CHAPTER 3

Elementary Quantum Physics

The triumph of modern physics is the triumph of quantum mechanics. Even the simplest experimental observation that the resistivity of a metal depends linearly on the temperature can only be explained by quantum physics, simply because we must take the mean speed of the conduction electrons to be nearly independent of temperature. The modern definitions of voltage and ohm, adopted in January 1990 and now part of the IEEE standards, are based on Josephson and quantum Hall effects, both of which are quantum mechanical phenomena.

One of the most important discoveries in physics has been the wave–particle duality of nature. The electron, which we have so far considered to be a particle and hence to be obeying Newton's second law ($F = ma$), can also exhibit wave-like properties quite contrary to our intuition. An electron beam can give rise to diffraction patterns and interference fringes, just like a light wave. Interference and diffraction phenomena displayed by light can only be explained by treating light as an electromagnetic wave. But light can also exhibit particle-like properties in which it behaves as if it were a stream of discrete entities ("photons"), each carrying a linear momentum and each interacting discretely with electrons in matter (just like a particle colliding with another particle).

3.1 PHOTONS

3.1.1 LIGHT AS A WAVE

In introductory physics courses, light is considered to be a wave. Indeed, such phenomena as interference, diffraction, refraction, and reflection can all be explained by the theory of waves. In all these phenomena, a ray of light is considered to be an **electromagnetic (EM) wave** with a given frequency, as depicted in Figure 3.1. The electric and magnetic fields, $\mathcal{E}_y$ and B_z, of this wave are perpendicular to each other and to the direction of propagation x. The electric field $\mathcal{E}_y$ at position x at time t may be

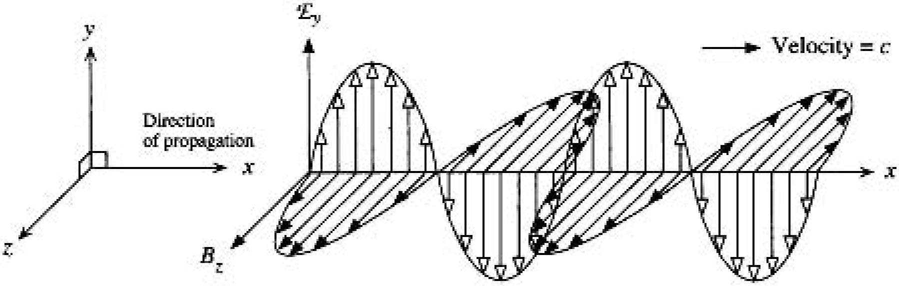

Figure 3.1 The classical view of light as an electromagnetic wave.
An electromagnetic wave is a traveling wave with time-varying electric and magnetic fields that are perpendicular to each other and to the direction of propagation.

described by

Traveling wave

$$\mathcal{E}_y(x, t) = \mathcal{E}_o \sin(kx - \omega t) \qquad [3.1]$$

where k is the wavenumber (propagation constant) related to the wavelength λ by $k = 2\pi/\lambda$, and ω is the angular frequency of the wave (or $2\pi\nu$, where ν is the frequency). A similar equation describes the variation of the magnetic field B_z (directed along z) with x at any time t. Equation 3.1 represents a traveling wave in the x direction, which, in the present example, is a sinusoidally varying function (Figure 3.1). The velocity of the wave (strictly the phase velocity) is

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

where ν is the frequency. The intensity $\mathcal{I}$, that is, the energy flowing per unit area per second, of the wave represented by Equation 3.1 is given by

Intensity of light wave

$$\mathcal{I} = \frac{1}{2}c\varepsilon_o\mathcal{E}_o^2 \qquad [3.2]$$

where ε_o is the absolute permittivity.

Understanding the wave nature of light is fundamental to understanding interference and diffraction, two phenomena that we experience with sound waves almost on a daily basis. Figure 3.2 illustrates how the interference of secondary waves from the two slits S_1 and S_2 gives rise to the dark and bright fringes (called **Young's fringes**) on a screen placed at some distance from the slits. At point P on the screen, the waves emanating from S_1 and S_2 interfere constructively, if they are in phase. This is the case if the path difference between the two rays is an integer multiple of the wavelength λ, or

$$S_1P - S_2P = n\lambda$$

where n is an integer. If the two waves are out of phase by a path difference of $\lambda/2$, or

$$S_1P - S_2P = \left(n + \frac{1}{2}\right)\lambda$$

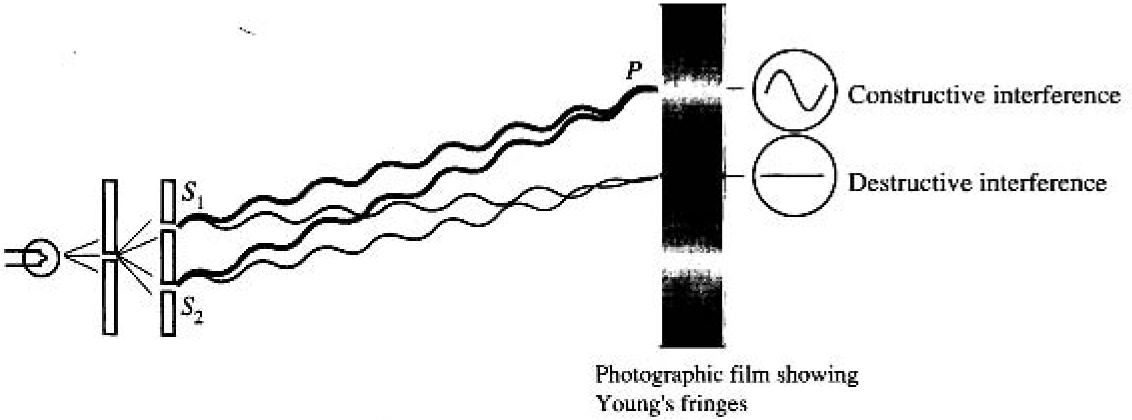

Figure 3.2 Schematic illustration of Young's double-slit experiment.

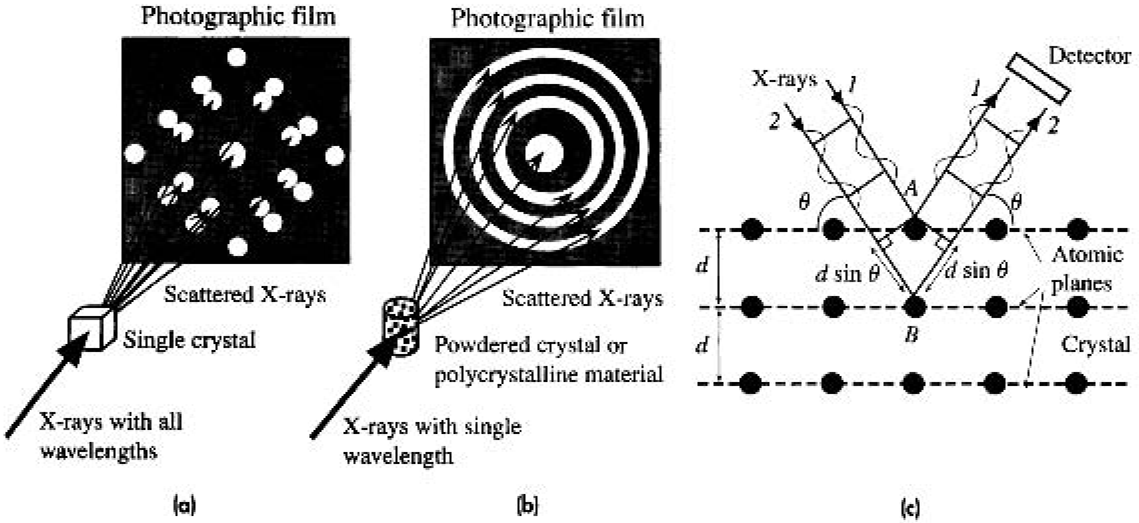

Figure 3.3 Diffraction patterns obtained by passing X-rays through crystals can only be explained by using ideas based on the interference of waves.

(a) Diffraction of X-rays from a single crystal gives a diffraction pattern of bright spots on a photographic film.

(b) Diffraction of X-rays from a powdered crystalline material or a polycrystalline material gives a diffraction pattern of bright rings on a photographic film.

(c) X-ray diffraction involves the constructive interference of waves being "reflected" by various atomic planes in the crystal.

then the waves interfere destructively and the intensity at point P vanishes. Thus, in the y direction, the observer sees a pattern of bright and dark fringes.

When X-rays are incident on a crystalline material, they give rise to typical diffraction patterns on a photographic plate, as shown in Figure 3.3a and b, which can only be explained by using wave concepts. For simplicity, consider two waves, *1* and *2*, in an X-ray beam. The waves are initially in phase, as shown in Figure 3.3c. Suppose that wave *1* is "reflected" from the first plane of atoms in the crystal, whereas wave 2 is "reflected" from the second plane.[1] After reflection, wave 2 has traveled an additional distance equivalent to $2d \sin\theta$ before reaching wave 1. The path difference between the two waves is $2d \sin\theta$, where d is the separation of the atomic planes. For constructive interference, this must be $n\lambda$, where n is an integer. Otherwise, waves 1 and 2 will interfere destructively and will cancel each other. Waves reflected from adjacent atomic planes interfere constructively to constitute a diffracted beam *only* when the path difference between the waves is an integer multiple of the wavelength, and this will only be the case for certain directions. Therefore the *condition* for the existence of a diffracted beam is

Bragg diffraction condition

$$2d \sin\theta = n\lambda \qquad n = 1, 2, 3, \ldots \tag{3.3}$$

The condition expressed in Equation 3.3, for observing a diffracted beam, forms the whole basis for identifying and studying various crystal structures (the science of crystallography). The equation is referred to as **Bragg's law,** and arises from the constructive interference of waves.

Aside from exhibiting wave-like properties, light can behave like a stream of "particles" of zero rest-mass. As it turns out, the only way to explain a vast number of experiments is to view light as a stream of discrete entities or energy packets called **photons,** each carrying a quantum of energy $h\nu$, and momentum h/λ, where h is a universal constant that can be determined experimentally, and ν is the frequency of light. This photonic view of light is drastically different than the simple wave picture and must be examined closely to understand its origin.

3.1.2 THE PHOTOELECTRIC EFFECT

Consider a quartz glass vacuum tube with two metal electrodes, a photocathode and an anode, which are connected externally to a voltage supply V (variable and reversible) via an ammeter, as schematically illustrated in Figure 3.4. When the cathode is illuminated with light, if the frequency ν of the light is greater than a certain critical value ν_0, the ammeter registers a current I, even when the anode voltage is zero (*i.e.*, the supply is bypassed). When light strikes the cathode, electrons are emitted with sufficient kinetic energy to reach the opposite electrode. Applying a positive voltage to the anode helps to collect more of the electrons and thus increases the current, until it saturates because all the photoemitted electrons have been collected. The current, then, is limited by the rate of supply of photoemitted electrons. If, on the other hand, we apply a negative voltage to the anode, we can "push" back the photoemitted electrons and hence reduce the current I. Figure 3.5a shows the dependence of the photocurrent on the anode voltage, for one particular frequency of light.

Recall that when an electron traverses a voltage difference V, its potential energy changes by eV (potential difference is defined as work done per unit charge). When a negative voltage is applied to the anode, the electron has to do work to get to this electrode, and this work comes from its kinetic energy just after photoemission. When the negative anode voltage V is equal to V_0, which just "extinguishes" the current I, we

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[1] Strictly, one must consider the scattering of waves from the electrons in individual atoms (*e.g.*, atoms *A* and *B* in Figure 3.3c) and examine the constructive interference of these scattered waves, which leads to the same condition as that derived in Equation 3.3.

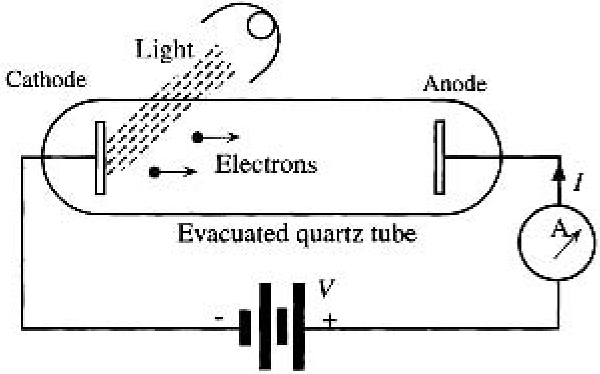
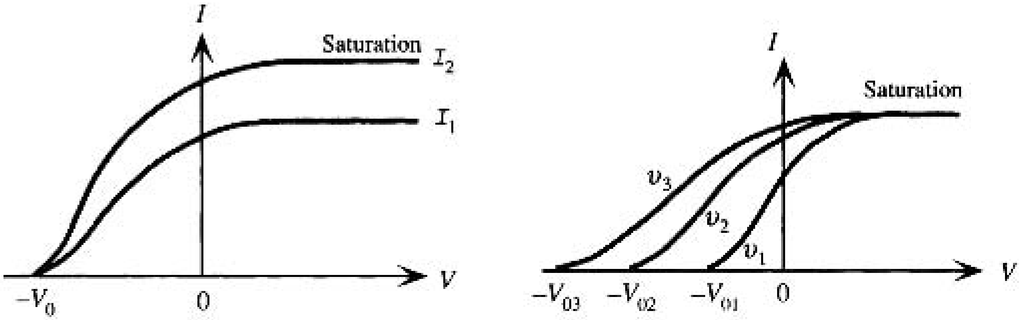


Figure 3.4 The photoelectric effect.



