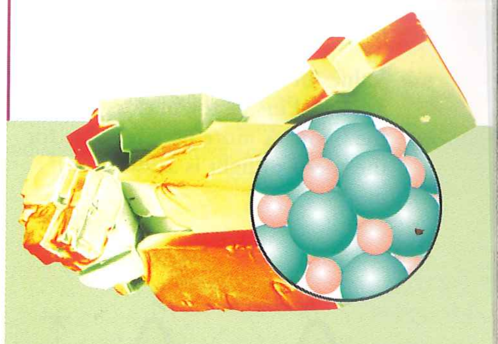
combustion were 1.811 g of CO_2 and 0.3172 g of H_2O. (a) Determine the empirical formula of the compound. (b) The molar mass was found to be 170.12 g·mol^{-1}. What is the molecular formula of gallic acid?

M.17 An industrial by-product consists of C, H, O, and Cl. When 0.100 g of the compound was analyzed by combustion analysis, 0.0682 g of CO_2 and 0.0140 g of H_2O were produced. The mass percentage of Cl in the compound was found to be 55.0%. What are the empirical and molecular formulas of the compound?

M.18 A mixture of 4.94 g of 85.0% pure phosphine, PH_3, and 0.110 kg of $CuSO_4 \cdot 5H_2O$ (of molar mass 249.68 g·mol^{-1}) is placed in a reaction vessel. (a) Balance the chemical equation for the reaction that takes place, given the skeletal form $CuSO_4 \cdot 5H_2O(s) + PH_3(g) \rightarrow Cu_3P_2(s) + H_2SO_4(aq) + H_2O(l)$. (b) Name each reactant and product. (c) Determine the limiting reactant. (d) Calculate the mass (in grams) of Cu_3P_2 (of molar mass 252.56 g·mol^{-1}) produced, given that the percentage yield of the reaction is 6.31%.

ATOMS: *The Quantum World*

1



What Are the Key Ideas? Matter is composed of atoms. The structures of atoms can be understood in terms of the theory of matter known as quantum mechanics, in which the properties of particles and waves merge together.

Why Do We Need to Know This Material? Atoms are the fundamental building blocks of matter. They are the currency of chemistry in the sense that almost all the explanations of chemical phenomena are expressed in terms of atoms. This chapter explores the structures and properties of atoms and the periodic variation of their properties. Quantum mechanics is central to this discussion because it accounts for the structures and therefore the properties of atoms.

What Do We Need to Know Already? We need to be familiar with the nuclear model of the atom and the general layout of the periodic table (Fundamentals Section B). We also need the concepts of kinetic and potential energy (Section A).

OBSERVING ATOMS
1.1 The Characteristics of Electromagnetic Radiation
1.2 Radiation, Quanta, and Photons
1.3 The Wave–Particle Duality of Matter
1.4 The Uncertainty Principle
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MODELS OF ATOMS
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THE PERIODICITY OF ATOMIC PROPERTIES
1.14 Atomic Radius
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1.18 The Inert-Pair Effect
1.19 Diagonal Relationships
THE IMPACT ON MATERIALS
1.20 The Main-Group Elements
1.21 The Transition Metals

We need insight to think like a chemist. Chemical insight means that, when we look at an everyday object or a sample of a chemical, we can imagine the atoms that make it up. Not only that, we need to be able to plunge, in our mind's eye, deep into the center of matter and discover the internal structure of atoms. To be able to understand this structure and how it relates to the chemical properties of elements, we need to understand the **electronic structure** of an atom, the description of how electrons are arranged around its nucleus.

As soon as we start this journey into the atom, we encounter an extraordinary feature of our world. When Rutherford proposed the nuclear model of the atom in the early twentieth century (Section B), he expected to be able to use **classical mechanics**, the laws of motion proposed by Newton in the seventeenth century, to describe its electronic structure. After all, classical mechanics had been tremendously successful for describing the motion of visible objects such as balls and planets. However, it soon became clear that classical mechanics fails when applied to electrons in atoms. New laws, which came to be known as **quantum mechanics**, had to be developed.

The opening sections of this chapter follow the development of quantum mechanics and the modern nuclear model of the atom. First, we see how experiments have led to our modern concepts of the nature of matter and radiation. Next, we see how additional experiments led to a profound refinement of Dalton's model of an atom as an uncuttable sphere and have clarified the structure of Rutherford's nuclear model of the atom (Section B).

OBSERVING ATOMS

To investigate the internal structures of objects as small as atoms, we observe them indirectly through the properties of the electromagnetic radiation they emit. We then propose a model of the structure of the atom that accounts for these properties. The analysis of the electromagnetic radiation emitted or absorbed by substances is a branch of chemistry called **spectroscopy.** We shall see how to use atomic spectroscopy—spectroscopy applied to atoms—to determine their structures.

1.1 The Characteristics of Electromagnetic Radiation

As we saw in Section A, we can think of a *field* as a region of influence, like the gravitational field of the Earth.

Values of the fundamental constants are listed inside the back cover of the book. A more precise value for the speed of light is 2.998×10^8 m·s^{-1}.

A ray of **electromagnetic radiation** consists of oscillating (time-varying) electric and magnetic fields that travel through empty space at 3.00×10^8 m·s^{-1}, or at just over 670 million miles per hour. This speed is denoted c and called the "speed of light." Visible light is a form of electromagnetic radiation, as are radio waves, microwaves, and x-rays. All these forms of radiation transfer energy from one region of space to another. The warmth we feel from the Sun is a tiny proportion of the total energy it emits, and it is carried to us through space as electromagnetic radiation.

One reason why electromagnetic radiation is a good tool for the study of atoms is that an electric field pushes on charged particles such as electrons. As a light ray passes an electron, its electric field pushes the electron first in one direction and then in the opposite direction, over and over again. That is, the field oscillates in both direction and strength (Fig. 1.1). The number of **cycles** (complete reversals of direction away from and back to the initial strength and direction) per second is called the **frequency,** ν (the Greek letter nu), of the radiation. The unit of frequency, 1 hertz (1 Hz), is defined as 1 cycle per second:

$$1 \text{ Hz} = 1 \text{ s}^{-1}$$

Electromagnetic radiation of frequency 1 Hz pushes a charge in one direction, then the opposite direction, and returns to the original direction once per second. The frequency of electromagnetic radiation that we see as visible light is close to 10^{15} Hz, and so its electric field changes direction at about a thousand trillion (10^{15}) times a second as it travels past a given point.

