have the lowest energy possible. According to **Hund's rule,** *orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin.* Applying this rule shows, for example, that one electron will enter each of the three *p* orbitals in a main energy level before a second electron enters any of them. This is illustrated in Figure 4-18. What is the maximum number of unpaired electrons in a *d* sublevel?

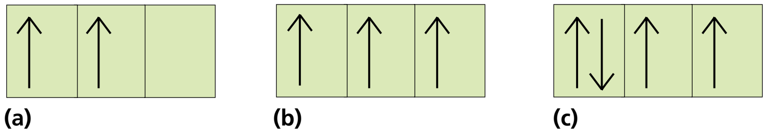


FIGURE 4-18 The figure shows how (a) two, (b) three, and (c) four electrons fill the *p* sublevel of a given main energy level according to Hund's rule.

Representing Electron Configurations

Three methods, or notations, are used to indicate electron configurations. Two of these notations will be discussed in the next two sections for the first-period elements, hydrogen and helium. The third notation applies mostly to elements of the third period and higher. It will be discussed in the section on third-period elements.

In a ground-state hydrogen atom, the single electron is in the lowest-energy orbital, the 1*s* orbital. The electron can be in either one of its two spin states. Helium has two electrons, which are paired in the 1*s* orbital.

Orbital Notation

In orbital notation, an unoccupied orbital is represented by a line, ____, with the orbital's name written underneath the line. An orbital containing one electron is represented as $\underline{\ \uparrow\ }$. An orbital containing two electrons is represented as $\underline{\ \uparrow\downarrow\ }$, showing the electrons paired and with opposite spins. The lines are labeled with the principal quantum number and sublevel letter. For example, the orbital notations for hydrogen and helium are written as follows.

$$\mathrm{H}\ \underset{1s}{\underline{\;\uparrow\;}}\qquad\qquad \mathrm{He}\ \underset{1s}{\underline{\;\uparrow\downarrow\;}}$$

Electron-Configuration Notation

CHEMISTRY INTERACTIVE TUTOR

Module 2: Models of the Atom

Electron-configuration notation eliminates the lines and arrows of orbital notation. Instead, the number of electrons in a sublevel is shown by adding a superscript to the sublevel designation. The hydrogen configuration is represented by $1s^1$. The superscript indicates that one electron is present in hydrogen's 1*s* orbital. The helium configuration is represented by $1s^2$. Here the superscript indicates that there are two electrons in helium's 1*s* orbital.

SAMPLE PROBLEM 4-1

The electron configuration of boron is $1s^22s^22p^1$. How many electrons are present in an atom of boron? What is the atomic number for boron? Write the orbital notation for boron.

SOLUTION

The number of electrons in a boron atom is equal to the sum of the superscripts in its electron-configuration notation: $2 + 2 + 1 = 5$ electrons. The number of protons equals the number of electrons in a neutral atom. So we know that boron has 5 protons and thus has an atomic number of 5. To write the orbital notation, first draw the lines representing orbitals.

$$\underset{1s}{\underline{\qquad}}\quad \underset{2s}{\underline{\qquad}}\quad \underset{2p_x}{\underline{\qquad}}\,\underset{2p_y}{\underline{\qquad}}\,\underset{2p_z}{\underline{\qquad}}$$

Next, add arrows showing the electron locations. The first two electrons occupy $n = 1$ energy level and fill the 1*s* orbital.

$$\underset{1s}{\underline{\;\uparrow\downarrow\;}}\quad \underset{2s}{\underline{\qquad}}\quad \underset{2p_x}{\underline{\qquad}}\,\underset{2p_y}{\underline{\qquad}}\,\underset{2p_z}{\underline{\qquad}}$$

The next three electrons occupy the $n = 2$ main energy level. According to the Aufbau principle, two of these occupy the lower-energy 2*s* orbital. The third occupies a higher-energy *p* orbital.

$$\underset{1s}{\underline{\;\uparrow\downarrow\;}}\quad \underset{2s}{\underline{\;\uparrow\downarrow\;}}\quad \underset{2p_x}{\underline{\;\uparrow\;}}\,\underset{2p_y}{\underline{\qquad}}\,\underset{2p_z}{\underline{\qquad}}$$

PRACTICE

1. The electron configuration of nitrogen is $1s^22s^22p^3$. How many electrons are present in a nitrogen atom? What is the atomic number of nitrogen? Write the orbital notation for nitrogen.	*Answer* 7, 7, $\underset{1s}{\underline{\;\uparrow\downarrow\;}}\ \underset{2s}{\underline{\;\uparrow\downarrow\;}}\ \underset{2p_x}{\underline{\;\uparrow\;}}\,\underset{2p_y}{\underline{\;\uparrow\;}}\,\underset{2p_z}{\underline{\;\uparrow\;}}$
2. The electron configuration of fluorine is $1s^22s^22p^5$. What is the atomic number of fluorine? How many of its *p* orbitals are filled? How many unpaired electrons does a fluorine atom contain?	*Answer* 9, 2, 1

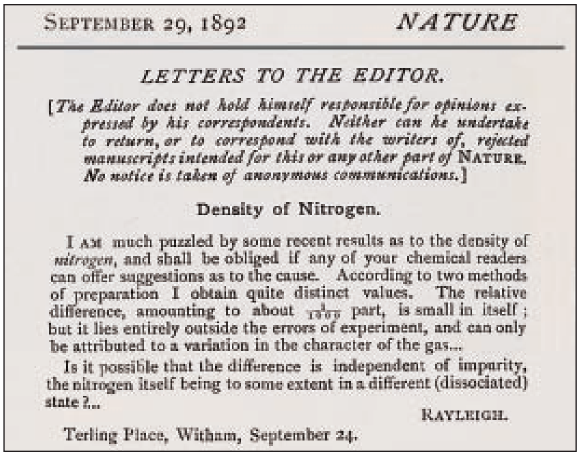
The Noble Decade

HISTORICAL PERSPECTIVE

By the late nineteenth century, the science of chemistry had begun to be organized. The first international congress of chemistry, in 1860, established the field's first standards. And Dmitri Mendeleev's periodic table of elements gave chemists across the globe a systematic understanding of matter's building blocks. But many important findings were yet to come, including the discovery of a family of rare, unreactive gases that were unlike any substances known at the time.