(a) Photoelectric current versus voltage when the cathode is illuminated with light of identical wavelength but different intensities ($\mathcal{I}$). The saturation current is proportional to the light intensity.

(b) The stopping voltage and therefore the maximum kinetic energy of the emitted electron increases with the frequency of light, ν. (The light intensity is not the same; it is adjusted to keep the saturation current the same.)

Figure 3.5 Results from the photoelectric experiment.

know that the potential energy "gained" by the electron is just the kinetic energy lost by the electron, or

$$eV_0 = \frac{1}{2}m_e v^2 = KE_m$$

where v is the velocity and KE_m is the kinetic energy of the electron just after photoemission. Therefore, we can conveniently measure the maximum kinetic energy KE_m of the emitted electrons.

For a given frequency of light, increasing the intensity of light $\mathcal{I}$ requires the *same* voltage V_0 to extinguish the current; that is, the KE_m of emitted electrons is independent of the light intensity $\mathcal{I}$. This is quite surprising. However, increasing the intensity does increase the saturation current. Both of these effects are noted in the I–V results shown in Figure 3.5a.

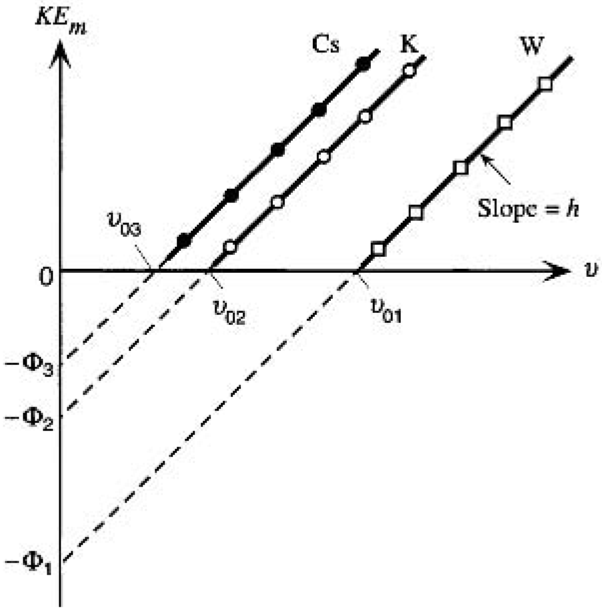


Figure 3.6 The effect of varying the frequency of light and the cathode material in the photoelectric experiment. The lines for the different materials have the same slope h but different intercepts.

Since the magnitude of the saturation photocurrent depends on the light intensity I, whereas the KE of the emitted electron is independent of I, we are forced to conclude that only the *number* of electrons ejected depends on the light intensity. Furthermore, if we plot KE_m (from the V_0 value) against the light frequency ν for different electrode metals for the cathode, we find the typical behavior shown in Figure 3.6. This shows that the KE of the emitted electron depends on the frequency of light. The experimental results shown in Figure 3.6 can be summarized by a statement that relates the KE_m of the electron to the frequency of light and the electrode metal, as follows:

Photoemitted electron maximum KE

$$KE_m = h\nu - h\nu_0 \qquad [3.4]$$

where h is the slope of the straight line and is independent of the type of metal, whereas ν_0 depends on the electrode material for the photocathode (*e.g.*, ν_{01}, ν_{02}, etc.). Equation 3.4 is essentially a succinct statement of the experimental observations of the photoelectric effect as exhibited in Figure 3.6. The constant h is called **Planck's constant**, which, from the slope of the straight lines in Figure 3.6, can be shown to be about 6.6×10^{-34} J s. This was beautifully demonstrated by Millikan in 1915, in an excellent series of photoelectric experiments using different photocathode materials.

The successful interpretation of the photoelectric effect was first given in 1905 by Einstein, who proposed that light consists of "energy packets," each of which has the magnitude $h\nu$. We can call these energy quanta **photons.** When one photon strikes an electron, its energy is transferred to the electron. The whole photon becomes absorbed by the electron. Yet, an electron in a metal is in a lower state of potential energy (PE) than in vacuum, by an amount Φ, which we call the **work function** of the metal, as illustrated in Figure 3.7. The lower PE is what keeps the electron in the metal; otherwise, it would "drop out."

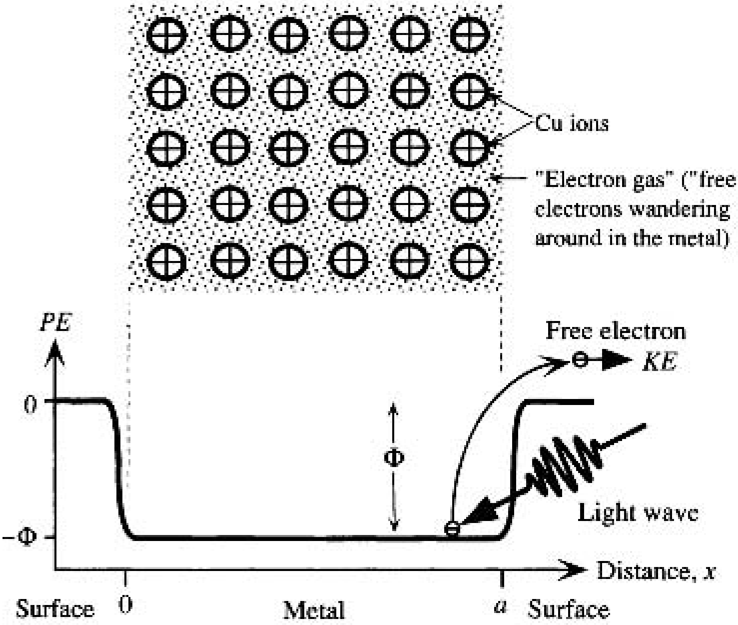


Figure 3.7 The *PE* of an electron inside the metal is lower than outside by an energy called the workfunction of the metal.
Work must be done to remove the electron from the metal.

This lower *PE* is a result of the Coulombic attraction interaction between the electron and the positive metal ions. Some of the photon energy $h\nu$ therefore goes toward overcoming this *PE* barrier. The energy that is left ($h\nu - \Phi$) gives the electron its *KE*. The work function Φ changes from one metal to another. Photoemission only occurs when $h\nu$ is greater than Φ. This is clearly borne out by experiment, since a critical frequency ν_0 is needed to register a photocurrent. When ν is less than ν_0, even if we use an extremely intense light, no current exists because no photoemission occurs, as demonstrated by the experimental results in Figure 3.6. Inasmuch as Φ depends on the metal, so does ν_0. Therefore, in Einstein's interpretation $h\nu_0 = \Phi$. In fact, the measurement of ν_0 constitutes one method of determining the work function of the metal.

This explanation for the photoelectric effect is further supported by the fact that the work function Φ from $h\nu_0$ is in good agreement with that from thermionic emission experiments. There is an apparent similarity between the *I–V* characteristics of the phototube and that of the vacuum tube used in early radios. The only difference is that in the vacuum tube, the emission of electrons from the cathode is achieved by heating the cathode. Thermal energy ejects some electrons over the *PE* barrier Φ. The measurement of Φ by this thermionic emission process agrees with that from photoemission experiments.

In the photonic interpretation of light, we still have to resolve the meaning of the intensity of light, because the classical intensity in Equation 3.2

$$I = \frac{1}{2}c\varepsilon_o\mathcal{E}_o^2$$

Classical light intensity

is obviously not acceptable. Increasing the intensity of illumination in the photoelectric experiment increases the saturation current, which means that more electrons are

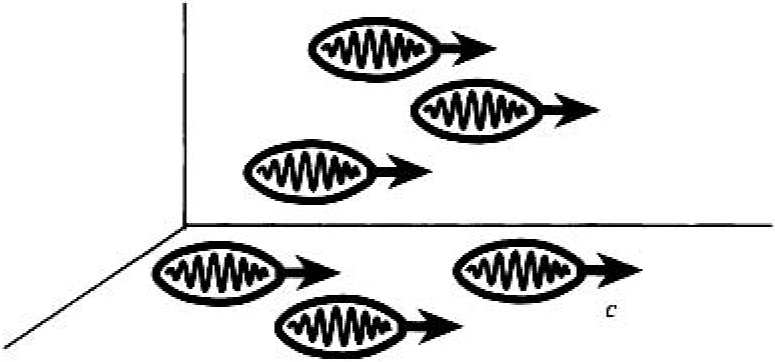


Figure 3.8 Intuitive visualization of light consisting of a stream of photons (not to be taken too literally).
SOURCE: R. Serway, C. J. Moses, and C. A. Moyer, *Modern Physics*, Saunders College Publishing, 1989, p. 56, figure 2.16(b).

emitted per unit time. We therefore infer that the cathode must be receiving more photons per unit time at higher intensities. By definition, "intensity" refers to the amount of energy flowing through a unit area per unit time. If the number of photons crossing a unit area per unit time is the **photon flux,** denoted by Γ_{ph}, then the flow of energy through a unit area per unit time, the **light intensity,** is the product of this photon flux and the energy per photon, that is,

Light intensity

$$I = \Gamma_{ph} h\nu \tag{3.5}$$

where

Photon flux

$$\Gamma_{ph} = \frac{\Delta N_{ph}}{A\Delta t} \tag{3.6}$$

in which ΔN_{ph} is the net number of photons crossing an area A in time Δt. With the energy of a photon given as $h\nu$ and the intensity of light defined as $\Gamma_{ph}h\nu$, the explanation for the photoelectric effect becomes self-consistent. The interpretation of light as a stream of photons can perhaps be intuitively imagined as depicted in Figure 3.8.

EXAMPLE 3.1 **ENERGY OF A BLUE PHOTON** What is the energy of a blue photon that has a wavelength of 450 nm?

SOLUTION

The energy of the photon is given by

$$E_{ph} = h\nu = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{450 \times 10^{-9}\ \text{m}} = 4.4 \times 10^{-19}\ \text{J}$$

Generally, with such small energy values, we prefer electron–volts (eV), so the energy of the photon is

$$\frac{4.4 \times 10^{-19}\ \text{J}}{1.6 \times 10^{-19}\ \text{J/eV}} = 2.75\ \text{eV}$$

EXAMPLE 3.2

THE PHOTOELECTRIC EXPERIMENT In the photoelectric experiment, green light, with a wavelength of 522 nm, is the longest-wavelength radiation that can cause the photoemission of electrons from a clean sodium surface.

a. What is the work function of sodium, in electron–volts?

b. If UV (ultraviolet) radiation of wavelength 250 nm is incident to the sodium surface, what will be the kinetic energy of the photoemitted electrons, in electron–volts?

c. Suppose that the UV light of wavelength 250 nm has an intensity of 20 mW cm^{-2}. If the emitted electrons are collected by applying a positive bias to the opposite electrode, what will be the photoelectric current density?