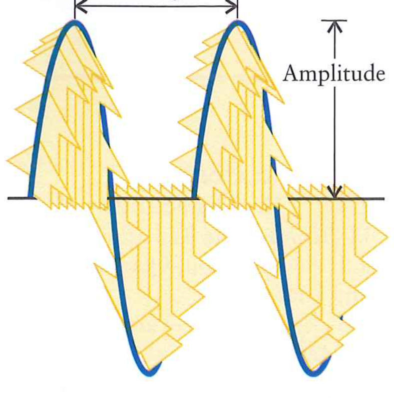


FIGURE 1.1 The electric field of electromagnetic radiation oscillates in space and time. This diagram represents a "snapshot" of an electromagnetic wave at a given instant. The length of an arrow at any point represents the strength of the force that the field exerts on a charged particle at that point. The distance between the peaks is the wavelength of the radiation, and the height of the wave above the center line is the amplitude.

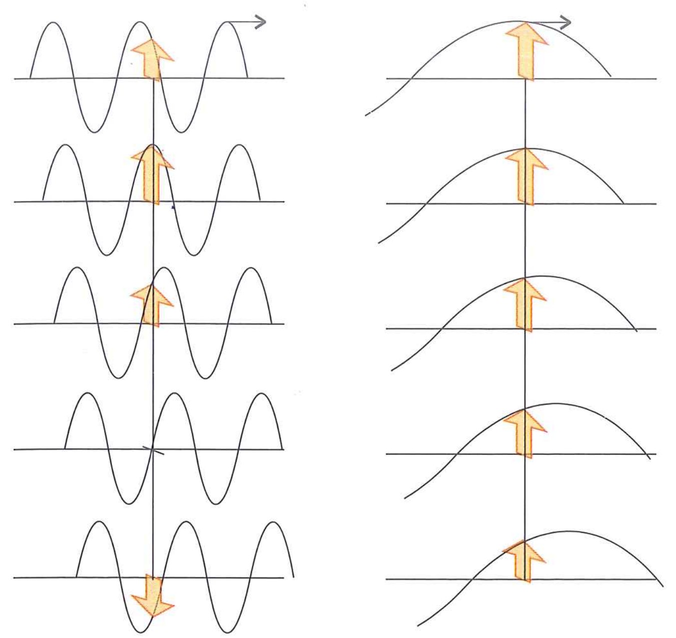
An instantaneous snapshot of a wave of electromagnetic radiation spread through space would look like Fig. 1.1. The wave is characterized by its amplitude and wavelength. The **amplitude** is the height of the wave above the center line. The square of the amplitude determines the **intensity,** or brightness, of the radiation. The **wavelength,** λ (the Greek letter lambda), is the peak-to-peak distance. The wavelengths of visible light are close to 500 nm. Although 500 nm is only half of one-thousandth of a millimeter (so you might *just* be able to imagine it), it is much longer than the diameters of atoms, which are typically close to 0.2 nm.

Different wavelengths of electromagnetic radiation correspond to different regions of the spectrum (see Table 1.1). Our eyes detect electromagnetic radiation with wavelengths in the range from 700 nm (red light) to 400 nm (violet light). Radiation in this range is called **visible light,** and the frequency of visible light determines its color. White light, which includes sunlight, is a mixture of all wavelengths of visible light.

TABLE 1.1 Color, Frequency, and Wavelength of Electromagnetic Radiation

Radiation type	Frequency (10^{14} Hz)	Wavelength (nm, 2 sf)*	Energy per photon (10^{-19} J)
x-rays and γ-rays	$\geq 10^3$	≤ 3	$\geq 10^3$
ultraviolet	8.6	350	5.7
visible light			
violet	7.1	420	4.7
blue	6.4	470	4.2
green	5.7	530	3.8
yellow	5.2	580	3.4
orange	4.8	620	3.2
red	4.3	700	2.8
infrared	3.0	1000	2.0
microwaves and radio waves	$\leq 10^{-3}$	$\geq 3 \times 10^6$	$\leq 10^{-3}$

*The abbreviation sf denotes the number of significant figures in the data. The frequencies, wavelengths, and energies are typical values; they should not be regarded as precise.



(a) Short wavelength, high frequency (b) Long wavelength, low frequency

FIGURE 1.2 (a) Short-wavelength radiation: the vertical arrow shows how the electric field changes markedly at five successive instants. (b) For the same five instants, the electric field of the long-wavelength radiation changes much less. The horizontal arrows in the uppermost images show that in each case the wave has traveled the same distance. Short-wavelength radiation has a high frequency, whereas long-wavelength radiation has a low frequency.

Now imagine the wave in Fig. 1.1 zooming along at its actual speed, the speed of light, c. If the wavelength of the light is very short, very many complete oscillations pass a given point in a second (Fig. 1.2a). If the wavelength is long, the light still travels at the speed c, but fewer complete oscillations pass the point in a second (Fig. 1.2b). A short wavelength therefore corresponds to high-frequency radiation and a long wavelength corresponds to low-frequency radiation. The precise relation is

$$\text{Wavelength} \times \text{frequency} = \text{speed of light, or } \lambda\nu = c \qquad (1)^*$$

For instance, suppose we want to find the wavelength of blue light of frequency 6.4×10^{14} Hz. Then,

$$\text{From } \lambda = \frac{c}{\nu}, \quad \lambda = \frac{2.998 \times 10^8 \text{ m·s}^{-1}}{6.4 \times 10^{14} \text{ s}^{-1}} = \frac{2.998 \times 10^8}{6.4 \times 10^{14}} \text{ m} = 4.7 \times 10^{-7} \text{ m}$$

or about 470 nm. Blue light, which has a relatively high frequency, has a shorter wavelength than that of red light, which has a frequency near 700 nm.