Cross-Disciplinary Correspondence

In 1888, the British physicist Lord Rayleigh encountered a small but significant discrepancy in the results of one of his experiments. In an effort to redetermine the atomic mass of nitrogen, he measured the densities of several samples of nitrogen gas. Each sample had been prepared by a different method. The samples that had been isolated from chemical reactions all exhibited similar densities. But they were about one-tenth of a percent lighter than the nitrogen isolated from air, which at the time was believed to be a mixture of nitrogen, oxygen, water vapor, and carbon dioxide.



SEPTEMBER 29, 1892 *NATURE*

LETTERS TO THE EDITOR.

[*The Editor does not hold himself responsible for opinions expressed by his correspondents. Neither can he undertake to return, or to correspond with the writers of, rejected manuscripts intended for this or any other part of* NATURE. *No notice is taken of anonymous communications.*]

Density of Nitrogen.

I AM much puzzled by some recent results as to the density of *nitrogen*, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to two methods of preparation I obtain quite distinct values. The relative difference, amounting to about $\frac{1}{1000}$ part, is small in itself; but it lies entirely outside the errors of experiment, and can only be attributed to a variation in the character of the gas...

Is it possible that the difference is independent of impurity, the nitrogen itself being to some extent in a different (dissociated) state ?...

RAYLEIGH.

Terling Place, Witham, September 24.

An excerpt of Lord Rayleigh's letter as originally published in Nature *magazine in 1892*

Rayleigh was at a loss to explain his discovery. Finally, in 1892, he published a letter in *Nature* magazine appealing to his colleagues for an explanation. A month later he received a reply from a Scottish chemist named William Ramsay. Ramsay related that he too had been stumped by the density difference between chemical and atmospheric nitrogen. Rayleigh decided to report his findings to the Royal Society of Chemistry, adding:

> *Until the questions arising out of these observations are thoroughly cleared up, the above number [density] for nitrogen must be received with a certain reserve.*

A Chemist's Approach

With Rayleigh's permission, Ramsay attempted to remove all the known components from a sample of air and analyze what, if anything, remained. First he heated magnesium in the air to remove all of the nitrogen in the form of magnesium nitride. Then he removed the oxygen, water vapor, and carbon dioxide factions. What remained was a minuscule portion of a mysterious gas.

Ramsay tried to cause the gas to react with chemically active substances, such as hydrogen, sodium, and caustic soda, but the gas remained unaltered. He decided to name this new atmospheric component argon (Greek for "inert" or "idle"):

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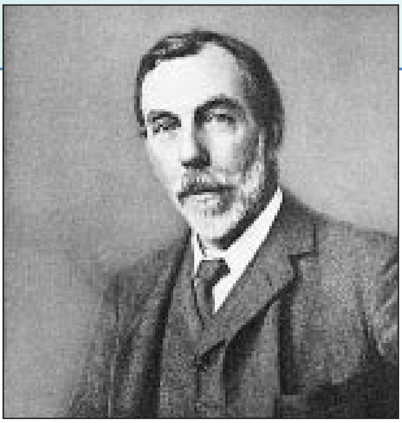


In 1893, Scottish chemist William Ramsay isolated a previously unknown component of the atmosphere.

> *The gas deserves the name "argon," for it is a most astonishingly indifferent body. . . .*

Periodic Problems

Rayleigh and Ramsay were sure that they had discovered a new element. But this created a problem. Their calculations indicated that argon had an atomic mass of about 40. However, there was no space in the periodic table as it appeared in 1894 for such an element. The elements with atomic masses closest to that of argon were chlorine and potassium. Unfortunately, the chemical properties of the families of each of these elements were completely dissimilar to those of the strange gas.

Ramsay contemplated argon's lack of reactivity. He knew that Mendeleev had created the periodic table on the basis of valence, or the number of atomic partners an element bonds with in forming a compound. As Ramsay could not cause argon to form any compounds, he assigned it a valence of zero. And because the valence of the elements in the families of both chlorine and potassium was one, perhaps argon fit in between them. In May 1894, Ramsay wrote to Rayleigh:

> *Has it occurred to you that there is room for gaseous elements at the end of the first column of the periodic table?…Such elements should have the density 20 or thereabouts, and 0.8 pc [percent] (1/120th about) of the nitrogen of the air could so raise the density of nitrogen that it would stand to pure [chemical] nitrogen in the ratio of 230:231.*

Ramsay's insight that argon merited a new spot in the periodic table, between the chlorine family and the potassium family, was correct. And, as he would soon confirm, his newly discovered gas was indeed one of a previously unknown family of elements.

New Neighbors

In 1895, Ramsay isolated a light, inert gas from a mineral called cleveite. Physical analysis revealed that the gas was the same as one that had been identified in the sun in 1868—helium. Helium was the second zero-valent element found on Earth, and its discovery made chemists aware that the periodic table had been missing a whole column of elements.