SOLUTION

a. At threshold, the photon energy just causes photoemissions; that is, the electron just overcomes the potential barrier Φ. Thus, $hc/\lambda_0 = e\Phi$, where Φ is the work function in eV, and λ_0 is the longest wavelength.

$$\Phi = \frac{hc}{e\lambda_0} = \frac{(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^8\ \text{m s}^{-1})}{(1.6 \times 10^{-19}\ \text{J/eV})(522 \times 10^{-9}\ \text{m})} = 2.38\ \text{eV}$$

b. The energy of the incoming photon E_{ph} is (hc/λ), so the excess energy over $e\Phi$ goes to the kinetic energy of the electron. Thus,

$$KE = \frac{hc}{e\lambda} - \Phi = \frac{(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^8\ \text{m s}^{-1})}{(1.6 \times 10^{-19}\ \text{J/eV})(250 \times 10^{-9}\ \text{m})} - 2.38\ \text{eV} = 2.58\ \text{eV}$$

c. The light intensity (defined as energy flux) is given by $I = \Gamma_{ph}(hc/\lambda)$, where Γ_{ph} is the number of photons arriving per unit area per unit time; that is, photon flux and (hc/λ) is the energy per photon. Thus, if each photon releases one electron, the electron flux will be equal to the photon flux, and the current density, which is the charge flux, will be

$$J = e\Gamma_{ph} = \frac{eI\lambda}{hc} = \frac{(1.6 \times 10^{-19}\ \text{C})(20 \times 10^{-3} \times 10^4\ \text{J s}^{-1}\ \text{m}^{-2})(250 \times 10^{-9}\ \text{m})}{(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^8\ \text{m s}^{-1})}$$

$$= 40.3\ \text{A m}^{-2} \quad \text{or} \quad 4.0\ \text{mA cm}^{-2}$$

3.1.3 COMPTON SCATTERING

When an X-ray strikes an electron, it is deflected, or "scattered." In addition, the electron moves away after the interaction, as depicted in Figure 3.9. The wavelength of the incoming and scattered X-rays can readily be measured. The frequency ν' of the scattered X-ray is less than the frequency ν of the incoming X-ray. When the KE of the electron is determined, we find that

$$KE = h\nu - h\nu'$$

Since the electron now also has a momentum p_e, then from the conservation of linear momentum law, we are forced to accept that the X-ray also has a momentum. The Compton effect experiments showed that the momentum of the photon is related to its wavelength by

$$p = \frac{h}{\lambda} \qquad [3.7]$$

Momentum of a photon

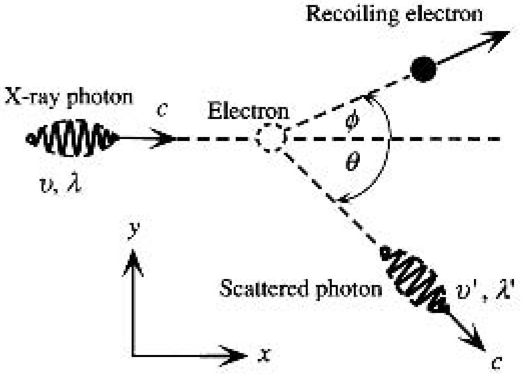


Figure 3.9 Scattering of an X-ray photon by a "free" electron in a conductor.

We see that a photon not only has an energy $h\upsilon$, but also a momentum p, and it interacts as if it were a discrete entity like a particle. Therefore, when discussing the properties of a photon, we must consider its energy and momentum as if it were a particle.

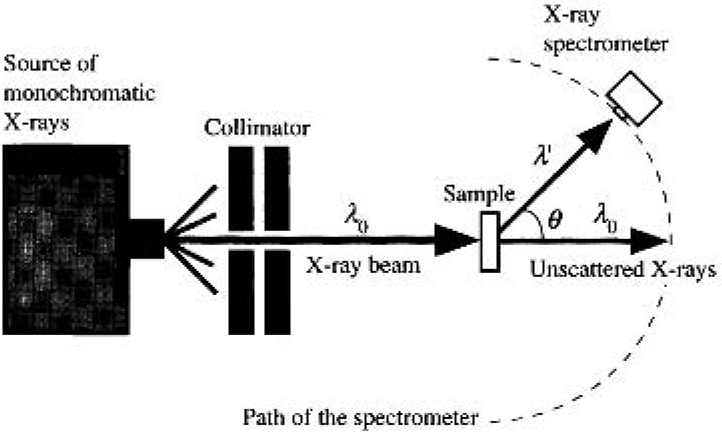
We should mention that the description of the Compton effect shown in Figure 3.9 is, in fact, the inference from a more practical experiment involving the scattering of X-rays from a metal target. A collimated monochromatic beam of X-rays of wavelength λ_0 strikes a conducting target, such as graphite, as illustrated in Figure 3.10a. A conducting target contains a large number of nearly "free" electrons (conduction electrons), which can scatter the X-rays. The scattered X-rays are detected at various angles θ with respect to the original direction, and their wavelength λ' is measured. The result of the experiment is therefore the scattered wavelength λ' measured at various scattering angles θ, as shown in Figure 3.10b. It turns out that the λ' versus θ results agree with the conservation of linear momentum law applied to an X-ray photon colliding with an electron with the momentum of the photon given precisely by Equation 3.7.

The photoelectric experiment and the Compton effect are just two convincing experiments in modern physics that force us to accept that light can have particle-like properties. We already know that it can also exhibit wave-like properties, in such experiments as Young's interference fringes. We are then faced with what is known as the wave–particle dilemma. How do we know whether light is going to behave like a wave or a particle? The properties exhibited by light depend very much on the nature of the experiment. Some experiments will require the wave model, whereas others may use the particulate interpretation of light. We should perhaps view the two interpretations as two complementary ways of modeling the behavior of light when it interacts with matter, accepting the fact that light has a dual nature. Both models are needed for a full description of the behavior of light.

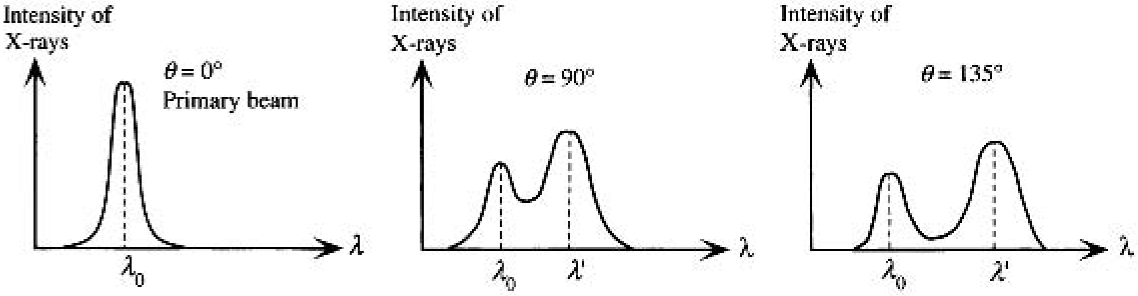
The expressions for the energy and momentum of the photon, $E = h\upsilon$ and $p = h/\lambda$, can also be written in terms of the angular frequency $\omega(= 2\pi\upsilon)$ and the wave number k, defined as $k = 2\pi/\lambda$. If we define $\hbar = h/2\pi$, then

Photon energy and momentum

$$E = h\upsilon = \hbar\omega \qquad \text{and} \qquad p = \frac{h}{\lambda} = \hbar k \qquad [3.8]$$



(a) A schematic diagram of the Compton experiment



(b) Results from the Compton experiment

Figure 3.10 The Compton experiment and its results.

EXAMPLE 3.3

X-RAY PHOTON ENERGY AND MOMENTUM X-rays are photons with very short wavelengths that can penetrate or pass through objects, hence their use in medical imaging, security scans at airports, and many other applications including X-ray diffraction studies of crystal structures. Typical X-rays used in mammography (medical imaging of breasts) have a wavelength of about 0.6 angstrom (1 Å $= 10^{-10}$ m). Calculate the energy and momentum of an X-ray photon with this wavelength, and the velocity of a *corresponding* electron that has the same momentum.

SOLUTION

The photon energy E_{ph} is given by

$$E_{ph} = h\upsilon = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{0.6 \times 10^{-10}\ \text{m}} \times \frac{\text{eV J}^{-1}}{1.6 \times 10^{-19}}$$

$$= 2.06 \times 10^{4}\ \text{eV} \qquad \text{or} \qquad 20.6\ \text{keV}$$

The momentum p of this X-ray photon is

$$p = \frac{h}{\lambda} = \frac{6.6 \times 10^{-34}\ \text{J s}}{0.6 \times 10^{-10}\ \text{m}} = 1.1 \times 10^{-23}\ \text{kg m s}^{-1}$$

A corresponding electron with the same momentum, $m_e v_{\text{electron}} = p$, would have a velocity

$$v_{\text{electron}} = \frac{p}{m_e} = \frac{1.1 \times 10^{-23}\ \text{kg m s}^{-1}}{9.1 \times 10^{-31}\ \text{kg}} = 1.2 \times 10^{7}\ \text{m s}^{-1}$$

This is much greater than the average speed of conduction (free) electrons whizzing around inside a metal, which is $\sim 10^{6}\ \text{m s}^{-1}$.

3.1.4 BLACK BODY RADIATION

Experiments indicate that all objects emit and absorb energy in the form of radiation, and the intensity of this radiation depends on the radiation wavelength and temperature of the object. This radiation is frequently termed **thermal radiation.** When the object is in thermal equilibrium with its surroundings, that is, at the same temperature, the object absorbs as much radiation energy as it emits. On the other hand, when the temperature of the object is above the temperature of its surroundings, there is a net emission of radiation energy. The maximum amount of radiation energy that can be emitted by an object is called the **black body radiation.** Although, in general, the intensity of the radiated energy depends on the material's surface, the radiation emitted from a cavity with a small aperture is independent of the material of the cavity and corresponds very closely to black body radiation.

The intensity of the emitted radiation has the spectrum (*i.e.*, intensity vs. wavelength characteristic), and the temperature dependence illustrated in Figure 3.11. It is useful to define a **spectral irradiance** I_λ as the emitted radiation intensity (power per unit area) per unit wavelength, so that $I_\lambda\, \delta\lambda$ is the intensity in a small range of wavelengths $\delta\lambda$. Figure 3.11 shows the typical I_λ versus λ behavior of black body radiation at two temperatures. We assume that the characteristics of the radiation emerging from the aperture represent those of the radiation within the cavity.

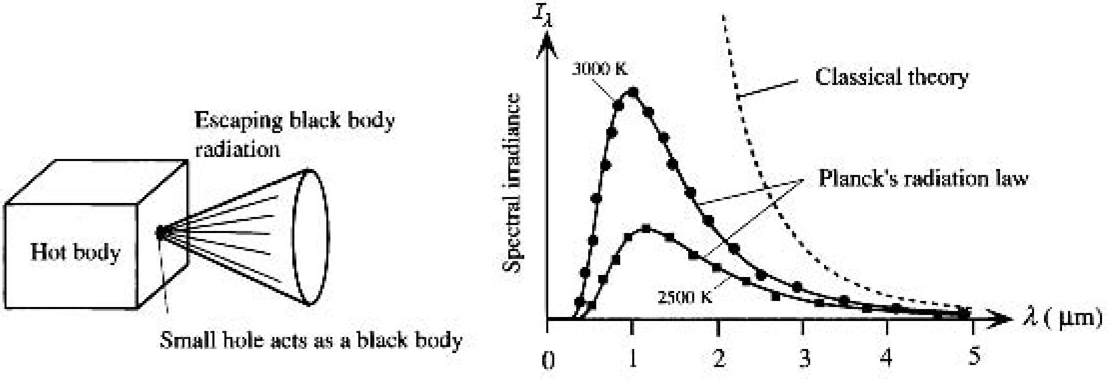


Figure 3.11 Schematic illustration of black body radiation and its characteristics.
Spectral irradiance versus wavelength at two temperatures (3000 K is about the temperature of the incandescent tungsten filament in a light bulb).

Classical physics predicts that the acceleration and deceleration of the charges due to various thermal vibrations, oscillations, or motions of the atoms in the surface region of the cavity material result in electromagnetic waves of the emissions. These waves then interfere with each other, giving rise to many types of standing electromagnetic waves with different wavelengths in the cavity. Each wave contributes an energy kT to the emitted intensity. If we calculate the number of standing waves within a small range of wavelength, the classical prediction leads to the **Rayleigh–Jeans law** in which $\mathcal{I}_\lambda \propto 1/\lambda^4$ and $\mathcal{I}_\lambda \propto T$, which are not in agreement with the experiment, especially in the short-wavelength range (see Figure 3.11).

Max Planck (1900) was able to show that the experimental results can be explained if we assume that the radiation within the cavity involves the emission and absorption of discrete amounts of light energy by the oscillation of the molecules of the cavity material. He assumed that oscillating molecules emit and absorb a quantity of energy that is an integer multiple of a discrete energy quantum that is determined by the frequency ν of the radiation and given by $h\nu$. This is what we now call a photon. He then considered the energy distribution (the statistics) in the molecular oscillations and took the probability of an oscillator possessing an energy $nh\nu$ (where n is an integer) to be proportional to the Boltzmann factor, $\exp(-nh\nu/kT)$. He eventually derived the mathematical form of the black body radiation characteristics in Figure 3.11. Planck's black body radiation formula for $\mathcal{I}_\lambda$ is generally expressed as

$$\mathcal{I}_\lambda = \frac{2\pi hc^2}{\lambda^5\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]} \qquad [3.9]$$

Planck's radiation law

where k is the Boltzmann constant. Planck's radiation law based on the emission and absorption of photons is in excellent agreement with all observed black body radiation characteristics as depicted in Figure 3.11.

Planck's radiation law is undoubtedly one of the major successes of modern physics. We can take Equation 3.9 one step further and derive *Stefan's black body radiation law* that was used in Chapter 2 to calculate the rate of radiation energy emitted from the hot filament of a light bulb. If we integrate $\mathcal{I}_\lambda$ over all wavelengths,[2] we will obtain the total radiative power P_S emitted by a black body per unit surface area at a temperature T,

$$P_S = \int_0^\infty \mathcal{I}_\lambda \, d\lambda = \left(\frac{2\pi^5k^4}{15c^2h^3}\right)T^4 = \sigma_S T^4 \qquad [3.10]$$

Stefan's black body radiation law

where $$\sigma_S = \frac{2\pi^5k^4}{15c^2h^3} = 5.670 \times 10^{-8}\ \mathrm{W\ m^{-2}\ K^{-4}} \qquad [3.11]$$

Stefan's constant

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[2] The integration of Equation 3.9 can be done by looking up definite integral tables in math handbooks—we only need the result of the mathematics, which is Equation 3.10. The P_S in Equation 3.10 is sometimes called the *radiant emittance*. Stefan's law is also known as the Stefan-Boltzmann law.