SELF-TEST 1.1A Calculate the wavelengths of the light from traffic signals as they change. Assume that the lights emit the following frequencies: green, 5.75×10^{14} Hz; yellow, 5.15×10^{14} Hz; red, 4.27×10^{14} Hz.

[*Answer:* Green, 521 nm; yellow, 582 nm; red, 702 nm]

SELF-TEST 1.1B What is the wavelength of a radio station transmitting at 98.4 MHz?

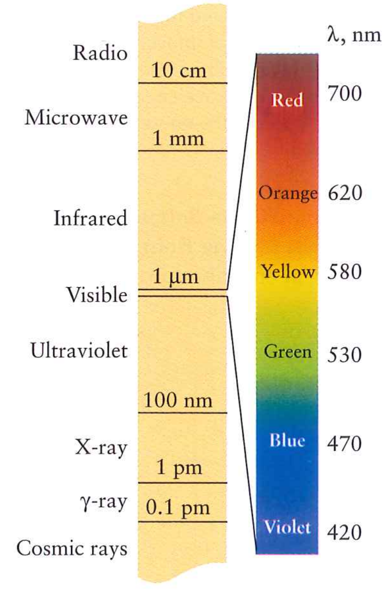


FIGURE 1.3 The electromagnetic spectrum and the names of its regions. The region we call "visible light" occupies a very narrow range of wavelengths. The regions are not drawn to scale.

As far as we know, there is neither an upper limit nor a lower limit to the wavelength of electromagnetic radiation (Fig. 1.3). **Ultraviolet radiation** is radiation at higher frequency than violet light; its wavelength is less than about 400 nm. This damaging component of radiation from the Sun is responsible for sunburn and tanning, but it is largely prevented from reaching the surface of the Earth by the ozone layer. **Infrared radiation,** the radiation we experience as heat, has a lower frequency and longer wavelength than red light; its wavelength is greater than about 800 nm. Microwaves, which are used in radar and microwave ovens, have wavelengths in the millimeter-to-centimeter range.

Modern theories suggest that our concept of space breaks down on a scale of 10^{-34} m, so that may constitute a lower bound to electromagnetic radiation wavelength.

The color of light depends on its frequency and wavelength; long-wavelength radiation has a lower frequency than that of short-wavelength radiation.

1.2 Radiation, Quanta, and Photons

As an object is heated to high temperatures, it glows more brightly—the phenomenon of **incandescence**—and the color of light it gives off changes from red through orange and yellow toward white. Those are *qualitative* observations. To study the effect *quantitatively,* scientists had to measure the intensity of radiation at each wavelength and repeat the measurements at a variety of different temperatures. These experiments caused one of the greatest revolutions that has ever occurred in science. Figure 1.4 shows some of the experimental results. The "hot object" is known as a **black body** (even though it might be glowing white hot!). The name signifies that the object does not favor one wavelength over another in the sense of absorbing a particular wavelength preferentially or emitting one preferentially. The curves in Fig. 1.4 show the intensity of **black-body radiation,** the radiation emitted at different wavelengths by a heated black body, for a series of temperatures.

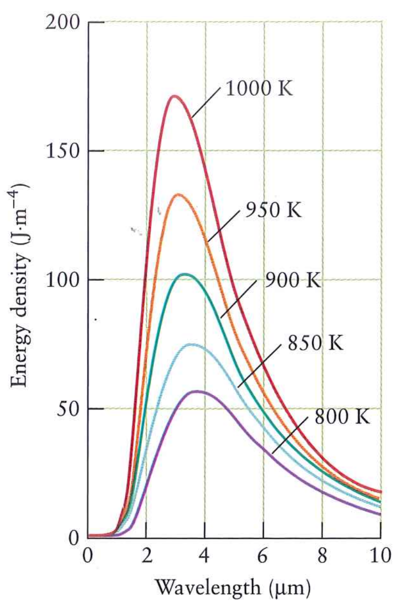


FIGURE 1.4 The intensity of radiation emitted by a heated black body as a function of wavelength. As the temperature increases, the total energy emitted (the area under the curve) increases sharply, and the maximum intensity of emission moves to shorter wavelengths. (To obtain the energy in a volume V and at wavelengths λ and $\lambda + \Delta\lambda$, multiply the energy density by V and $\Delta\lambda$.)

The name *Stefan–Boltzmann law* recognizes Ludwig Boltzmann's theoretical contribution.

Two crucial pieces of experimental information that had to be incorporated into any model of black-body radiation were discovered in the late nineteenth century. In 1879, Josef Stefan investigated the increasing brightness of a black body as it is heated and discovered that the total intensity of radiation emitted over all wavelengths increases as the fourth power of the temperature (Fig. 1.5). This quantitative relation is now called the **Stefan–Boltzmann law** and is usually written

$$\frac{\overset{\text{watts}}{\text{Power emitted}}}{\underset{\text{meter}^2}{\text{Surface area}}} = \text{constant} \times T^4 \qquad (2)$$

where T signifies an absolute temperature, one reported on the Kelvin scale (Appendix 1B). The experimental value of the constant is 5.67×10^{-8} W·m^{-2}·K^{-4}, where W denotes watts (1 W = 1 J·s^{-1}). A few years later, in 1893, Wilhelm Wien examined the shift in color of black-body radiation as the temperature increases and discovered that the wavelength corresponding to the maximum in the intensity, λ_{max}, is inversely proportional to the temperature, $\lambda_{max} \propto 1/T$, and therefore that $\lambda_{max} \times T$ is a constant (Fig. 1.6). This quantitative result is now called **Wien's law** and is normally written

$$T\lambda_{max} = \tfrac{1}{5}c_2 \qquad (3)$$

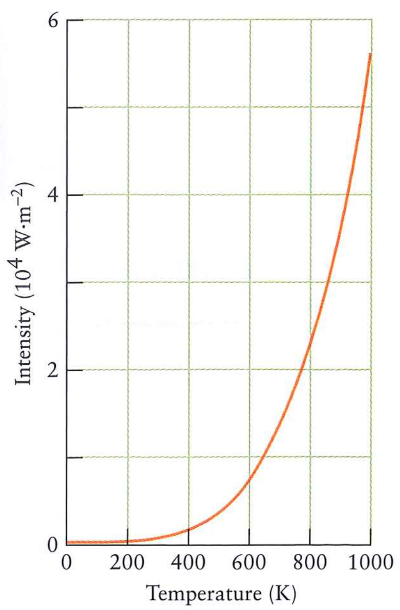


FIGURE 1.5 The total intensity of radiation emitted by a heated black body increases as the fourth power of the temperature, so a body at 1000 K emits more than 120 times as much energy as that emitted by the same body at 300 K.