Over the next three years, Ramsay and his assistant, Morris Travers, identified three more inert gases present in the atmosphere: neon (Greek for "new"), krypton ("hidden"), and xenon ("stranger"). Finally in 1900, German chemist Friedrich Ernst Dorn discovered radon, the last of the new family of elements known today as the noble gases. For his discovery, Ramsay received the Nobel Prize in 1904.

Groups	III	IV	V	VI	VII	VIII	I	II	III	IV	V	VI	VII	0	I	II
Periods	b	b	b	b	b	b	b	b	a	a	a	a	a		a	a
1															H	He
2															Li	Be
3									B	C	N	O	F	Ne	Na	Mg
4									Al	Si	P	S	Cl	Ar	K	Ca
5	Sc	Ti	V	Cr	Mn	Fe Co Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr
6	Y	Zr	Nb	Mo	Tc	Ru Rh Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba
7	La	Hf	Ta	W	Re	Os Ir Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra
8	Ac															
	Transition elements								Main-group elements							

One version of the periodic table as it appeared after the discovery of the noble gases. The placement of the Group 1 and 2 elements at the far right of the table shows clearly how the noble gases fit in between the chlorine family and the potassium family of elements. The "0" above the noble-gas family indicates the zero valency of the gases.

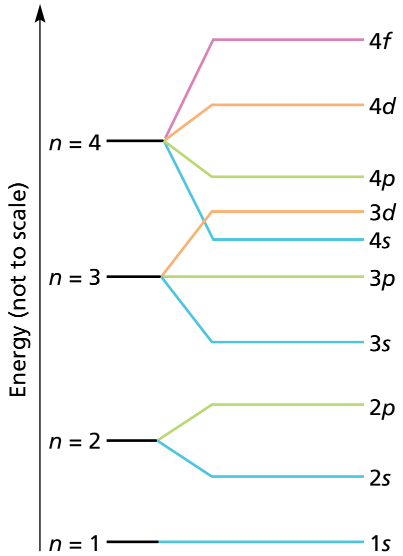


FIGURE 4-19 The direction of the arrow indicates the order in which atomic orbitals are filled according to the Aufbau principle.

Elements of the Second Period

In the first-period elements, hydrogen and helium, electrons occupy the first main energy level. The ground-state configurations in Table 4-3 illustrate how the Aufbau principle, the Pauli exclusion principle, and Hund's rule are applied to atoms of elements in the second period. Figure 4-19 shows the first four main energy levels in order of increasing energy for applying the Aufbau principle.

According to the Aufbau principle, after the 1*s* orbital is filled, the next electron occupies the *s* sublevel in the second main energy level. Thus, lithium, Li, has a configuration of $1s^22s^1$. The electron occupying the 2*s* level of a lithium atom is in the atom's highest, or outermost, occupied level. *The* **highest occupied level** *is the electron-containing main energy level with the highest principal quantum number*. The two electrons in the 1*s* sublevel of lithium are no longer in the outermost main energy level. They have become **inner-shell electrons,** *which are electrons that are not in the highest occupied energy level.*

The fourth electron in an atom of beryllium, Be, must complete the pair in the 2*s* sublevel because this sublevel is of lower energy than the 2*p* sublevel. With the 2*s* sublevel filled, the 2*p* sublevel, which has three vacant orbitals of equal energy, can be occupied. Hund's rule applies here, as is shown in the orbital notations in Table 4-3. One of the three *p* orbitals is occupied by a single electron in an atom of boron, B. Two of the three *p* orbitals are occupied by unpaired electrons in an atom of carbon, C. And all three *p* orbitals are occupied by unpaired electrons in an atom of nitrogen, N.

According to the Aufbau principle, the next electron must pair with another electron in one of the 2*p* orbitals rather than enter the third main energy level. The Pauli exclusion principle allows the electron to pair with

TABLE 4-3 ***Electron Configurations of Atoms of Second-Period Elements Showing Two Notations***

		Orbital notation					**Electron-configuration notation**
Name	**Symbol**	**1*s***	**2*s***	**2*p***			
Lithium	Li	↑↓	↑				$1s^22s^1$
Beryllium	Be	↑↓	↑↓				$1s^22s^2$
Boron	B	↑↓	↑↓	↑			$1s^22s^22p^1$
Carbon	C	↑↓	↑↓	↑	↑		$1s^22s^22p^2$
Nitrogen	N	↑↓	↑↓	↑	↑	↑	$1s^22s^22p^3$
Oxygen	O	↑↓	↑↓	↑↓	↑	↑	$1s^22s^22p^4$
Fluorine	F	↑↓	↑↓	↑↓	↑↓	↑	$1s^22s^22p^5$
Neon	Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^22s^22p^6$

one of the electrons occupying the 2*p* orbitals as long as the spins of the paired electrons are opposite. Thus, atoms of oxygen, O, have the configuration $1s^22s^22p^4$. Oxygen's orbital notation is shown in Table 4-3.

Two 2*p* orbitals are filled in fluorine, F, and all three are filled in neon, Ne. Atoms such as those of neon, which have the *s* and *p* sublevels of their highest occupied level filled with eight electrons, are said to have an *octet* of electrons. Examine the periodic table inside the back cover of the text. Notice that neon is the last element in the second period.

Elements of the Third Period

After the outer octet is filled in neon, the next electron enters the *s* sublevel in the $n = 3$ main energy level. Thus, atoms of sodium, Na, have the configuration $1s^22s^22p^63s^1$. Compare the configuration of a sodium atom with that of an atom of neon in Table 4-3. Notice that the first 10 electrons in a sodium atom have the same configuration as a neon atom, $1s^22s^22p^6$. In fact, the first 10 electrons in an atom of each of the third-period elements have the same configuration as neon. This similarity allows us to use a shorthand notation for the electron configurations of the third-period elements.