Equation 3.10 in which $P_S = \sigma_S T^4$ is **Stefan's law** for black body radiation, and the σ_S in Equation 3.11 is the **Stefan constant** with a value of approximately 5.67×10^{-8} W m^{-2} K^{-4}. Stefan's law was known before Planck used quantum physics to derive his black body radiation law embedded in I_λ. A complete explanation of Stefan's law and the value for σ_S however had to wait for Planck's law. The h in Equation 3.10 or 3.11 is a clear pointer that the origin of Stefan's law lies in quantum physics.

EXAMPLE 3.4

STEFAN'S LAW AND THE LIGHT BULB Stefan's law as stated in Equation 3.10 applies to a perfect black body that is emitting radiation into its environment which is at absolute zero. If the environment or the surroundings of the black body is at a finite temperature T_o, than the surroundings would also be emitting radiation. The same black body will then also absorb radiation from its environment. By definition, a black body is not only a perfect emitter of radiation but also a perfect absorber of radiation. The rate of radiation absorbed from the environment per unit surface is again given by Equation 3.10 but with T_o instead of T since it is the surroundings that are emitting the radiation. Thus, $\sigma_S T_o^4$ is the absorbed radiation rate from the surroundings, so

$$\text{Net rate of radiative power emission per unit surface} = \sigma_S T^4 - \sigma_S T_o^4$$

Further, not all surfaces are perfect black bodies. Black body emission is the maximum possible emission from a surface at a given temperature. A real surface emits less than a black body. **Emissivity** ε of a surface measures the efficiency of a surface in terms of a black body emitter; it is the ratio of the emitted radiation from a real surface to that emitted from a black body at a given temperature and over the same wavelength range. The *total* net rate of radiative power emission becomes

Stefan's law for a real surface

$$P_{\text{radiation}} = S\varepsilon\sigma_S(T^4 - T_o^4) \qquad [3.12]$$

where S is the surface area that is emitting the radiation. Consider the tungsten filament of a 100 W light bulb in a lamp. When we switch the lamp on, the current through the filament generates heat which quickly heats up the filament to an operating temperature T_f. At this temperature, the electric energy that is input into the bulb is radiated away from the filament as radiation energy. A typical 100 W bulb filament has a length of 57.9 cm and a diameter of 63.5 μm. Its surface area is then

$$S = \pi(63.5 \times 10^{-6}\text{ m})(0.579\text{ m}) = 1.155 \times 10^{-4}\text{ m}^2$$

The emissivity ε of tungsten is about 0.35. Assuming that under steady-state operation all the electric power that is input into the bulb's filament is radiated away,

$$\begin{aligned} 100\text{ W} = P_{\text{radiation}} &= S\varepsilon\sigma_S(T_f^4 - T_o^4) \\ &= (1.155 \times 10^{-4}\text{ m}^2)(0.35)(5.67 \times 10^{-8}\text{ W m}^{-2}\text{ K}^{-4})(T_f^4 - 300^4) \end{aligned}$$

Solving we find,

$$T_f = 2570\text{ K} \qquad \text{or} \qquad 2297\ ^\circ\text{C}$$

which is well below the melting temperature of tungsten which is 3422 °C. The second term that has T_o^4 has very little effect on the calculation as radiation absorption from the environment is practically nil compared with the emitted radiation at T_f.

The shift in the spectral intensity emitted from a black body with temperature is of particular interest to many photoinstrumention engineers. The peak spectral intensity in Figure 3.11 occurs at a wavelength $\lambda_{\max}$, which, by virtue of Equation 3.9, depends on the temperature of the black body. By substituting a new variable $x = hc/(kT\lambda)$ into Equation 3.9 and differentiating it, or plotting it against x, we can show that the peak occurs when

Wien's displacement law

$$\lambda_{\max} T \approx 2.89 \times 10^{-3} \text{ m K}$$

which is known as **Wien's displacement law.** The peak emission shifts to lower wavelengths as the temperature increases. We can calculate the wavelength $\lambda_{\max}$ corresponding to the peak in the spectral distribution of emitted radiation from our 100 W lamp: $\lambda_{\max} = (2.89 \times 10^{-3} \text{ m K})/(2570 \text{ K}) = 1.13\ \mu\text{m}$ (in the infrared).

3.2 THE ELECTRON AS A WAVE

3.2.1 DE BROGLIE RELATIONSHIP

It is apparent from the photoelectric and Compton effects that light, which we thought was a wave, can behave as if it were a stream of particulate-like entities called photons. Can electrons exhibit wave-like properties? Again, this depends on the experiment and on the energy of the electrons.

When the interference and diffraction experiments in Figures 3.2 and 3.3 are repeated with an electron beam, very similar results are found to those obtainable with light and X-rays. When we use an electron beam in Young's double-slit experiment, we observe high- and low-intensity regions (*i.e.*, Young's fringes), as illustrated in Figure 3.12. The interference pattern is viewed on a fluorescent TV screen. When an energetic electron beam hits an Al polycrystalline sample, it produces diffraction rings on a fluorescent screen (Figure 3.13), just like X-rays do on a photographic

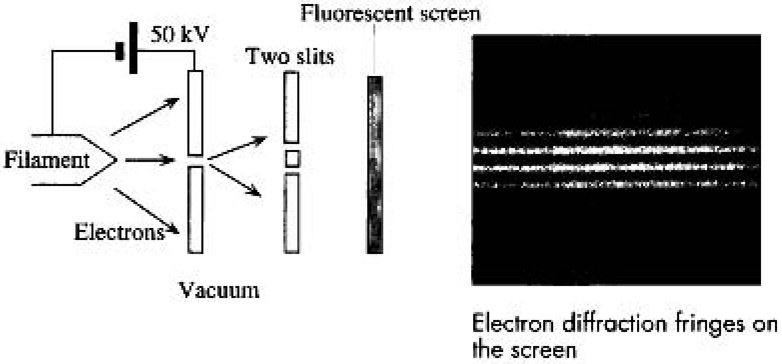
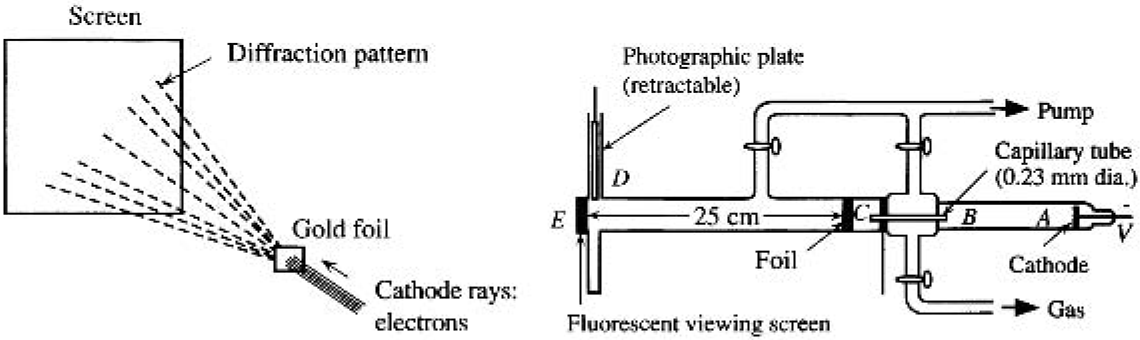


Figure 3.12 Young's double-slit experiment with electrons involves an electron gun and two slits in a cathode ray tube (CRT) (hence, in vacuum).

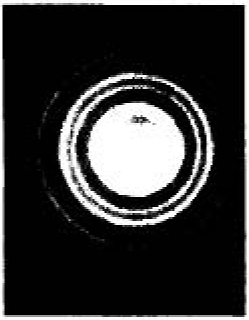
Electrons from the filament are accelerated by a 50 kV anode voltage to produce a beam that is made to pass through the slits. The electrons then produce a visible pattern when they strike a fluorescent screen (e.g., a TV screen), and the resulting visual pattern is photographed.

SOURCE: Pattern from C. Jönsson, D. Brandt, and S. Hirschi, *Am. J. Physics*, **42**, 1974, p. 9, figure 8. Used with permission.

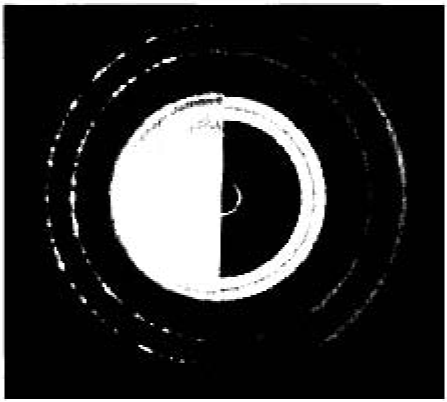


(a) Thomson diffracted electrons by using a thin gold foil and produced a diffraction pattern on the screen of his apparatus in (b). The foil was polycrystalline, so the diffraction pattern was circular rings.

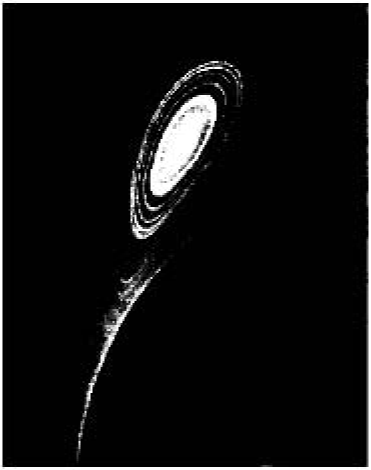
(b) In Thomson's electron diffraction apparatus a beam of electrons is generated in tube *A*, passed through collimating tube *B*, and made to impinge on a thin gold foil *C*. The transmitted electrons impinge on the fluorescent screen *E*, or a photographic plate *D*, which could be lowered into the path. The entire apparatus was evacuated during the experiment.



(c) Electron diffraction pattern obtained by G. P. Thomson using a gold foil target.



(d) Composite photograph showing diffraction patterns produced with an aluminum foil by X-rays and electrons of similar wavelength. Left: X-rays of $\lambda = 0.071$ nm. Right: Electrons of energy 600 eV.



(e) Diffraction pattern produced by 40 keV electrons passing through zinc oxide powder. The distortion of the pattern was produced by a small magnet placed between the sample and the photographic plate. An X-ray diffraction pattern would not be affected by a magnetic field.

Figure 3.13 The diffraction of electrons by crystals gives typical diffraction patterns that would be expected if waves were being diffracted, as in X-ray diffraction with crystals.

SOURCE: (b) from G. P. Thomson, *Proceedings of the Royal Society*, A117, no. 600, 1928; (c) and (d) from A. P. French and F. Taylor, *An Introduction to Quantum Mechanics*, Norton, New York, 1978, p. 75; (e) from R. B. Leighton, *Principles of Modern Physics*, New York: McGraw-Hill, 1959, p. 84.

plate. The diffraction pattern obtained with an electron beam (Figure 3.13) means that the electrons are obeying the Bragg diffraction condition $2d \sin\theta = n\lambda$ just as much as the X-ray waves.

Since we know the interatomic spacing d and we can measure the angle of diffraction 2θ, we can readily evaluate the wavelength λ associated with the wave-like behavior of the electrons. Furthermore, from the accelerating voltage V in the electron tube, we can also determine the momentum of the electrons, because the kinetic energy gained by the electrons, $(p^2/2m_e)$, is equal to eV. Simply by adjusting the accelerating voltage V, we can therefore study how the wavelength of the electron depends on the momentum.

As a result of such studies and other similar experiments, it has been found that an electron traveling with a momentum p behaves like a wave of wavelength λ given by

Wavelength of the electron

$$\lambda = \frac{h}{p} \tag{3.13}$$

This is just the reverse of the equation for the momentum of a photon given its wavelength. The same equation therefore relates wave-like and particle-like properties to and from each other. Thus,

De Broglie relations

$$\lambda = \frac{h}{p} \qquad \text{or} \qquad p = \frac{h}{\lambda}$$

is an equation that exposes the wave–particle duality of nature. It was first hypothesized by De Broglie in 1924. As an example, we can calculate the wavelengths of a number of particle-like objects:

a. A 50 gram golf ball traveling at a velocity of 20 m s^{-1}.

The wavelength is

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{J s}}{(50 \times 10^{-3}\ \text{kg})(20\ \text{m s}^{-1})} = 6.63 \times 10^{-34}\ \text{m}$$

The wavelength is so small that this golf ball will not exhibit any wave effects. Firing a stream of golf balls at a wall will not result in "diffraction rings" of golf balls.

b. A proton traveling at 2200 m s^{-1}.