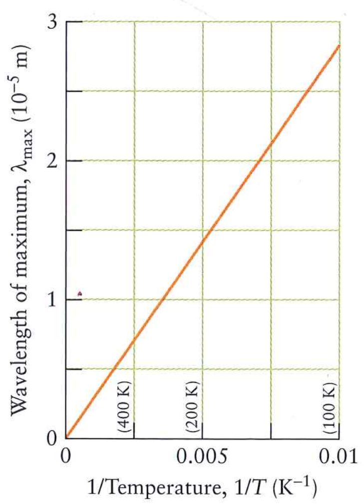


FIGURE 1.6 As the temperature is raised ($1/T$ decreases), the wavelength of maximum emission shifts to smaller values.

where c_2 is called the **second radiation constant.** The empirical (experimental) value of c_2 is 1.44×10^{-2} K·m.

EXAMPLE 1.1 **Sample exercise: Determining the temperature of the surface of a star**

The maximum intensity of solar radiation occurs at 490. nm. What is the temperature of the surface of the Sun?

SOLUTION We can use Wien's law to determine the surface temperature of stars treated as hot black bodies:

$$\text{From } T\lambda_{max} = \tfrac{1}{5}c_2 \text{ written as } T = \frac{c_2}{5\lambda_{max}},$$

$$T = \frac{1.44 \times 10^{-2}\ \text{K·m}}{5 \times 4.90 \times 10^{-7}\ \text{m}} = \frac{1.44 \times 10^{-2}}{5 \times 4.90 \times 10^{-7}}\ \text{K} = 5.88 \times 10^3\ \text{K}$$

That is, the surface temperature of the Sun is about 6000 K.

SELF-TEST 1.2A In 1965, electromagnetic radiation with a maximum at 1.05 mm (in the microwave region) was discovered to pervade the universe. What is the temperature of "empty" space?

[*Answer:* 2.74 K]

SELF-TEST 1.2B A red giant is a late stage in the evolution of a star. The average wavelength maximum at 700. nm shows that a red giant cools as it dies. What is the surface temperature of a red giant?

For nineteenth-century scientists, the obvious way to account for the laws of black-body radiation was to set up a model of electromagnetic radiation in terms of waves and to use classical physics to derive its characteristics. However, much to their dismay, they found that the characteristics they deduced did not match their observations. Worst of all was the **ultraviolet catastrophe:** classical physics predicted that any black body at any nonzero temperature should emit intense ultraviolet radiation and even x-rays and γ-rays! According to classical physics, any warm object would devastate the countryside with high-frequency radiation. Even a human body at 37°C would glow in the dark. There would, in fact, be no darkness.

The suggestion that resolved the problem came in 1900 from the German physicist Max Planck. He proposed that the exchange of energy between matter and radiation occurs in **quanta,** or packets of energy. Planck focused his attention on the hot, rapidly oscillating atoms of the black body. His central idea was that an atom oscillating at a frequency ν can exchange energy with its surroundings only in packets of magnitude

The word *quantum* comes from the Latin for amount—literally, "How much?"

$$E = h\nu \qquad (4)^*$$

The constant h, now called **Planck's constant,** has the value 6.626×10^{-34} J·s. If the oscillating atom releases an energy E into the surroundings, radiation of frequency $\nu = E/h$ will be detected.

Planck's hypothesis implies that radiation of frequency ν can be generated only if an oscillator of that frequency has acquired the minimum energy required to start oscillating. At low temperatures, there is not enough energy available to stimulate oscillations at very high frequencies, and so the object does not generate high-frequency, ultraviolet radiation. As a result, the intensity curves in Fig. 1.4 die away at high frequencies (short wavelengths) and the ultraviolet catastrophe is avoided. In contrast, in classical physics it was assumed that an oscillator could oscillate with any energy and therefore, even at low temperatures, high-frequency oscillators could contribute to the emitted radiation. The hypothesis is *quantitatively* successful, too, because Planck was able to use his proposal to derive the Stefan–Boltzmann and Wien laws. He was also able to calculate the variation of

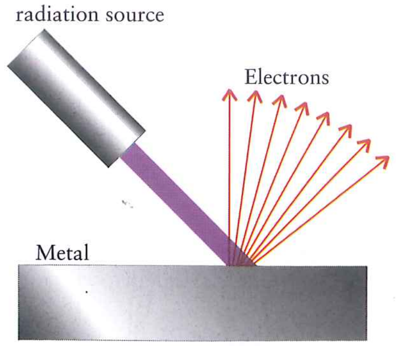


FIGURE 1.7 When a metal is illuminated with ultraviolet radiation, electrons are ejected, provided the frequency is above a threshold frequency that is characteristic of the metal.

We say that a property y varies linearly with x if the relation between y and x can be written $y = b + mx$, where b and m are constants. See Appendix 1E.

intensity with wavelength and obtained a curve that matched the experimental curve almost exactly.

To achieve this successful theory, Planck had to discard classical physics, which puts no restriction on how small an energy may be transferred from one object to another. He proposed that energy is transferred in discrete packets. To justify such a dramatic revolution, more evidence was needed. That evidence came from the **photoelectric effect,** the ejection of electrons from a metal when its surface is exposed to ultraviolet radiation (Fig. 1.7). The experimental observations were as follows:

1 No electrons are ejected unless the radiation has a frequency above a certain threshold value characteristic of the metal.
2 Electrons are ejected immediately, however low the intensity of the radiation.
3 The kinetic energy of the ejected electrons increases linearly with the frequency of the incident radiation.