Noble-Gas Notation

Neon is a member of the Group 18 elements. *The Group 18 elements (helium, neon, argon, krypton, xenon, and radon) are called the* **noble gases.** To simplify sodium's notation, the symbol for neon, enclosed in square brackets, is used to represent the complete neon configuration: $[Ne] = 1s^22s^22p^6$. This allows us to write sodium's electron configuration as $[Ne]3s^1$, which is called sodium's *noble-gas notation.* Table 4-4 shows the noble-gas notation of the electron configuration of each of the third-period elements.

TABLE 4-4 ***Electron Configurations of Atoms of Third-Period Elements***

Name	Symbol	Atomic number	Number of electrons in sublevels 1*s*	2*s*	2*p*	3*s*	3*p*	Noble-gas notation
Sodium	Na	11	2	2	6	1		$[Ne]3s^1$
Magnesium	Mg	12	2	2	6	2		$[Ne]3s^2$
Aluminum	Al	13	2	2	6	2	1	$[Ne]3s^23p^1$
Silicon	Si	14	2	2	6	2	2	$[Ne]3s^23p^2$
Phosphorus	P	15	2	2	6	2	3	$[Ne]3s^23p^3$
Sulfur	S	16	2	2	6	2	4	$[Ne]3s^23p^4$
Chlorine	Cl	17	2	2	6	2	5	$[Ne]3s^23p^5$
Argon	Ar	18	2	2	6	2	6	$[Ne]3s^23p^6$

The last element in the third period is argon, Ar, which is a noble gas. As in neon, the highest-occupied energy level of argon has an octet of electrons, [Ne]$3s^2 3p^6$. In fact, each noble gas other than He has an electron octet in its highest energy level. *A* **noble-gas configuration** *is an outer main energy level fully occupied, in most cases, by eight electrons.*

Elements of the Fourth Period

The electron configurations of atoms in the fourth-period elements are shown in Table 4-5. The period begins by filling the 4*s* orbital, the empty orbital of lowest energy. Thus, the first element in the fourth period is potassium, K, which has the electron configuration [Ar]$4s^1$. The next element is calcium, Ca, which has the electron configuration [Ar]$4s^2$.

With the 4*s* sublevel filled, the 4*p* and 3*d* sublevels are the next available vacant orbitals. Figure 4-19 on page 110 shows that the 3*d* sublevel

TABLE 4-5 ***Electron Configuration of Atoms of Elements in the Fourth Period***

Name	Symbol	Atomic number	Number of electrons in sublevels above 2*p*: 3*s*	3*p*	3*d*	4*s*	4*p*	Noble-gas notation
Potassium	K	19	2	6		1		*[Ar]$4s^1$
Calcium	Ca	20	2	6		2		[Ar]$4s^2$
Scandium	Sc	21	2	6	1	2		[Ar]$3d^1 4s^2$
Titanium	Ti	22	2	6	2	2		[Ar]$3d^2 4s^2$
Vanadium	V	23	2	6	3	2		[Ar]$3d^3 4s^2$
Chromium	Cr	24	2	6	5	1		[Ar]$3d^5 4s^1$
Manganese	Mn	25	2	6	5	2		[Ar]$3d^5 4s^2$
Iron	Fe	26	2	6	6	2		[Ar]$3d^6 4s^2$
Cobalt	Co	27	2	6	7	2		[Ar]$3d^7 4s^2$
Nickel	Ni	28	2	6	8	2		[Ar]$3d^8 4s^2$
Copper	Cu	29	2	6	10	1		[Ar]$3d^{10} 4s^1$
Zinc	Zn	30	2	6	10	2		[Ar]$3d^{10} 4s^2$
Gallium	Ga	31	2	6	10	2	1	[Ar]$3d^{10} 4s^2 4p^1$
Germanium	Ge	32	2	6	10	2	2	[Ar]$3d^{10} 4s^2 4p^2$
Arsenic	As	33	2	6	10	2	3	[Ar]$3d^{10} 4s^2 4p^3$
Selenium	Se	34	2	6	10	2	4	[Ar]$3d^{10} 4s^2 4p^4$
Bromine	Br	35	2	6	10	2	5	[Ar]$3d^{10} 4s^2 4p^5$
Krypton	Kr	36	2	6	10	2	6	[Ar]$3d^{10} 4s^2 4p^6$

*[Ar] = $1s^2 2s^2 2p^6 3s^2 3p^6$

is lower in energy than the 4p sublevel. Therefore, the five 3d orbitals are next to be filled. A total of 10 electrons can occupy the 3d orbitals. These are filled successively in the 10 elements from scandium (atomic number 21) to zinc (atomic number 30).

Scandium, Sc, has the electron configuration $[\mathrm{Ar}]3d^14s^2$. Titanium, Ti, has the configuration $[\mathrm{Ar}]3d^24s^2$. And vanadium, V, has the configuration $[\mathrm{Ar}]3d^34s^2$. Up to this point, three electrons with the same spin have been added to three separate d orbitals, as required by Hund's rule.