Using $m_p = 1.67 \times 10^{-27}$ kg, we have $\lambda = (h/mv) \approx 0.18$ nm. This is only slightly smaller than the interatomic distance in crystals, so firing protons at a crystal can result in diffraction. (Recall that to get a diffraction peak, we must satisfy the Bragg condition, $2d \sin\theta = n\lambda$.) Protons, however, are charged, so they can penetrate only a small distance into the crystal. Hence, they are not used in crystal diffraction studies.

c. Electron accelerated by 100 V.

This voltage accelerates the electron to a KE equal to eV. From $KE = p^2/2m_e = eV$, we can calculate p and hence $\lambda = h/p$. The result is $\lambda = 0.123$ nm. Since this is comparable to typical interatomic distances in solids, we would see a diffraction pattern when an electron beam strikes a crystal. The actual pattern is determined by the Bragg diffraction condition.

3.2.2 TIME-INDEPENDENT SCHRÖDINGER EQUATION

The experiments in which electrons exhibit interference and diffraction phenomena show quite clearly that, under certain conditions, the electron can behave as a wave; in other words, it can exhibit wave-like properties. There is a general equation that describes this wave-like behavior and, with the appropriate potential energy and boundary conditions, will predict the results of the experiments. The equation is called the **Schrödinger equation** and it forms the foundations of quantum theory. Its fundamental nature is analogous to the classical physics assertion of Newton's second law, $F = ma$, which of course cannot be proved. As a fundamental equation, Schrödinger's has been found to successfully predict every observable physical phenomenon at the atomic scale. Without this equation, we will not be able to understand the properties of electronic materials and the principles of operation of many semiconductor devices. We introduce the equation through an analogy.

A traveling electromagnetic wave resulting from sinusoidal current oscillations, or the traveling voltage wave on a long transmission line, can generally be described by a traveling-wave equation of the form

$$\mathcal{E}(x, t) = \mathcal{E}_o \exp j(kx - \omega t) = \mathcal{E}(x) \exp(-j\omega t) \qquad [3.14]$$

where $\mathcal{E}(x) = \mathcal{E}_0 \exp(jkx)$ represents the spatial dependence, which is separate from the time variation. We assume that no transients exist to upset this perfect sinusoidal propagation. We note that the time dependence is harmonic and therefore predictable. For this reason, in ac circuits we put aside the $\exp(-j\omega t)$ term until we need the instantaneous magnitude of the voltage.

The average intensity $\mathcal{I}_{av} = \frac{1}{2}c\varepsilon_o\mathcal{E}_o^2$ depends on the square of the amplitude. In Young's double-slit experiment, the intensity varies along the y direction, which means that $\mathcal{E}_o^2$ for the resultant wave depends on y. In the electron version of this experiment in Figure 3.12, what changes in the y direction is the probability of observing electrons; that is, there are peaks and troughs in the probability of finding electrons along y, just like the $\mathcal{E}_o^2$ variation along y. We should therefore attach some probability interpretation to the wave description of the electron.

In 1926, Max Born suggested a probability wave interpretation for the wave-like behavior of the electron.

$$\mathcal{E}(x, t) = \mathcal{E}_o \sin(kx - \omega t)$$

is a plane traveling **wavefunction** for an electric field; experimentally, we measure and interpret the *intensity* of a wave, namely $|\mathcal{E}(x, t)|^2$. There may be a similar wave function for the electron, which we can represent by a function $\Psi(x, t)$. According to Born, the significance of $\Psi(x, t)$ is that its amplitude squared represents the probability of finding the electron per unit distance. Thus, in three dimensions, if $\Psi(x, y, z, t)$ represents the wave property of the electron, it must have one of the following interpretations:

> $|\Psi(x, y, z, t)|^2$ is the probability of finding the electron per unit volume at x, y, z at time t.
>
> $|\Psi(x, y, z, t)|^2\, dx\, dy\, dz$ is the probability of finding the electron in a small elemental volume $dx\, dy\, dz$ at x, y, z at time t.

If we are just considering one dimension, then the wavefunction is $\Psi(x, t)$, and $|\Psi(x, t)|^2\,dx$ is the probability of finding the electron between x and $(x + dx)$ at time t.

We should note that since only $|\Psi|^2$ has meaning, not Ψ, the latter function need not be real; it can be a complex function with real and imaginary parts. For this reason, we tend to use $\Psi^*\,\Psi$, where Ψ^* is the complex conjugate of Ψ, instead of $|\Psi|^2$, to represent the probability per unit volume.

To obtain the wavefunction $\Psi(x, t)$ for the electron, we need to know how the electron interacts with its environment. This is embodied in its potential energy function $V = V(x, t)$, because the net force the electron experiences is given by

$$F = -dV/dx.$$

For example, if the electron is attracted by a positive charge (*e.g.*, the proton in a hydrogen atom), then it clearly has an electrostatic potential energy given by

$$V(r) = -\frac{e^2}{4\pi\varepsilon_o r}$$

where $r = \sqrt{x^2 + y^2 + z^2}$ is the distance between the electron and the proton.

If the *PE* of the electron is time independent, which means that $V = V(x)$ in one dimension, then the spatial and time dependences of $\Psi(x, t)$ can be separated, just as in Equation 3.14, and the **total wavefunction** $\Psi(x, t)$ of the electron can be written as

Steady-state total wave function

$$\Psi(x, t) = \psi(x)\exp\left(-\frac{jEt}{\hbar}\right) \qquad [3.15]$$

where $\psi(x)$ is the electron wavefunction that describes only the spatial behavior, and E is the energy of the electron. The temporal behavior is simply harmonic, by virtue of $\exp(-jEt/\hbar)$, which corresponds to $\exp(-j\omega t)$ with an angular frequency $\omega = E/\hbar$. The fundamental equation that describes the electron's behavior by determining $\psi(x)$ is called the **time-independent Schrödinger equation.** It is given by the famous equation

Schrödinger's equation for one dimension

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad [3.16a]$$

where m is the mass of the electron.

This is a second-order differential equation. It should be reemphasized that the potential energy V in Equation 3.16a depends only on x. If the potential energy of the electron depends on time as well, that is, if $V = V(x, t)$, then in general $\Psi(x, t)$ cannot be written as $\psi(x)\exp(-jEt/\hbar)$. Instead, we must use the full version of the Schrödinger equation, which is discussed in more advanced textbooks.

In three dimensions, there will be derivatives of ψ with respect to x, y, and z. We use the calculus notation $(\partial\psi/\partial x)$, differentiating $\psi(x, y, z)$ with respect to x but keeping y and z constant. Similar notations $\partial\psi/\partial y$ and $\partial\psi/\partial z$ are used for derivatives with respect to y alone and with respect to z alone, respectively. In three dimensions, Equation 3.16a becomes

Schrödinger's equation for three dimensions

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad [3.16b]$$

where $V = V(x, y, z)$ and $\psi = \psi(x, y, z)$.

Equation 3.16b is a fundamental equation, called the time-independent Schrödinger equation, the solution of which gives the steady-state behavior of the electron in a time-independent potential energy environment described by $V = V(x, y, z)$. By solving Equation 3.16b, we will know the probability distribution and the energy of the electron. Once $\psi(x, y, z)$ has been determined, the total wavefunction for the electron is given by Equation 3.15 so that

$$|\Psi(x, y, z, t)|^2 = |\psi(x, y, z)|^2$$

which means that the steady-state probability distribution of the electron is simply $|\psi(x, y, z)|^2$.

The time-independent Schrödinger equation can be viewed as a "mathematical crank." We input the potential energy of the electron and the boundary conditions, turn the crank, and get the probability distribution and the energy of the electron under steady-state conditions.

Two important boundary conditions are often used to solve the Schrödinger equation. First, as an analogy, when we stretch a string between two fixed points and put it into a steady-state vibration, there are no discontinuities or kinks along the string. We can therefore intelligently guess that because $\psi(x)$ represents wave-like behavior, it must be a smooth function without any discontinuities.

The first boundary condition is that Ψ must be continuous, and the second is that $d\Psi/dx$ must be continuous. In the steady state, these two conditions translate directly to ψ and $d\psi/dx$ being continuous. Since the probability of finding the electron is represented by $|\psi|^2$, this function must be single-valued and smooth, without any discontinuities, as illustrated in Figure 3.14. The enforcement of these boundary conditions results in strict requirements on the wavefunction $\psi(x)$, as a result of which only certain wavefunctions are acceptable. These wavefunctions are called the **eigenfunctions** (characteristic functions) of the system, and they determine the behavior and energy of the electron under steady-state conditions. The eigenfunctions $\psi(x)$ are also called **stationary states,** inasmuch as we are only considering steady-state behavior.

It is important to note that the Schrödinger equation is generally applicable to all matter, not just the electron. For example, the equation can also be used to describe the behavior of a proton, if the appropriate potential energy $V(x, y, z)$ and mass (m_{proton}) are used. Wavefunctions associated with particles are frequently called **matter waves.**

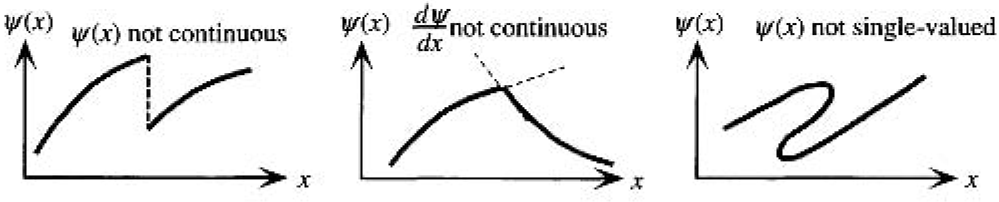


Figure 3.14 Unacceptable forms of $\psi(x)$.

EXAMPLE 3.5

THE FREE ELECTRON Solve the Schrödinger equation for a free electron whose energy is E. What is the uncertainty in the position of the electron and the uncertainty in the momentum of the electron?

SOLUTION

Since the electron is free, its potential energy is zero, $V = 0$. In the Schrödinger equation, this leads to

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

We can write this as

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

where we defined $k^2 = (2m/\hbar^2)E$. Solving the differential equation, we get

$$\psi(x) = A\exp(jkx) \qquad \text{or} \qquad B\exp(-jkx)$$

The total wavefunction is obtained by multiplying $\psi(x)$ by $\exp(-jEt/\hbar)$. We can define a fictitious frequency for the electron by $\omega = E/\hbar$ and multiply $\psi(x)$ by $\exp(-j\omega t)$:

$$\Psi(x, t) = A\exp j(kx - \omega t) \qquad \text{or} \qquad B\exp j(-kx - \omega t)$$

Each of these is a traveling wave. The first solution is a traveling wave in the $+x$ direction, and the second one is in the $-x$ direction. Thus, the free electron has a traveling wave solution with a wavenumber $k = 2\pi/\lambda$, that can have any value. The energy E of the electron is simply *KE*, so

$$KE = E = \frac{(\hbar k)^2}{2m}$$

When we compare this with the classical physics expression $KE = (p^2/2m)$, we see that the momentum is given by

$$p = \hbar k \qquad \text{or} \qquad p = \frac{h}{\lambda}$$

This is the de Broglie relationship. The latter therefore results naturally from the Schrödinger equation for a free electron.

The probability distribution for the electron is

$$|\psi(x)|^2 = |A\exp j(kx)|^2 = A^2$$

which is constant over the entire space. Thus, the electron can be anywhere between $x = -\infty$ and $x = +\infty$. The uncertainty Δx in its position is infinite. Since the electron has a well-defined wavenumber k, its momentum p is also well-defined by virtue of $p = \hbar k$. The uncertainty Δp in its momentum is thus zero.

EXAMPLE 3.6

WAVELENGTH OF AN ELECTRON BEAM Electrons are accelerated through a 100 V potential difference to strike a polycrystalline aluminum sample. The diffraction pattern obtained indicates that the highest intensity and smallest angle diffraction, corresponding to diffraction from the (111) planes, has a diffraction angle of 30.4°. From X-ray studies, the separation of the (111) planes is 0.234 nm. What is the wavelength of the electron and how does it compare with that from the de Broglie relationship?

SOLUTION

Since we know the angle of diffraction $2\theta (= 30.4^\circ)$ and the interplanar separation $d (= 0.234\text{ nm})$, we can readily calculate the wavelength of the electron from the Bragg condition for diffraction, $2d \sin\theta = n\lambda$. With $n = 1$,

$$\lambda = 2d \sin\theta = 2(0.234\text{ nm})\sin(15.2^\circ) = 0.1227\text{ nm}$$

This is the wavelength of the electron.