Einstein found an explanation of these observations and, in the process, profoundly changed our conception of the electromagnetic field. He proposed that electromagnetic radiation consists of particles, which were later called **photons.** Each photon can be regarded as a packet of energy, and the energy of a single photon is related to the frequency of the radiation by Eq. 4 ($E = h\nu$). For example, ultraviolet photons are more energetic than photons of visible light, which has lower frequencies. According to this photon model of electromagnetic radiation, we can visualize a beam of red light as a stream of photons of one particular energy, yellow light as a stream of photons of higher energy, and green light as a stream of photons of higher energy still. It is important to note that the intensity of radiation is an indication of the *number* of photons present, whereas $E = h\nu$ is a measure of the *energy* of each individual photon. For instance, the energy of a single photon of blue light of frequency 6.4×10^{14} Hz is

$$E = (6.626 \times 10^{-34}\ \text{J·s}) \times (6.4 \times 10^{14}\ \text{Hz}) = 4.2 \times 10^{-19}\ \text{J}$$

To derive this value, we have used 1 Hz = 1 s^{-1}, so J·s × Hz = J·s × s^{-1} = J.

SELF-TEST 1.3A What is the energy of a photon of yellow light of frequency 5.2×10^{14} Hz?

[*Answer:* 3.4×10^{-19} J]

SELF-TEST 1.3B What is the energy of a photon of orange light of frequency 4.8×10^{14} Hz?

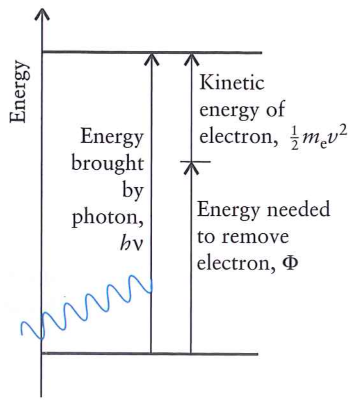


FIGURE 1.8 In the photoelectric effect, a photon with energy $h\nu$ strikes the surface of a metal and its energy is absorbed by an electron. If the energy of the photon is greater than the work function, Φ, of the metal, the electron absorbs enough energy to break away from the metal. The kinetic energy of the ejected electron is the difference between the energy of the photon and the work function: $\frac{1}{2}m_e v^2 = h\nu - \Phi$.

Be careful to distinguish the symbol for speed, v (for velocity), from the symbol for frequency, ν (the Greek letter nu).

The characteristics of the photoelectric effect are easy to explain if we visualize electromagnetic radiation as photons. If the incident radiation has frequency ν, it consists of a stream of photons of energy $h\nu$. These particles collide with the electrons in the metal. The energy required to remove an electron from the surface of a metal is called the **work function** of the metal and denoted Φ (uppercase phi). If the energy of a photon is less than the energy required to remove an electron from the metal, then an electron will not be ejected, regardless of the intensity of the radiation. However, if the energy of the photon, $h\nu$, is greater than Φ, then an electron is ejected with a kinetic energy, $E_K = \frac{1}{2}m_e v^2$, equal to the difference between the energy of the incoming photon and the work function: $E_K = h\nu - \Phi$ (Fig. 1.8). It follows that

$$\underbrace{\tfrac{1}{2}m_e v^2}_{\text{kinetic energy of ejected electron}} = \underbrace{h\nu}_{\text{energy supplied by photon}} - \underbrace{\Phi}_{\text{energy required to eject electron}} \qquad (5)^*$$

This expression tells us that a plot of the kinetic energy of the ejected electrons against the frequency of the radiation should be a straight line of slope h, the same for all metals, and an extrapolated intercept with the vertical axis at $-\Phi$, different

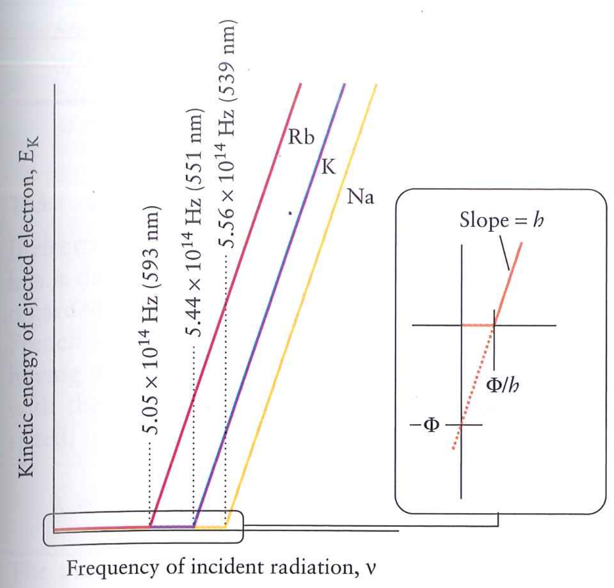


FIGURE 1.9 When photons strike a metal, no electrons are ejected unless the incident radiation has a frequency above a value characteristic of the metal. The kinetic energy of the ejected electrons varies linearly with the frequency of the incident radiation. The inset shows the relation of the slope and the two intercepts to the parameters in Eq. 5.

for each metal. The intercept with the horizontal axis (corresponding to zero kinetic energy of the ejected electron) is at Φ/h in each case.

We can now interpret the experimental observations of the photoelectric effect in light of Einstein's theory:

1 An electron can be driven out of the metal only if it receives at least a certain minimum energy, Φ, from the photon during the collision. Therefore, the frequency of the radiation must have a certain minimum value if electrons are to be ejected. This minimum frequency depends on the work function and hence on the identity of the metal (Fig. 1.9).
2 Provided a photon has enough energy, a collision results in the immediate ejection of an electron.
3 The kinetic energy of the electron ejected from the metal increases linearly with the frequency of the incident radiation according to Eq. 5.

The photoelectric effect strongly supports the view that electromagnetic radiation consists of photons that behave like particles. However, there is plenty of evidence to show that electromagnetic radiation behaves like waves! The most compelling evidence is the observation of **diffraction,** the pattern of high and low intensities generated by an object in the path of a ray of light (Fig. 1.10). A diffraction pattern results when the peaks and troughs of waves traveling along one path interfere with the peaks and troughs of waves traveling along another path. If the peaks coincide, the amplitude of the wave (its height) is enhanced; we call this enhancement **constructive interference** (Fig. 1.11a). If the peaks of one wave coincide with the troughs of another wave, the amplitude of the wave is diminished by **destructive interference** (Fig. 1.11b). This effect is the basis of a useful technique for studying matter. For example, x-ray diffraction is one of the most important tools for studying the structures of molecules (see Major Technique 3, following Chapter 5).