Surprisingly, chromium, Cr, has the electron configuration $[\mathrm{Ar}]3d^54s^1$. Not only did the added electron go into the fourth 3d orbital, but an electron also moved from the 4s orbital into the fifth 3d orbital, leaving the 4s orbital with a single electron. Chromium's electron configuration is contrary to what is expected according to the Aufbau principle. However, in reality the $[\mathrm{Ar}]3d^54s^1$ configuration is of lower energy than a $[\mathrm{Ar}]3d^44s^2$ configuration. For chromium, having six outer orbitals with unpaired electrons is a more stable arrangement than having four unpaired electrons in the 3d orbitals and forcing two electrons to pair up in the 4s orbital. On the other hand, for tungsten, W, which is in the same group as chromium, having four electrons in the 5d orbitals and two electrons paired in the 6s orbital is the most stable arrrangement. Unfortunately, there is no simple explanation for such deviations from the ideal order given in Figure 4-19.

Manganese, Mn, has the electron configuration $[\mathrm{Ar}]3d^54s^2$. The added electron goes to the 4s orbital, completely filling this orbital while leaving the 3d orbitals still half-filled. Beginning with the next element, electrons continue to pair in the d orbitals. Thus, iron, Fe, has the configuration $[\mathrm{Ar}]3d^64s^2$; cobalt, Co, has the configuration $[\mathrm{Ar}]3d^74s^2$; and nickel, Ni, has the configuration $[\mathrm{Ar}]3d^84s^2$. Next is copper, Cu, in which an electron moves from the 4s orbital to pair with the electron in the fifth 3d orbital. The result is an electron configuration of $[\mathrm{Ar}]3d^{10}4s^1$—the lowest-energy configuration for Cu.

In atoms of zinc, Zn, the 4s sublevel is filled to give the electron configuration $[\mathrm{Ar}]3d^{10}4s^2$. In atoms of the next six elements, electrons add one by one to the three 4p orbitals. According to Hund's rule, one electron is added to each of the three 4p orbitals before electrons are paired in any 4p orbital.

Elements of the Fifth Period

In the 18 elements of the fifth period, sublevels fill in a similar manner as in elements of the fourth period. However, they start at the 5s orbital instead of the 4s. Successive electrons are added first to the 5s orbital, then to the 4d orbitals, and finally to the 5p orbitals. This can be seen in Table 4-6 on page 114. There are occasional deviations from the predicted configurations here also. The deviations differ from those for fourth-period elements, but in each case the preferred configuration has the lowest possible energy.

TABLE 4-6 *Electron Configurations of Atoms of Elements in the Fifth Period*

			Number of electrons in sublevels above $3d$					
Name	**Symbol**	**Atomic number**	**$4s$**	**$4p$**	**$4d$**	**$5s$**	**$5p$**	**Noble-gas notation**
Rubidium	Rb	37	2	6		1		*$[Kr]5s^1$
Strontium	Sr	38	2	6		2		$[Kr]5s^2$
Yttrium	Y	39	2	6	1	2		$[Kr]4d^15s^2$
Zirconium	Zr	40	2	6	2	2		$[Kr]4d^25s^2$
Niobium	Nb	41	2	6	4	1		$[Kr]4d^45s^1$
Molybdenum	Mo	42	2	6	5	1		$[Kr]4d^55s^1$
Technetium	Tc	43	2	6	6	1		$[Kr]4d^65s^1$
Ruthenium	Ru	44	2	6	7	1		$[Kr]4d^75s^1$
Rhodium	Rh	45	2	6	8	1		$[Kr]4d^85s^1$
Palladium	Pd	46	2	6	10			$[Kr]4d^{10}$
Silver	Ag	47	2	6	10	1		$[Kr]4d^{10}5s^1$
Cadmium	Cd	48	2	6	10	2		$[Kr]4d^{10}5s^2$
Indium	In	49	2	6	10	2	1	$[Kr]4d^{10}5s^25p^1$
Tin	Sn	50	2	6	10	2	2	$[Kr]4d^{10}5s^25p^2$
Antimony	Sb	51	2	6	10	2	3	$[Kr]4d^{10}5s^25p^3$
Tellurium	Te	52	2	6	10	2	4	$[Kr]4d^{10}5s^25p^4$
Iodine	I	53	2	6	10	2	5	$[Kr]4d^{10}5s^25p^5$
Xenon	Xe	54	2	6	10	2	6	$[Kr]4d^{10}5s^25p^6$

*$[Kr] = 1s^22s^22p^63s^23p^63d^{10}4s^24p^6$

SAMPLE PROBLEM 4-2

a. **Write both the complete electron-configuration notation and the noble-gas notation for iron, Fe.**

b. **How many electron-containing orbitals are in an atom of iron? How many of these orbitals are completely filled? How many unpaired electrons are there in an atom of iron? In which sublevel are the unpaired electrons located?**

SOLUTION

a. The complete electron-configuration notation of iron is $1s^22s^22p^63s^23p^63d^64s^2$. The periodic table inside the back cover of the text reveals that $1s^22s^22p^63s^23p^6$ is the electron configuration of the noble gas argon, Ar. Therefore, as shown in Table 4-5 on page 112, iron's noble-gas notation is $[Ar]3d^64s^2$.

b. An iron atom has 15 orbitals that contain electrons. They consist of one 1s orbital, one $2s$ orbital, three $2p$ orbitals, one $3s$ orbital, three $3p$ orbitals, five $3d$ orbitals, and one $4s$ orbital. Eleven of these orbitals are filled. The notation $3d^6$ represents $3d$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$, so there are four unpaired electrons. They are located in the $3d$ sublevel.