When an electron is accelerated through a voltage V, it gains KE equal to eV, so $p^2/2m = eV$ and $p = (2meV)^{1/2}$. This is the momentum imparted by the potential difference V. From the de Broglie relationship, the wavelength should be

$$\lambda = \frac{h}{p} = \frac{h}{(2meV)^{1/2}}$$

or

$$\lambda = \left(\frac{h^2}{2meV}\right)^{1/2}$$

Substituting for e, h, and m, we obtain

$$\lambda = \frac{1.226\text{ nm}}{V^{1/2}}$$

The experiment uses 100 V, so the de Broglie wavelength is

$$\lambda = \frac{1.226\text{ nm}}{V^{1/2}} = \frac{1.226\text{ nm}}{100^{1/2}} = 0.1226\text{ nm}$$

which is in excellent agreement with that determined from the Bragg condition.

3.3 INFINITE POTENTIAL WELL: A CONFINED ELECTRON

Consider the behavior of the electron when it is confined to a certain region, $0 < x < a$. Its PE is zero inside that region and infinite outside, as shown in Figure 3.15. The electron cannot escape, because it would need an infinite PE. Clearly the probability $|\psi|^2$ of finding the electron per unit volume is zero outside $0 < x < a$. Thus, $\psi = 0$ when $x \le 0$ and $x \ge a$, and ψ is determined by the Schrödinger equation in $0 < x < a$ with $V = 0$. Therefore, in the region $0 < x < a$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \qquad [3.17]$$

This is a second-order linear differential equation. As a general solution, we can take

$$\psi(x) = A\exp(jkx) + B\exp(-jkx)$$

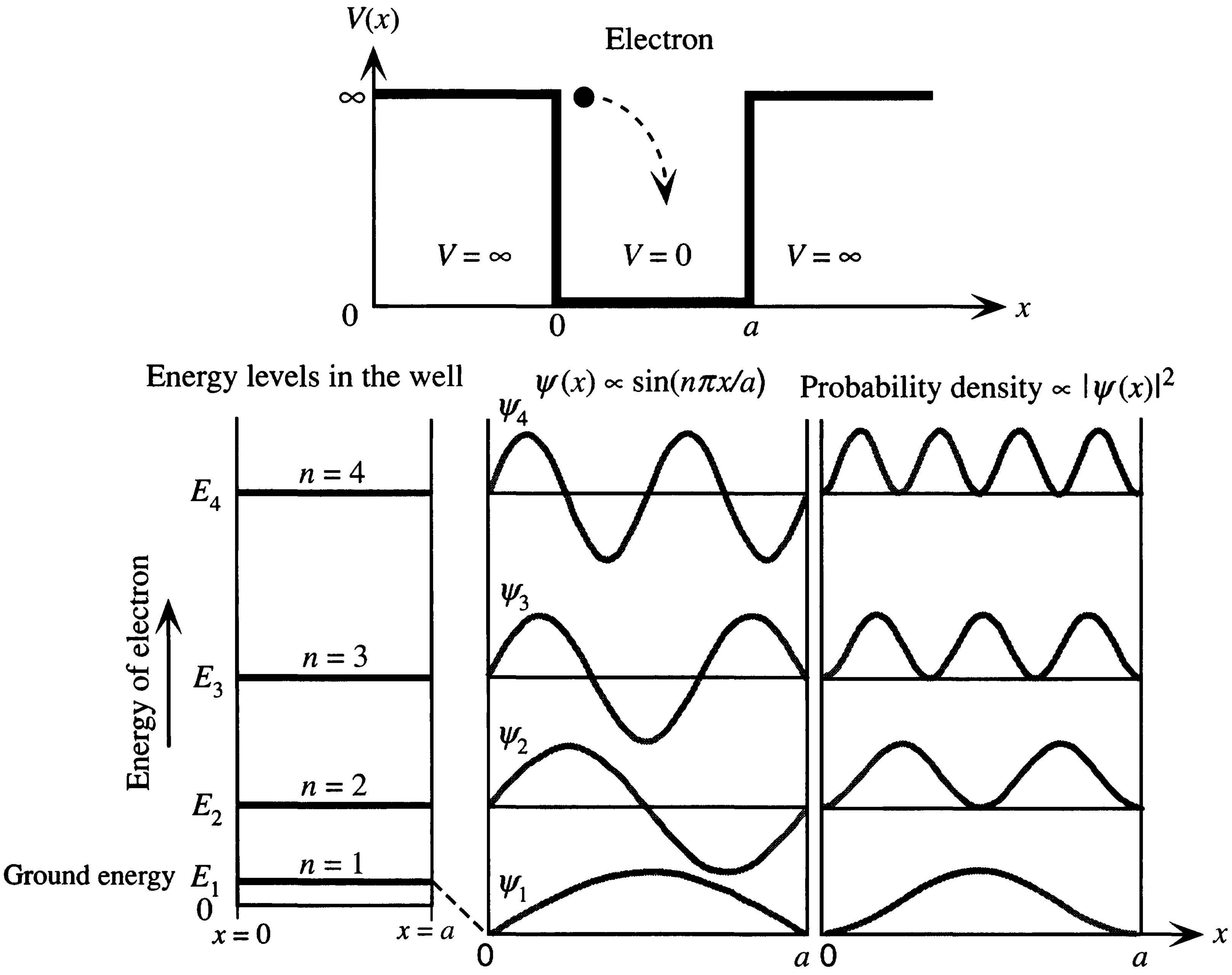


Figure 3.15 Electron in a one-dimensional infinite *PE* well.

The energy of the electron is quantized. Possible wavefunctions and the probability distributions for the electron are shown.

where k is some constant (to be determined) and substitute this in Equation 3.17 to find k. We first note that $\psi(0) = 0$; therefore, $B = -A$, so that

$$\psi(x) = A[\exp(jkx) - \exp(-jkx)] = 2Aj \sin kx \qquad [3.18]$$

We now substitute this into the Schrödinger Equation 3.17 to relate the energy E to k. Thus, Equation 3.17 becomes

$$-2Ajk^2(\sin kx) + \left(\frac{2m}{\hbar^2}\right)E(2Aj \sin kx) = 0$$

which can be rearranged to obtain the energy of the electron:

$$E = \frac{\hbar^2 k^2}{2m} \qquad [3.19]$$

Since the electron has no PE within the well, its total energy E is kinetic energy KE, and we can write

$$E = KE = \frac{p_x^2}{2m}$$

where p_x is its momentum. Comparing this with Equation 3.19, we see that the momentum of the electron must be

$$p_x = \pm\hbar k \tag{3.20}$$

The momentum p_x may be in the $+x$ direction or the $-x$ direction (which is the reason for ±), so the **average momentum** is actually zero, $p_{av} = 0$.

We have already seen this relationship, when we defined k as $2\pi/\lambda$ (wavenumber) for a free traveling wave. So the constant k here is a wavenumber-type quantity even though there is no distinct traveling wave. Its value is determined by the boundary condition at $x = a$ where $\psi = 0$, or

$$\psi(a) = 2Aj \sin ka = 0$$

The solution to $\sin ka = 0$ is simply $ka = n\pi$, where $n = 1, 2, 3, \ldots$ is an integer. We exclude $n = 0$ because it will result in $\psi = 0$ everywhere (no electron at all).

We notice immediately that k, and therefore the energy of the electron, can only have certain values; they are **quantized** by virtue of n being an integer. Here, n is called a **quantum number.** For each n, there is a special wavefunction

Wavefunction in infinite PE well

$$\psi_n(x) = 2Aj \sin\left(\frac{n\pi x}{a}\right) \tag{3.21}$$

which is called an eigenfunction.[3] All ψ_n for $n = 1, 2, 3 \ldots$ constitute the eigenfunctions of the system. Each eigenfunction identifies a possible state for the electron. For each n, there is one special k value, $k_n = n\pi/a$, and hence a special energy value E_n, since

$$E_n = \frac{\hbar^2 k_n^2}{2m}$$

that is,

Electron energy in infinite PE well

$$E_n = \frac{\hbar^2(\pi n)^2}{2ma^2} = \frac{h^2 n^2}{8ma^2} \tag{3.22}$$

The energies E_n defined by Equation 3.22 with $n = 1, 2, 3 \ldots$ are called **eigenenergies** of the system.

We still have not completely solved the problem, because A has yet to be determined. To find A, we use what is called the **normalization condition.** The total probability of finding the electron in the whole region $0 < x < a$ is unity, because we know the electron is somewhere in this region. Thus, $|\psi|^2\,dx$ summed between $x = 0$ and

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[3] From the German meaning "characteristic function."

$x = a$ must be unity, or

Normalization condition

$$\int_{x=0}^{x=a} |\psi(x)|^2\,dx = \int_{x=0}^{x=a} \left|2Aj\sin\left(\frac{n\pi x}{a}\right)\right|^2 dx = 1$$

Carrying out the simple integration, we find

$$A = \left(\frac{1}{2a}\right)^{1/2}$$

The resulting wavefunction for the electron is thus

$$\psi_n(x) = j\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{n\pi x}{a}\right) \qquad [3.23]$$

We can now summarize the behavior of an electron in a one-dimensional *PE* well. Its wavefunction and energy, shown in Figure 3.15, are given by Equations 3.23 and 3.22, respectively. Both depend on the quantum number n. The energy of the electron increases with n^2, so the minimum energy of the electron corresponds to $n = 1$. This is called the **ground state,** and the energy of the ground state is the lowest energy the electron can possess. Note also that the energy of the electron in this potential well cannot be zero, even though the *PE* is zero. Thus, the electron always has *KE*, even when it is in the ground state.

The **node** of a wavefunction is defined as the point where $\psi = 0$ inside the well. It is apparent from Figure 3.15 that the ground wavefunction ψ_1 with the lowest energy has no nodes, ψ_2 has one node, ψ_3 has two nodes, and so on. Thus, the energy increases as the number of nodes increases in a wavefunction.

It may seem surprising that the energy of the electron is quantized; that is, that it can only have finite values, given by Equation 3.22. The electron cannot be made to take on any value of energy, as in the classical case. If the electron behaved like a particle, then an applied force F could impart any value of energy to it, because $F = dp/dt$ (Newton's second law), or $p = \int F dt$. By applying a force F for a time t, we can give the electron a *KE* of

$$E = \frac{p^2}{2m} = \left(\frac{1}{2}m\right)\left[\int F\,dt\right]^2$$

However, Equation 3.22 tells us that, in the microscopic world, the energy can only have quantized values. The two conflicting views can be reconciled if we consider the energy difference between two consecutive energy levels, as follows:

Energy separation in infinite PE well

$$\Delta E = E_{n+1} - E_n = \frac{h^2(2n+1)}{8ma^2}$$

As a increases to macroscopic dimensions, $a \to \infty$, the electron is completely free and $\Delta E \to 0$. Since $\Delta E = 0$, the energy of a completely free electron ($a = \infty$) is continuous. The energy of a confined electron, however, is quantized, and ΔE depends on the dimension (or size) of the potential well confining the electron.

In general, an electron will be "contained" in a spatial region of three dimensions, within which the *PE* will be lower (hence the confinement). We must then solve the

Schrödinger equation in three dimensions. The result is three quantum numbers that characterize the behavior of the electron.

Examination of the wavefunctions ψ_n in Figure 3.15 shows that these are either *symmetric* or *antisymmetric* with respect to the center of the well at $x = \frac{1}{2}a$. The symmetry of a wavefunction is called its **parity.** Whenever the potential energy function $V(x)$ exhibits symmetry about a certain point C, for example, about $x = \frac{1}{2}a$ in Figure 3.15, then the wavefunctions have either **even parity** (such as $\psi_1, \psi_3, \ldots$ that are symmetric) or have **odd parity** (such as $\psi_2, \psi_4, \ldots$ that are antisymmetric).

EXAMPLE 3.7

ELECTRON CONFINED WITHIN ATOMIC DIMENSIONS Consider an electron in an infinite potential well of size 0.1 nm (typical size of an atom). What is the ground energy of the electron? What is the energy required to put the electron at the third energy level? How can this energy be provided?

SOLUTION

The electron is confined in an infinite potential well, so its energy is given by

$$E_n = \frac{h^2 n^2}{8ma^2}$$

We use $n = 1$ for the ground level and $a = 0.1$ nm. Therefore,

$$E_1 = \frac{(6.6 \times 10^{-34}\ \text{J s})^2(1)^2}{8(9.1 \times 10^{-31}\ \text{kg})(0.1 \times 10^{-9}\ \text{m})^2} = 6.025 \times 10^{-18}\ \text{J} \qquad \text{or} \qquad 37.6\ \text{eV}$$

The frequency of the electron associated with this energy is

$$\omega = \frac{E}{\hbar} = \frac{6.025 \times 10^{-18}\ \text{J}}{1.055 \times 10^{-34}\ \text{J s}} = 5.71 \times 10^{16}\ \text{rad s}^{-1} \qquad \text{or} \qquad \nu = 9.092 \times 10^{15}\ \text{s}^{-1}$$

The third energy level E_3 is

$$E_3 = E_1 n^2 = (37.6\ \text{eV})(3)^2 = 338.4\ \text{eV}$$

The energy required to take the electron from 37.6 eV to 338.4 eV is 300.8 eV. This can be provided by a photon of exactly that energy; no less, and no more. Since the photon energy is $E = h\nu = hc/\lambda$, or

$$\lambda = \frac{hc}{E} = \frac{(6.6 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{300.8\ \text{eV} \times 1.6 \times 10^{-19}\ \text{C}}$$

$$= 4.12\ \text{nm}$$

which is an X-ray photon.