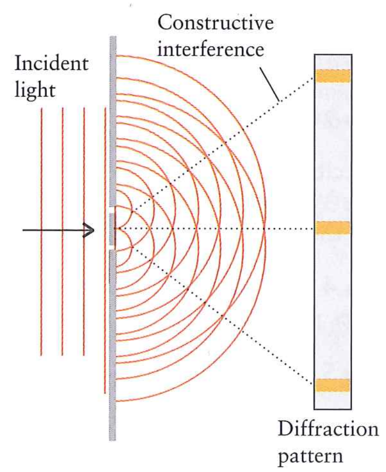


FIGURE 1.10 In this illustration, the peaks of the waves of electromagnetic radiation are represented by orange lines. When radiation coming from the left (the vertical lines) passes through a pair of closely spaced slits, circular waves are generated at each slit. These waves interfere with each other. Where they interfere constructively (as indicated by the positions of the dotted lines), a bright line is seen on the screen behind the slits; where the interference is destructive, the screen is dark.

Let's review the evidence for the nature of electromagnetic radiation. The results of some experiments (the photoelectric effect) compel us to the view that electromagnetic radiation is particlelike. Those of other experiments (diffraction) compel us equally firmly to the view that electromagnetic radiation is wavelike. Thus we are brought to the heart of modern physics. Experiments oblige us to accept the **wave–particle duality** of electromagnetic radiation, in which the concepts of waves and particles blend together. In the wave model, the intensity of the radiation is proportional to the square of the amplitude of the wave. In the particle model, intensity is proportional to the number of photons present at each instant.

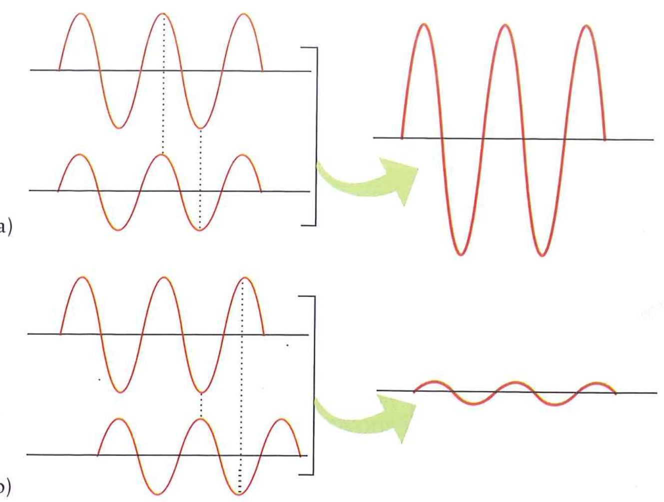


FIGURE 1.11 (a) Constructive interference. The two component waves (left) are "in phase" in the sense that their peaks and troughs coincide. The resultant (right) has an amplitude that is the sum of the amplitudes of the components. The wavelength of the radiation is not changed by interference, only the amplitude is changed. (b) Destructive interference. The two component waves are "out of phase" in the sense that the troughs of one coincide with the peaks of the other. The resultant has a much lower amplitude than either component.

EXAMPLE 1.2 Interpreting a light ray in terms of photons

A discharge lamp rated at 25 W ($1\ \text{W} = 1\ \text{J·s}^{-1}$) emits yellow light of wavelength 580 nm. How many photons of yellow light does the lamp generate in 1.0 s?

STRATEGY We should expect a large number of photons because the energy of a single photon is very small. The number of photons generated in a given time interval is the total energy emitted in that interval divided by the energy of a single photon. We calculate the energy of a photon from its wavelength by using Eq. 1 to convert the given wavelength into a frequency and Eq. 4 to convert frequency into energy. To reduce rounding errors, it is good practice to work through a calculation symbolically as far as possible and to introduce numerical data at the last possible stage.

SOLUTION

Step 1 Find the frequency of the light from Eq. 1

From $\lambda\nu = c$, $\nu = \dfrac{c}{\lambda}$

Step 2 Calculate the energy, E_{photon}, of each photon of wavelength λ.

From $E = h\nu$, $E_{\text{photon}} = \dfrac{hc}{\lambda}$

Step 3 Divide the total energy, E_{total}, by the energy of one photon to find the number of photons, N, that account for the total energy.

From $N = \dfrac{E_{\text{total}}}{E_{\text{photon}}}$, $N = \dfrac{E_{\text{total}}}{(hc/\lambda)} = \dfrac{\lambda E_{\text{total}}}{hc}$

Step 4 The total energy emitted by the lamp is its power (P in watts, or joules per second) multiplied by the time, t, for which it is turned on.

Substitute $E_{\text{total}} = P \times t$: $N = \dfrac{\lambda P t}{hc}$

Step 5 Express the wavelength in meters and insert the data.

$$N = \frac{(5.80 \times 10^{-7}\ \text{m}) \times (25\ \text{J·s}^{-1}) \times (1.0\ \text{s})}{(6.626 \times 10^{-34}\ \text{J·s}) \times (3.00 \times 10^{8}\ \text{m·s}^{-1})}$$
$$= \frac{5.80 \times 10^{-7} \times 25 \times 1.0}{6.626 \times 10^{-34} \times 3.00 \times 10^{8}}$$
$$= 7.3 \times 10^{19}$$

This result means that, when you turn on the lamp, it generates about 10^{20} photons of yellow light each second. As predicted, this is a very large number.

SELF-TEST 1.4A Another discharge lamp produces 5.0 J of energy per second in the blue region of the spectrum. How many photons of blue (470 nm) light would the lamp generate if it were left on for 8.5 s?

[*Answer:* 1.0×10^{20}]

SELF-TEST 1.4B In 1.0 s, a lamp that produces 25 J of energy per second in a certain region of the spectrum emits 5.5×10^{19} photons of light in that region. What is the wavelength of the emitted light?