PRACTICE

	Answer
1. a. Write both the complete electron-configuration notation and the noble-gas notation for iodine, I. How many inner-shell electrons does an iodine atom contain?	1. a. $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$, $[Kr]4d^{10}5s^25p^5$, 46
b. How many electron-containing orbitals are in an atom of iodine? How many of these orbitals are filled? How many unpaired electrons are there in an atom of iodine?	b. 27, 26, 1
2. a. Write the noble-gas notation for tin, Sn. How many unpaired electrons are there in an atom of tin?	2. a. $[Kr]4d^{10}5s^25p^2$, 2
b. How many electron-containing *d* orbitals are there in an atom of tin? Name the element in the fourth period whose atoms have the same number of highest-energy-level electrons as tin.	b. 10, germanium
3. a. Without consulting the periodic table or a table in this chapter, write the complete electron configuration for the element with atomic number 25.	3. a. $1s^22s^22p^63s^23p^63d^54s^2$
b. Identify the element described in item 3a.	b. manganese

Elements of the Sixth and Seventh Periods

The sixth period consists of 32 elements. It is much longer than the periods that precede it in the periodic table. To build up electron configurations for elements of this period, electrons are added first to the 6*s* orbital in cesium, Cs, and barium, Ba. Then, in lanthanum, La, an electron is added to the 5*d* orbital.

With the next element, cerium, Ce, the 4*f* orbitals begin to fill, giving cerium atoms a configuration of $[Xe]4f^15d^16s^2$. In the next 13 elements, the 4*f* orbitals are filled. Next the 5*d* orbitals are filled and the period is completed by filling the 6*p* orbitals. Because the 4*f* and the 5*d* orbitals are very close in energy, numerous deviations from the simple rules occur as these orbitals are filled. The electron configurations of the sixth-period elements can be found in the periodic table inside the back cover of the text.

The seventh period is incomplete and consists largely of synthetic elements, which will be discussed in Chapter 22.

SAMPLE PROBLEM 4-3

a. Write both the complete electron-configuration notation and the noble-gas notation for a rubidium atom.

b. Identify the elements in the second, third, and fourth periods that have the same number of highest-energy-level electrons as rubidium.

SOLUTION

a. $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$, $[\mathrm{Kr}]5s^1$

b. Rubidium has one electron in its highest energy level (the fifth). The elements with the same outermost configuration are, in the second period, lithium, Li; in the third period, sodium, Na; and in the fourth period, potassium, K.

PRACTICE

	Answer
1. a. Write both the complete electron-configuration notation and the noble-gas notation for a barium atom.	1. **a.** $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$ $5p^66s^2$, $[\mathrm{Xe}]6s^2$
b. Identify the elements in the second, third, fourth, and fifth periods that have the same number of highest-energy-level electrons as barium.	**b.** Be, Mg, Ca, Sr
2. a. Write the noble-gas notation for a gold atom.	2. **a.** $[\mathrm{Xe}]4f^{14}5d^{10}6s^1$
b. Identify the elements in the sixth period that have one unpaired electron in their 6*s* sublevel.	**b.** Au, Cs, Pt

SECTION REVIEW

1. a. What is an atom's electron configuration?
   b. What three principles guide the electron configuration of an atom?

2. What three methods are used to represent the arrangement of electrons in atoms?

3. What is an octet of electrons? Which elements contain an octet of electrons?

4. Write the complete electron-configuration notation, the noble-gas notation, and the orbital notation for the following elements:
a. carbon   b. neon   c. sulfur

5. Identify the elements having the following electron configurations:
a. $1s^22s^22p^63s^23p^3$
b. $[\mathrm{Ar}]4s^1$
c. contains four electrons in its third and outer main energy level
d. contains one set of paired and three unpaired electrons in its fourth and outer main energy level

CHAPTER 4 REVIEW

CHAPTER SUMMARY

4-1

- In the early twentieth century, light was determined to have a dual wave-particle nature.
- Quantum theory was developed to explain such observations as the photoelectric effect and the line-emission spectrum of hydrogen.
- Quantum theory states that electrons can exist in atoms only at specific energy levels.
- When an electron moves from one main energy level to a main energy level of lower energy, a photon is emitted. The photon's energy equals the energy difference between the two levels.
- An electron in an atom can move from one main energy level to a higher main energy level only by absorbing an amount of energy exactly equal to the difference between the two levels.

Vocabulary

continuous spectrum (94)
electromagnetic radiation (91)
electromagnetic spectrum (91)
excited state (94)
frequency (92)
ground state (94)
line-emission spectrum (94)
photoelectric effect (93)
photon (94)
quantum (93)
wavelength (91)

4-2

- In the early twentieth century, electrons were determined to have a dual wave-particle nature.
- The Heisenberg uncertainty principle states that it is impossible to determine simultaneously both the position and velocity of an electron or any other particle.
- Quantization of electron energies is a natural outcome of the Schrödinger wave equation, which treats an atom's electrons as waves surrounding the nucleus.
- An orbital is a three-dimensional region around the nucleus that shows the region of probable electron locations.
- The four quantum numbers that describe the properties of electrons in atomic orbitals are the principal quantum number, the angular momentum quantum number, the magnetic quantum number, and the spin quantum number.

Vocabulary

angular momentum quantum number (101)
Heisenberg uncertainty principle (99)
magnetic quantum number (102)
orbital (100)
principal quantum number (101)
quantum numbers (101)
quantum theory (99)
spin quantum number (104)

4-3

- Electrons occupy atomic orbitals in the ground state of an atom according to the Aufbau principle, the Pauli exclusion principle, and Hund's rule.
- Electron configurations can be depicted using different types of notation. In this book, three types of notation are used: orbital notation, electron-configuration notation, and noble-gas notation.
- Electron configurations of some atoms, such as chromium, do not strictly follow the Aufbau principle, but the ground-state configuration that results is the configuration with the minimum possible energy.