EXAMPLE 3.8

ENERGY OF AN APPLE IN A CRATE Consider a macroscopic object of mass 100 grams (say, an apple) confined to move between two rigid walls separated by 1 m (say, a typical size of a large apple crate). What is the minimum speed of the object? What should the quantum number n be if the object is moving with a speed 1 m s^{-1}? What is the separation of the energy levels of the object moving with that speed?

SOLUTION

Since the object is within rigid walls, we take the *PE* outside the walls as infinite and use

$$E_n = \frac{h^2 n^2}{8ma^2}$$

to find the ground-level energy. With $n = 1, a = 1$ m, $m = 0.1$ kg, we have

$$E_1 = \frac{(6.6 \times 10^{-34}\text{ J s})^2(1)^2}{8(0.1\text{ kg})(1\text{ m})^2} = 5.45 \times 10^{-67}\text{ J} = 3.4 \times 10^{-48}\text{ eV}$$

Since this is kinetic energy, $\frac{1}{2}mv_1^2 = E_1$, so the minimum speed is

$$v_1 = \sqrt{\frac{2E_1}{m}} = \sqrt{\frac{2(5.45 \times 10^{-67}\text{ J})}{0.1\text{ kg}}} = 3.3 \times 10^{-33}\text{ m s}^{-1}$$

This speed cannot be measured by any instrument; therefore, for all practical purposes, the apple is at rest in the crate (a relief for the fruit grocer). The time required for the object to move a distance of 1 mm is 3×10^{29} s or 10^{21} years, which is more than the present age of the universe!

When the object is moving with a speed 1 m s^{-1},

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}(0.1\text{ kg})(1\text{ m s}^{-1})^2 = 0.05\text{ J}$$

This must be equal to $E_n = h^2n^2/8ma^2$ for some value of n

$$n = \left(\frac{8ma^2E_n}{h^2}\right)^{1/2} = \left[\frac{8(0.1\text{ kg})(1\text{ m})^2(0.05\text{ J})}{(6.6 \times 10^{-34}\text{ J s})^2}\right]^{1/2} = 3.03 \times 10^{32}$$

which is an enormous number. The separation between two energy levels corresponds to a change in n from 3.03×10^{32} to $3.03 \times 10^{32} + 1$. This is such a negligibly small change in n that for all practical purposes, the energy levels form a continuum. Thus,

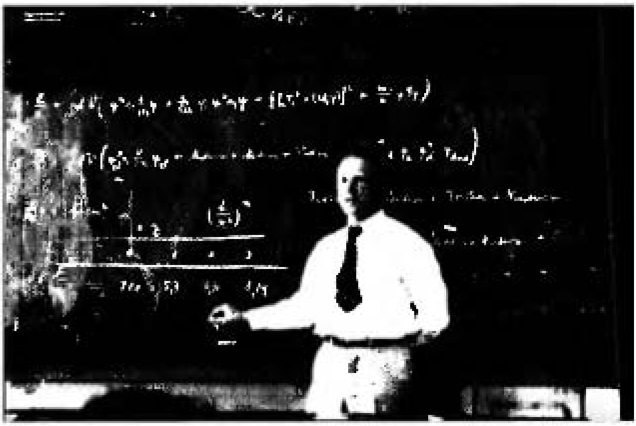
$$\begin{aligned}\Delta E = E_{n+1} - E_n &= \frac{h^2(2n+1)}{8ma^2} \\ &= \frac{[(6.6 \times 10^{-34}\text{ J s})^2(2 \times 3.03 \times 10^{32} + 1)]}{[8(0.1\text{ kg})(1\text{ m})^2]} \\ &= 3.30 \times 10^{-34}\text{ J} \quad\text{or}\quad 2.06 \times 10^{-15}\text{ eV}\end{aligned}$$

This energy separation is not detectable by any instrument. So for all practical purposes, the energy of the object changes continuously.

We see from this example that in the limit of large quantum numbers, quantum predictions agree with the classical results. This is the essence of **Bohr's correspondence principle.**

3.4 HEISENBERG'S UNCERTAINTY PRINCIPLE

The wavefunction of a free electron corresponds to a traveling wave with a single wavelength λ, as shown in Example 3.5. The traveling wave extends over all space, along all x, with the same amplitude, so the probability distribution function is uniform



Werner Heisenberg (1901–1976) received the Nobel prize in physics in 1932 for the uncertainty principle. This photo was apparently taken in 1936, while he was lecturing on quantum mechanics. "An expert is someone who knows some of the worst mistakes that can be made in his subject, and how to avoid them." W. Heisenberg.

SOURCE: AIP Emilio Segrè Visual Archives.

throughout the whole of space. The uncertainty Δx in the position of the electron is therefore infinite. Yet, the uncertainty Δp_x in the momentum of the electron is zero, because λ is well-defined, which means that we know p_x exactly from the de Broglie relationship, $p_x = h/\lambda$.

For an electron trapped in a one-dimensional infinite *PE* well, the wavefunction extends from $x = 0$ to $x = a$, so the uncertainty in the position of the electron is a. We know that the electron is within the well, but we cannot pinpoint with certainty exactly where it is. The momentum of the electron is either $p_x = \hbar k$ in the $+x$ direction or $-\hbar k$ in the $-x$ direction. The uncertainty Δp_x in the momentum is therefore $2\hbar k$; that is, $\Delta p_x = 2\hbar k$. For the ground-state wavefunction, which corresponds to $n = 1$, we have $ka = \pi$. Thus, $\Delta p_x = 2\hbar\pi/a$. Taking the product of the uncertainties in x and p, we get

$$(\Delta x)(\Delta p_x) = (a)\left(\frac{2\hbar\pi}{a}\right) = h$$

In other words, the product of the position and momentum uncertainties is simply h. This relationship is fundamental; and it constitutes a limit to our knowledge of the behavior of a system. *We cannot exactly and simultaneously know both the position and momentum of a particle along a given coordinate.* In general, if Δx and Δp_x are the respective uncertainties in the simultaneous measurement of the position and momentum of a particle along a particular coordinate (such as x), the **Heisenberg uncertainty principle** states that[4]

Heisenberg uncertainty principle for position and momentum

$$\Delta x \, \Delta p_x \gtrsim \hbar \qquad [3.24]$$

We are therefore forced to conclude that as previously stated, because of the wave nature of quantum mechanics, we are unable to determine exactly and simultaneously the position and momentum of a particle along a given coordinate. There will be an uncertainty Δx in the position and an uncertainty Δp_x in the momentum of the particle

---

[4] The Heisenberg uncertainty principle is normally written in terms of $\hbar$ rather than h. Further, in some physics texts, $\hbar$ in Equation 3.24 has a factor $\frac{1}{2}$ multiplying it.

and these uncertainties will be related by Heisenberg's uncertainty relationship in Equation 3.24.

These uncertainties are not in any way a consequence of the accuracy of a measurement or the precision of an instrument. Rather, they are the theoretical limits to what we can determine about a system. They are part of the quantum nature of the universe. In other words, even if we build the most perfectly engineered instrument to measure the position and momentum of a particle at one instant, we will still be faced with position and momentum uncertainties Δx and Δp_x such that $\Delta x \, \Delta p_x > \hbar$.

There is a similar uncertainty relationship between the uncertainty ΔE in the energy E (or angular frequency ω) of the particle and the time duration Δt during which it possesses the energy (or during which its energy is measured). We know that the kx part of the wave leads to the uncertainty relation $\Delta x \, \Delta p_x > \hbar$ or $\Delta x \, \Delta k \geq 1$. By analogy we should expect a similar relationship for the ωt part, or $\Delta\omega \, \Delta t \geq 1$. This hypothesis is true, and since $E = \hbar\omega$, we have the uncertainty relation for the particle energy and time:

Heisenberg uncertainty principle for energy and time

$$\Delta E \, \Delta t \gtrsim \hbar \tag{3.25}$$

Note that the uncertainty relationships in Equations 3.24 and 3.25 have been written in terms of $\hbar$, rather than h, as implied by the electron in an infinite potential energy well ($\Delta x \, \Delta p_x \geq h$). In general there is also a numerical factor of $\frac{1}{2}$ multiplying $\hbar$ in Equations 3.24 and 3.25 which comes about when we consider a Gaussian spread for all possible position and momentum values. The proof is not presented here, but can be found in advanced quantum mechanics books.

It is important to note that the uncertainty relationship applies only when the position and momentum are measured in the same direction (such as the x direction). On the other hand, the exact momentum, along, say, the y direction and the exact position, along, say, the x direction can be determined exactly, since $\Delta x \, \Delta p_y$ need not satisfy the Heisenberg uncertainty relationship (in other words, $\Delta x \, \Delta p_y$ can be zero).

EXAMPLE 3.9

THE MEASUREMENT TIME AND THE FREQUENCY OF WAVES: AN ANALOGY WITH $\Delta E \, \Delta t \geq \hbar$

Consider the measurement of the frequency of a sinusoidal wave of frequency 1000 Hz (or cycles/s). Suppose we can only measure the number of cycles to an accuracy of 1 cycle, because we need to receive a whole cycle to record it as one complete cycle. Then, in a time interval of $\Delta t = 1$ s, we will register 1000 ± 1 cycles. The uncertainty Δf in the frequency is 1 cycle/1 s or 1 Hz. If Δt is 2 s, we will measure 2000 ± 1 cycles, and the uncertainty Δf will be 1 cycle/2 s or $\frac{1}{2}$ cycle/s or $\frac{1}{2}$ Hz. Thus, Δf decreases with Δt.

Suppose that in a time interval Δt, we measure $N \pm 1$ cycles. Since the uncertainty is 1 cycle in a time interval Δt, the uncertainty in f will be

$$\Delta f = \frac{(1 \text{ cycle})}{\Delta t} = \frac{1}{\Delta t} \text{ Hz}$$

Since $\omega = 2\pi f$, we have

$$\Delta\omega \, \Delta t = 2\pi$$

In quantum mechanics, under steady-state conditions, an object has a time-oscillating wavefunction with a frequency ω which is related to its energy E by $\omega = E/\hbar$ (see Equation 3.15).

Substituting this into the previous relationship gives

$$\Delta E \, \Delta t = h$$

The uncertainty in the energy of a quantum object is therefore related, in a fundamental way, to the time duration during which the energy is observed. Notice that we again have h, as for $\Delta x \, \Delta p_x = h$, though the quantum mechanical uncertainty relationship in Equation 3.25 has $\hbar$.

EXAMPLE 3.10

THE UNCERTAINTY PRINCIPLE ON THE ATOMIC SCALE Consider an electron confined to a region of size 0.1 nm, which is the typical dimension of an atom. What will be the uncertainty in its momentum and hence its kinetic energy?

SOLUTION

We apply the Heisenberg uncertainty relationship, $\Delta x \, \Delta p_x \approx \hbar$, or

$$\Delta p_x \approx \frac{\hbar}{\Delta x} = \frac{1.055 \times 10^{-34}\,\text{J s}}{0.1 \times 10^{-9}\,\text{m}} = 1.055 \times 10^{-24}\ \text{kg m s}^{-1}$$

The uncertainty in the velocity is therefore

$$\Delta v = \frac{\Delta p_x}{m_e} = \frac{1.055 \times 10^{-24}\,\text{kg m s}^{-1}}{9.1 \times 10^{-31}\,\text{kg}} = 1.16 \times 10^{6}\,\text{m s}^{-1}$$

We can take this uncertainty to represent the order of magnitude of the actual speed. The kinetic energy associated with this momentum is

$$KE = \frac{\Delta p_x^2}{2m_e} = \frac{(1.055 \times 10^{-24}\,\text{kg m s}^{-1})^2}{2(9.1 \times 10^{-31}\,\text{kg})}$$

$$= 6.11 \times 10^{-19}\,\text{J} \qquad \text{or} \qquad 3.82\ \text{eV}$$

EXAMPLE 3.11

THE UNCERTAINTY PRINCIPLE WITH MACROSCOPIC OBJECTS Estimate the minimum velocity of an apple of mass 100 g confined to a crate of size 1 m.

SOLUTION

Taking the uncertainty in the position of the apple as 1 m, the apple is somewhere in the crate,

$$\Delta p_x \approx \frac{\hbar}{\Delta x} = \frac{1.05 \times 10^{-34}\,\text{J s}}{1\,\text{m}} = 1.05 \times 10^{-34}\,\text{kg m s}^{-1}$$

So the minimum uncertainty in the velocity is

$$\Delta v_x = \frac{\Delta p_x}{m} = \frac{1.05 \times 10^{-34}\,\text{kg m s}^{-1}}{0.1\,\text{kg}} = 1.05 \times 10^{-33}\,\text{m s}^{-1}$$

The quantum nature of the universe implies that the apple in the crate is moving with a velocity on the order of 10^{-33} m s^{-1}. This cannot be measured by any instrument; indeed, it would take the apple $\sim 10^{19}$ years to move an atomic distance of 0.1 nm.