Studies of black-body radiation led to Planck's hypothesis of the quantization of electromagnetic radiation. The photoelectric effect provides evidence of the particulate nature of electromagnetic radiation; diffraction provides evidence of its wave nature.

1.3 The Wave–Particle Duality of Matter

If electromagnetic radiation, which for a long time had been regarded as wavelike, has a dual character, could it be that matter, which since Dalton's day had been regarded as consisting of particles, also has wavelike properties? In 1925, the French scientist Louis de Broglie proposed that all particles should be regarded as having wavelike properties. He went on to suggest that the wavelength associated with the "matter wave" is inversely proportional to the particle's mass, m, and speed, v, and that

$$\lambda = \frac{h}{mv} \qquad (6a)$$

The product of mass and speed is called the **linear momentum,** p, of a particle, and so this expression is more simply written as the **de Broglie relation:**

$$\lambda = \frac{h}{p} \qquad (6b)^*$$

It is easy to see why the wavelike properties of particles had not been noticed. According to the de Broglie relation, a particle of mass 1 g traveling at $1\ \text{m·s}^{-1}$ has a wavelength of

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{J·s}}{(1 \times 10^{-3}\ \text{kg}) \times (1\ \text{m·s}^{-1})} = 7 \times 10^{-31}\ \frac{\text{kg·m}^2\text{·s}^{-1}}{\text{kg·m·s}^{-1}}$$
$$= 7 \times 10^{-31}\ \text{m}$$

This wavelength is undetectably small; the same is true for any macroscopic (visible) object traveling at normal speeds.

The wavelike character of electrons was detected by showing that they could be diffracted. The experiment was first performed in 1925 by two American scientists, Clinton Davisson and Lester Germer, who directed a beam of fast electrons at a single crystal of nickel. The regular array of atoms in the crystal, with centers separated by 250 pm, acts as a grid that diffracts waves; and a diffraction pattern was observed (Fig. 1.12). Electron diffraction is now an important technique for determining the structures of molecules and exploring the structures of solid surfaces.

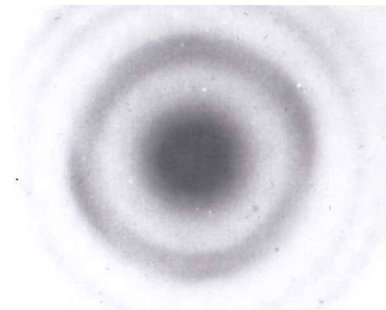


FIGURE 1.12 Davisson and Germer showed that electrons produce a diffraction pattern when reflected from a crystal. G. P. Thomson, working in Aberdeen, Scotland, showed that they also produce a diffraction pattern when they pass through a very thin gold foil. The latter is shown here. G. P. Thomson was the son of J. J. Thomson, who identified the electron (Section B). Both received Nobel prizes: J. J. for showing that the electron is a particle and G. P. for showing that it is a wave.

EXAMPLE 1.3 Estimating the wavelength of a particle

Estimate the wavelength of (a) a proton moving at 1/100 the speed of light; (b) a marble of mass 5.00 g traveling at $1.00\ \text{m·s}^{-1}$.

STRATEGY Use the de Broglie relation, Eq. 6a. The mass of a proton and the speed of light are given inside the back cover. Expect the macroscopic particle, the marble, to have a very short wavelength. Remember to express all quantities in kilograms, meters, and seconds, and use $1\ \text{J} = 1\ \text{kg·m}^2\text{·s}^{-2}$.

SOLUTION (a) The mass of a proton is 1.673×10^{-27} kg, and the speed of light is $2.998 \times 10^{8}\ \text{m·s}^{-1}$; therefore,

from $\lambda = \dfrac{h}{mv}$, $\lambda = \dfrac{6.626 \times 10^{-34}\ \text{J·s}}{(1.673 \times 10^{-27}\ \text{kg}) \times (2.998 \times 10^{8}\ \text{m·s}^{-1})/100}$

$$= 1.32 \times 10^{-13} \frac{(\text{kg·m}^2\text{·s}^{-2}) \times \text{s}}{\text{kg} \times (\text{m·s}^{-1})} = 1.32 \times 10^{-13}\ \text{m}$$

This wavelength corresponds to 0.132 pm. (b) The mass of the marble is 5.00×10^{-3} kg; so

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{J·s}}{(5.00 \times 10^{-3}\ \text{kg}) \times (1.00\ \text{m·s}^{-1})} = 1.33 \times 10^{-31}\ \text{m}$$

As expected, the wavelength of the marble is undetectably small. However, the wavelength of the rapidly moving proton is not very much smaller than the diameter of an atom (about 200 pm).

SELF-TEST 1.5A Calculate the wavelength of an electron traveling at 1/1000 the speed of light.

[*Answer:* 2.43 nm]

SELF-TEST 1.5B Calculate the wavelength of a rifle bullet of mass 5.0 g traveling at twice the speed of sound (the speed of sound is 331 m·s^{-1}).

Electrons (and matter in general) have both wavelike and particlelike properties.

1.4 The Uncertainty Principle

The wave–particle duality not only changes our understanding of electromagnetic radiation and matter, but also sweeps away the foundations of classical physics. In classical mechanics, a particle has a definite **trajectory**, or path on which location and linear momentum are specified at each instant. However, we cannot specify the precise location of a particle if it behaves like a wave: think of a wave in a guitar string, which is spread out all along the string, not localized at a precise point. A particle with a precise linear momentum has a precise wavelength; but, because it is meaningless to speak of the location of a wave, it follows that we cannot specify the location of a particle that has a precise linear momentum.