Vocabulary

Aufbau principle (105)
electron configuration (105)
highest occupied level (110)
Hund's rule (106)
inner-shell electrons (110)
noble gases (111)
noble-gas configuration (112)
Pauli exclusion principle (106)

REVIEWING CONCEPTS

1. a. List five examples of electromagnetic radiation.
   b. What is the speed of all forms of electromagnetic radiation in a vacuum?
   c. Relate the frequency and wavelength of any form of electromagnetic radiation. (4-1)

2. Prepare a two-column table. List the properties of light that can best be explained by the wave theory in one column. List those best explained by the particle theory in the second column. You may want to consult a physics textbook for reference. (4-1)

3. What are the frequency and wavelength ranges of visible light? (4-1)

4. List the colors of light in the visible spectrum in order of increasing frequency. (4-1)

5. In the early twentieth century, what two experiments involving light and matter could not be explained by the wave theory of light? (4-1)

6. a. How are the wavelength and frequency of electromagnetic radiation related?
   b. How are the energy and frequency of electromagnetic radiation related?
   c. How are the energy and wavelength of electromagnetic radiation related? (4-1)

7. Which theory of light, the wave or particle theory, best explains the following phenomena?
   a. the interference of light
   b. the photoelectric effect
   c. the emission of electromagnetic radiation by an excited atom (4-1)

8. Distinguish between the ground state and an excited state of an atom. (4-1)

9. According to the Bohr model of the hydrogen atom, how is hydrogen's emission spectrum produced? (4-1)

10. Describe two major shortcomings of the Bohr model of the atom. (4-2)

11. a. What is the principal quantum number?
   b. How is it symbolized?
   c. What are shells?
   d. How does *n* relate to the number of orbitals per main energy level and the number of electrons allowed per main energy level? (4-2)

12. a. What information is given by the angular momentum quantum number?
   b. What are sublevels, or subshells? (4-2)

13. For each of the following values of *n*, indicate the numbers and types of sublevels possible for that main energy level. (Hint: See Table 4-2.)
   a. $n = 1$
   b. $n = 2$
   c. $n = 3$
   d. $n = 4$
   e. $n = 7$ (number only) (4-2)

14. a. What information is given by the magnetic quantum number?
   b. How many orbital orientations are possible in each of the *s, p, d,* and *f* sublevels?
   c. Explain and illustrate the notation for distinguishing among the different *p* orbitals in a sublevel. (4-2)

15. a. What is the relationship between *n* and the total number of orbitals in a main energy level?
   b. How many total orbitals are contained in the third main energy level? in the fifth? (4-2)

16. a. What information is given by the spin quantum number?
   b. What are the possible values for this quantum number? (4-2)

17. How many electrons could be contained in the following main energy levels with *n* equal to:
   a. 1
   b. 3
   c. 4
   d. 6
   e. 7 (4-2)

18. a. In your own words, state the Aufbau principle.
   b. Explain the meaning of this principle in terms of an atom with many electrons. (4-3)

19. a. In your own words, state Hund's rule.
   b. What is the basis for this rule? (4-3)

20. a. In your own words, state the Pauli exclusion principle.
   b. What is the significance of the spin quantum number?

   c. Compare the values of the spin quantum number for two electrons in the same orbital. (4-3)

21. a. What is meant by the highest occupied energy level in an atom?
   b. What are inner-shell electrons? (4-3)

22. Determine the highest occupied energy level in the following elements:
   a. He
   b. Be
   c. Al
   d. Ca
   e. Sn (4-3)

23. Write the orbital notation for the following elements. (Hint: See Sample Problem 4-1.)
   a. P
   b. B
   c. Na
   d. C (4-3)

24. Write the electron-configuration notation for an unidentified element that contains the following number of electrons:
   a. 3
   b. 6
   c. 8
   d. 13 (4-3)

25. Given that the electron configuration for oxygen is $1s^2 2s^2 2p^4$, answer the following questions:
   a. How many electrons are in each atom?
   b. What is the atomic number of this element?
   c. Write the orbital notation for oxygen's electron configuration.
   d. How many unpaired electrons does oxygen have?
   e. What is the highest occupied energy level?
   f. How many inner-shell electrons does the atom contain?
   g. In which orbital(s) are these inner-shell electrons located? (4-3)

26. a. What are the noble gases?
   b. What is a noble-gas configuration?
   c. How does noble-gas notation simplify writing an atom's electron configuration? (4-3)

27. Write the noble-gas notation for the electron configuration of each of the elements that follow. (Hint: See Sample Problem 4-2.)
   a. Cl
   b. Ca
   c. Se (4-3)

28. a. What information is given by the noble-gas notation $[\mathrm{Ne}]3s^2$?
   b. What element does this represent? (4-3)

29. Write both the complete electron-configuration notation and the noble-gas notation for each of the following elements. (Hint: See Sample Problem 4-3.)
   a. Na
   b. Sr
   c. P (4-3)

30. Identify each of the following atoms on the basis of its electron configuration:
   a. $1s^2 2s^2 2p^1$
   b. $1s^2 2s^2 2p^5$
   c. $[\mathrm{Ne}]3s^2$
   d. $[\mathrm{Ne}]3s^2 3p^2$
   e. $[\mathrm{Ne}]3s^2 3p^5$
   f. $[\mathrm{Ar}]4s^1$
   g. $[\mathrm{Ar}]3d^6 4s^2$ (4-3)

PROBLEMS

Photons and Electromagnetic Radiation

31. Determine the frequency of light with a wavelength of 4.257×10^{-7} cm.

32. Determine the energy in joules of a photon whose frequency is 3.55×10^{17} Hz.

33. Using the two equations $E = h\nu$ and $c = \lambda\nu$, derive an equation expressing E in terms of h, c, and λ.

34. How long would it take a radio wave with a frequency of 7.25×10^5 Hz to travel from Mars to Earth if the distance between the two planets is approximately 8.00×10^7 km?