The difficulty will not go away. Wave–particle duality denies the possibility of specifying the location if the linear momentum is known, and so we cannot specify the trajectory of particles. If we know that a particle is *here* at one instant, we can say *nothing* about where it will be an instant later! The impossibility of knowing the position with arbitrarily great precision if the linear momentum is known precisely is an aspect of the **complementarity** of location and momentum, that if one property is known the other cannot be known. The **Heisenberg uncertainty principle** expresses this complementarity quantitatively: it states that, if the location of a particle is known to within an uncertainty Δx, then the linear momentum parallel to the x-axis can be known only to within an uncertainty Δp, where

$$\Delta p \Delta x \geq \tfrac{1}{2}\hbar \qquad (7)^*$$

The symbol $\hbar$, which is read "h bar," means $h/2\pi$, a useful combination that is found widely in quantum mechanics. From inside the back cover, we see that $\hbar = 1.054\,57 \times 10^{-34}$ J·s. Equation 7 tells us that, if the uncertainty in position is very small (Δx very small), then the uncertainty in linear momentum must be large, and vice versa (Fig. 1.13). The uncertainty principle has negligible practical consequences for macroscopic objects, but it is of profound importance for electrons in atoms and for a scientific understanding of the nature of the world.

(a)

(b)

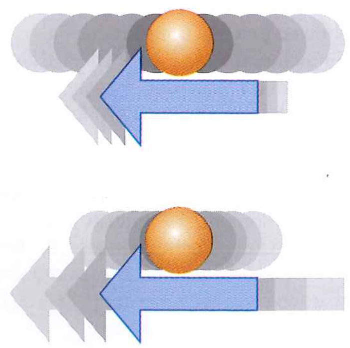


FIGURE 1.13 A representation of the uncertainty principle. (a) The location of the particle is ill defined, and so the momentum of the particle (represented by the arrow) can be specified reasonably precisely. (b) The location of the particle is well defined, and so the momentum cannot be specified very precisely.

EXAMPLE 1.4 Using the uncertainty principle

Estimate the minimum uncertainty in (a) the position of a marble of mass 1.0 g given that its speed is known to within $\pm 1.0\ \text{mm·s}^{-1}$ and (b) the speed of an electron confined to within the diameter of a typical atom (200. pm).

STRATEGY We expect the uncertainty in the position of an object as heavy as a marble to be very small but the uncertainty in the speed of an electron, which is very light and confined to a small region, to be very large. In each case, be sure to use units that match the units of $\hbar$. (a) We calculate the uncertainty Δp from $m\Delta v$, where Δv is the uncertainty in the speed; then we use Eq. 7 to estimate the minimum uncertainty in position, Δx, along the direction of its travel from $\Delta p \Delta x = \tfrac{1}{2}\hbar$ (the minimum value of the product of uncertainties). Because the reported uncertainty in speed is given to plus or minus a stated value, the value of Δv is equal to twice that value. (b) We assume Δx to be the diameter of the atom and use Eq. 7 to estimate Δp; by using the mass of the electron in Table B.1, we find Δv from $m\Delta v = \Delta p$.

SOLUTION (a) First we convert mass and speed into SI base units. The mass, m, is 1.0×10^{-3} kg, and the uncertainty in the speed, Δv, is $2 \times (1.0 \times 10^{-3}\ \text{m·s}^{-1})$. The minimum uncertainty in position, Δx, is

$$\text{from } \Delta p \Delta x \geq \tfrac{1}{2}\hbar, \qquad \Delta x = \frac{\hbar}{2m\Delta v}$$

Substitution of the data then gives

$$\begin{aligned}\Delta x &= \frac{1.05457 \times 10^{-34}\ \text{J·s}}{2 \times (1.0 \times 10^{-3}\ \text{kg}) \times (2.0 \times 10^{-3}\ \text{m·s}^{-1})} \\ &= \frac{1.05457 \times 10^{-34}}{2 \times 1.0 \times 10^{-3} \times 2.0 \times 10^{-3}}\ \frac{\text{J·s}}{\text{kg·m·s}^{-1}} = 2.6 \times 10^{-29}\ \text{m}\end{aligned}$$

Note that in the last step we have used $1\ \text{J} = 1\ \text{kg·m}^2\text{·s}^{-2}$. As predicted, this uncertainty is very small.

(b) The mass of the electron in Table B.1 is 9.109×10^{-31} kg; the diameter of the atom is $200. \times 10^{-12}$ m, or 2.00×10^{-10} m. The uncertainty in the speed, Δv, is equal to $\Delta p/m$:

$$\text{From } \Delta p \Delta x \geq \tfrac{1}{2}\hbar, \qquad \Delta v = \frac{\Delta p}{m} = \frac{\hbar}{2m\Delta x}$$

$$\begin{aligned}\Delta v &= \frac{1.05457 \times 10^{-34}\ \text{J·s}}{2 \times (9.109 \times 10^{-31}\ \text{kg}) \times (2.00 \times 10^{-10}\ \text{m})} \\ &= \frac{1.05457 \times 10^{-34}}{2 \times 9.109 \times 10^{-31} \times 2.00 \times 10^{-10}}\ \frac{\text{J·s}}{\text{kg·m}} \\ &= 2.89 \times 10^{5}\ \text{m·s}^{-1}\end{aligned}$$

As predicted, the uncertainty in the speed of the electron is very large, nearly $\pm 150\ \text{km·s}^{-1}$.

SELF-TEST 1.6A A proton is accelerated in a cyclotron to a very high speed that is known to within $3.0 \times 10^{2}\ \text{km·s}^{-1}$. What is the minimum uncertainty in its position?

[*Answer:* 0.10 pm]

SELF-TEST 1.6B The police are monitoring an automobile of mass 2.0 t (1 t = 10^3 kg) speeding along a highway. They are certain of the location of the vehicle only to within 1 m. What is the minimum uncertainty in the speed of the vehicle?

The location and momentum of a particle are complementary; that is, both the location and the momentum cannot be known simultaneously with arbitrary precision. The quantitative relation between the precision of each measurement is described by the Heisenberg uncertainty principle, Eq. 7.

1.5 Wavefunctions and Energy Levels

Twentieth-century scientists had to revise the nineteenth-century description of matter to take into account wave–particle duality. One of the first people to formulate a successful theory (in 1927) was the Austrian scientist Erwin Schrödinger.

Because particles have wavelike properties, we cannot expect them to behave like pointlike objects moving along precise trajectories. Schrödinger's approach was to replace the precise trajectory of a particle by a **wavefunction**, ψ (the Greek letter psi), a mathematical function with values that vary with position. There is