35. Cobalt-60 ($^{60}_{27}\mathrm{Co}$) is an artificial radioisotope that is produced in a nuclear reactor for use as a gamma-ray source in the treatment of certain types of cancer. If the wavelength of the gamma radiation from a cobalt-60 source is 1.00×10^{-3} nm, calculate the energy of a photon of this radiation.

Orbitals and Electron Configuration

36. List the order in which orbitals generally fill, from the 1*s* to the 7*p* orbital.

37. Write the noble-gas notation for the electron configurations of each of the following elements:
a. As
b. Pb
c. Lr
d. Hg
e. Sn
f. Xe
g. La

38. How do the electron configurations of chromium and copper contradict the Aufbau principle?

MIXED REVIEW

39. a. Which has a longer wavelength, green or yellow light?
b. Which has a higher frequency, an X ray or a microwave?
c. Which travels at a greater speed, ultraviolet or infrared light?

40. Write both the complete electron-configuration and noble-gas notation for each of the following:
a. Ar
b. Br
c. Al

41. Given the speed of light as 3.0×10^8 m/s, calculate the wavelength of the electromagnetic radiation whose frequency is 7.500×10^{12} Hz.

42. a. What is the electromagnetic spectrum?
b. What units are used to express wavelength?
c. What unit is used to express frequencies of electromagnetic waves?

43. Given that the electron configuration for phosphorus is $1s^22s^22p^63s^23p^3$, answer the following questions:
a. How many electrons are in each atom?
b. What is the atomic number of this element?
c. Write its orbital notation.
d. How many unpaired electrons does an atom of phosphorus have?
e. What is its highest occupied energy level?
f. How many inner-shell electrons does the atom contain?
g. In which orbital(s) are these inner-shell electrons located?

44. What is the frequency of a radio wave with an energy of 1.55×10^{-24} J/photon?

45. Write the noble-gas notation for the electron configurations of each of the following elements:
a. Hf
b. Sc
c. Fe
d. At
e. Ac
f. Zn

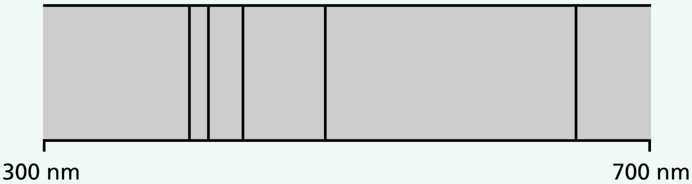
46. Describe the major similarities and differences between Schrödinger's model of the atom and the model proposed by Bohr.

47. When sodium is heated, a yellow spectral line whose energy is 3.37×10^{-19} J/photon is produced.
a. What is the frequency of this light?
b. What is its wavelength?

48. a. What is an orbital?
b. Describe an orbital in terms of an electron cloud.

CRITICAL THINKING

49. **Inferring Relationships** In the emission spectrum of hydrogen shown in Figure 4-5 on page 95, each colored line is produced by the emission of photons with specific energies. Substances also produce absorption spectra when electromagnetic radiation passes through them. Certain wavelengths are absorbed. Using the diagram below, predict what the wavelengths of the absorption lines will be when white light (all the colors of the visible spectrum) is passed through hydrogen gas.



Hydrogen absorption spectrum

50. **Applying Models** When discussing the photoelectric effect, the minimum energy needed to remove an electron from the metal is called the *work function* and is a characteristic of the metal. For example, chromium, Cr, will emit electrons when the wavelength of the radiation is 284 nm or less. Calculate the work function for chromium. (Hint: You will need to use the two equations that describe the relationships among wavelength, frequency, speed of light, and Planck's constant.)

TECHNOLOGY & LEARNING

51. **Graphing Calculator** Calculating Quantum Number Relationships

The graphing calculator can run a program that calculates relationships in atomic structure given the quantum number. Given the principal quantum number 3, you will calculate the number of orbitals, orbital shapes, and electrons. The program will then be used to make the calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. How many oribitals are there given the principle quantum number 12?

b. For the primary quantum number 3, how many possible combinations have a cloverleaf orbital shape (or orbital shape = 0)?

c. Name the total number of electrons for the principle quantum number 4.

HANDBOOK SEARCH

52. Sections 1 and 2 of the *Elements Handbook* (pages 728–739) contain information on an analytical test and a technological application for Group 1 and 2 elements that are based on the emission of light from atoms. Review these sections to answer the following:

a. What analytical technique utilizes the emission of light from excited atoms?

b. What elements in Groups 1 and 2 can be identified by this technique?

c. What types of compounds are used to provide color in fireworks?

d. What wavelengths within the visible spectrum would most likely contain emission lines for barium?

RESEARCH & WRITING

53. Neon signs do not always contain neon gas. The various colored lights produced by the signs are due to the emission of a variety of low-pressure gases in different tubes. Research other kinds of gases used in neon signs and list the colors that they emit.

54. Prepare a report about the photoelectric effect and cite some of its practical uses. Explain the basic operation of each device or technique mentioned.

ALTERNATIVE ASSESSMENT

55. **Performance Assessment** A spectroscope is a device used to produce and analyze spectra. Construct a simple spectroscope and determine the absorption spectra of several elemental gases. (Your teacher will provide you with the elemental samples.)