3.5 TUNNELING PHENOMENON: QUANTUM LEAK

To understand the tunneling phenomenon, let us examine the thrilling events experienced by the roller coaster shown in Figure 3.16a. Consider what the roller coaster can do when released from rest at a height *A*. The conservation of energy means that the carriage can reach *B* and at most *C*, but certainly not beyond *C* and definitely not *D* and *E*. Classically, there is no possible way the carriage will reach *E* at the other side of the potential barrier *D*. An extra energy corresponding to the height difference, $D - A$, is needed. Anyone standing at *E* will be quite safe. Ignoring frictional losses, the roller coaster will go back and forth between *A* and *C*.

Now, consider an analogous event on an atomic scale. An electron moves with an energy *E* in a region $x < 0$ where the potential energy *PE* is zero; therefore, *E* is solely kinetic energy. The electron then encounters a potential barrier of "height" V_o, which

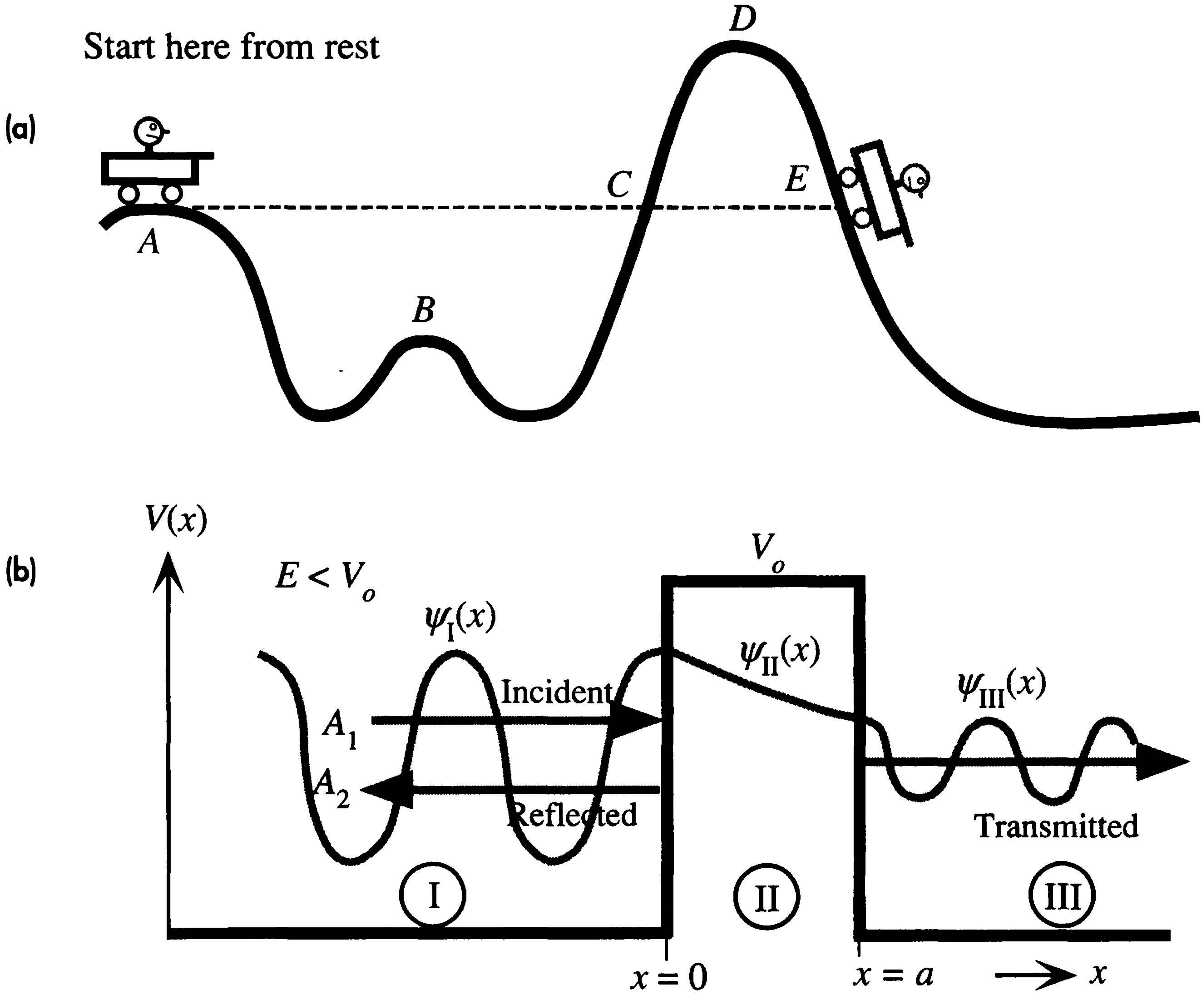


Figure 3.16

(a) The roller coaster released from *A* can at most make it to *C*, but not to *E*. Its *PE* at *A* is less than the *PE* at *D*. When the car is at the bottom, its energy is totally *KE*. *CD* is the energy barrier that prevents the car from making it to *E*. In quantum theory, on the other hand, there is a chance that the car could tunnel (leak) through the potential energy barrier between *C* and *E* and emerge on the other side of the hill at *E*.

(b) The wavefunction for the electron incident on a potential energy barrier (V_o). The incident and reflected waves interfere to give $\psi_I(x)$. There is no reflected wave in region III. In region II, the wavefunction decays with *x* because $E < V_o$.

is greater than E at $x = 0$. The extent (width) of the potential barrier is a. On the other side of the potential barrier, $x > a$, the *PE* is again zero. What will the electron do? Classically, just like the roller coaster, the electron should bounce back and thus be confined to the region $x < 0$, because its total energy E is less than V_o. In the quantum world, however, there is a distinct possibility that the electron will "tunnel" through the potential barrier and appear on the other side; it will leak through.

To show this, we need to solve the Schrödinger equation for the present choice of $V(x)$. Remember that the only way the Schrödinger equation will have the solution $\psi(x) = 0$ is if the *PE* is infinite, that is, $V = \infty$. Therefore, within any zero or finite *PE* region, there will always be a solution $\psi(x)$ and there always will be some probability of finding the electron.

We can divide the electron's space into three regions, I, II, and III, as indicated in Figure 3.16b. We can then solve the Schrödinger equation for each region, to obtain three wavefunctions $\psi_{\mathrm{I}}(x)$, $\psi_{\mathrm{II}}(x)$, and $\psi_{\mathrm{III}}(x)$. In regions I and III, $\psi(x)$ must be traveling waves, as there is no *PE* (the electron is free and moving with a kinetic energy E). In zone II, however, $E - V_o$ is negative, so the general solution of the Schrödinger equation is the sum of an exponentially decaying function and an exponentially increasing function. In other words,

$$\psi_{\mathrm{I}}(x) = A_1 \exp(jkx) + A_2 \exp(-jkx) \qquad [3.26a]$$

$$\psi_{\mathrm{II}}(x) = B_1 \exp(\alpha x) + B_2 \exp(-\alpha x) \qquad [3.26b]$$

$$\psi_{\mathrm{III}}(x) = C_1 \exp(jkx) + C_2 \exp(-jkx) \qquad [3.26c]$$

are the wavefunctions in which

$$k^2 = \frac{2mE}{\hbar^2} \qquad [3.27]$$

and

$$\alpha^2 = \frac{2m(V_o - E)}{\hbar^2} \qquad [3.28]$$

Both k^2 and α^2, and hence k and α, in Equations 3.26a to c are positive numbers. This means that $\exp(jkx)$ and $\exp(-jkx)$ represent traveling waves in opposite directions, and $\exp(-\alpha x)$ and $\exp(\alpha x)$ represent an exponential decay and rise, respectively. We see that in region I, $\psi_{\mathrm{I}}(x)$ consists of the incident wave $A_1 \exp(jkx)$ in the $+x$ direction, and a reflected wave $A_2 \exp(-jkx)$, in the $-x$ direction. Furthermore, because the electron is traveling toward the right in region III, there is no reflected wave, so $C_2 = 0$.

We must now apply the boundary conditions and the normalization condition to determine the various constants A_1, A_2, B_1, B_2, and C_1. In other words, we must match the three waveforms in Equations 3.26a to c at their boundaries ($x = 0$ and $x = a$) so that they form a continuous single-valued wavefunction. With the boundary conditions enforced onto the wavefunctions $\psi_{\mathrm{I}}(x)$, $\psi_{\mathrm{II}}(x)$, and $\psi_{\mathrm{III}}(x)$, all the constants can be determined in terms of the amplitude A_1 of the incoming wave. The relative probability that the electron will tunnel from region I through to III is defined as the **transmission**

coefficient *T*, and this depends very strongly on both the relative *PE* barrier height $(V_o - E)$ and the width a of the barrier. The final result that comes out from a tedious application of the boundary conditions is

Probability of tunneling

$$T = \frac{|\psi_{\mathrm{III}}(x)|^2}{|\psi_{\mathrm{I}}(\text{incident})|^2} = \frac{C_1^2}{A_1^2} = \frac{1}{1 + D\sinh^2(\alpha a)} \qquad [3.29]$$

where

$$D \doteq \frac{V_o^2}{4E(V_o - E)} \qquad [3.30]$$

and α is the rate of decay of $\psi_{\mathrm{II}}(x)$ as expressed in Equation 3.28. For a wide or high barrier, using $\alpha a \gg 1$ in Equation 3.29 and $\sinh(\alpha a) \approx \frac{1}{2}\exp(\alpha a)$, we can deduce

Probability of tunneling through

$$T = T_o \exp(-2\alpha a) \qquad [3.31]$$

where

$$T_o = \frac{16E(V_o - E)}{V_o^2} \qquad [3.32]$$

By contrast, the relative probability of reflection is determined by the ratio of the square of the amplitude of the reflected wave to that of the incident wave. This quantity is the **reflection coefficient *R*,** which is given by

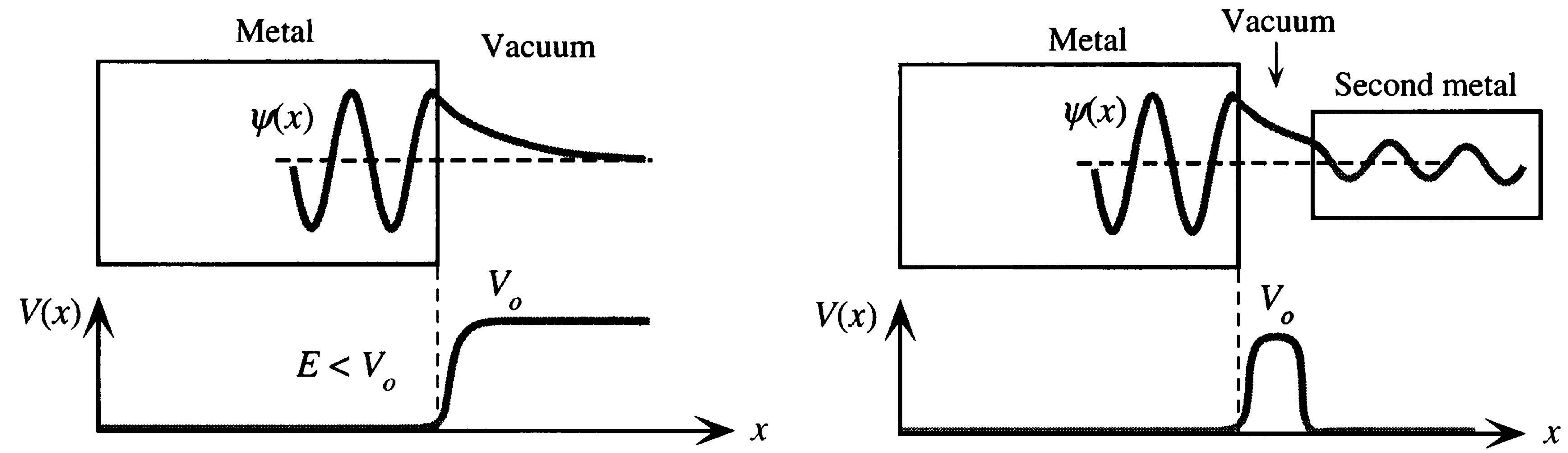
Reflection coefficient

$$R = \frac{A_2^2}{A_1^2} = 1 - T \qquad [3.33]$$

We can now summarize the entire tunneling affair as follows. When an electron encounters a potential energy barrier of height V_o greater than its energy E, there is a finite probability that it will leak through that barrier. This probability depends sensitively on the energy and width of the barrier. For a wide potential barrier, the probability of tunneling is proportional to $\exp(-2\alpha a)$, as in Equation 3.31. The wider or higher the potential barrier, the smaller the chance of the electron tunneling.

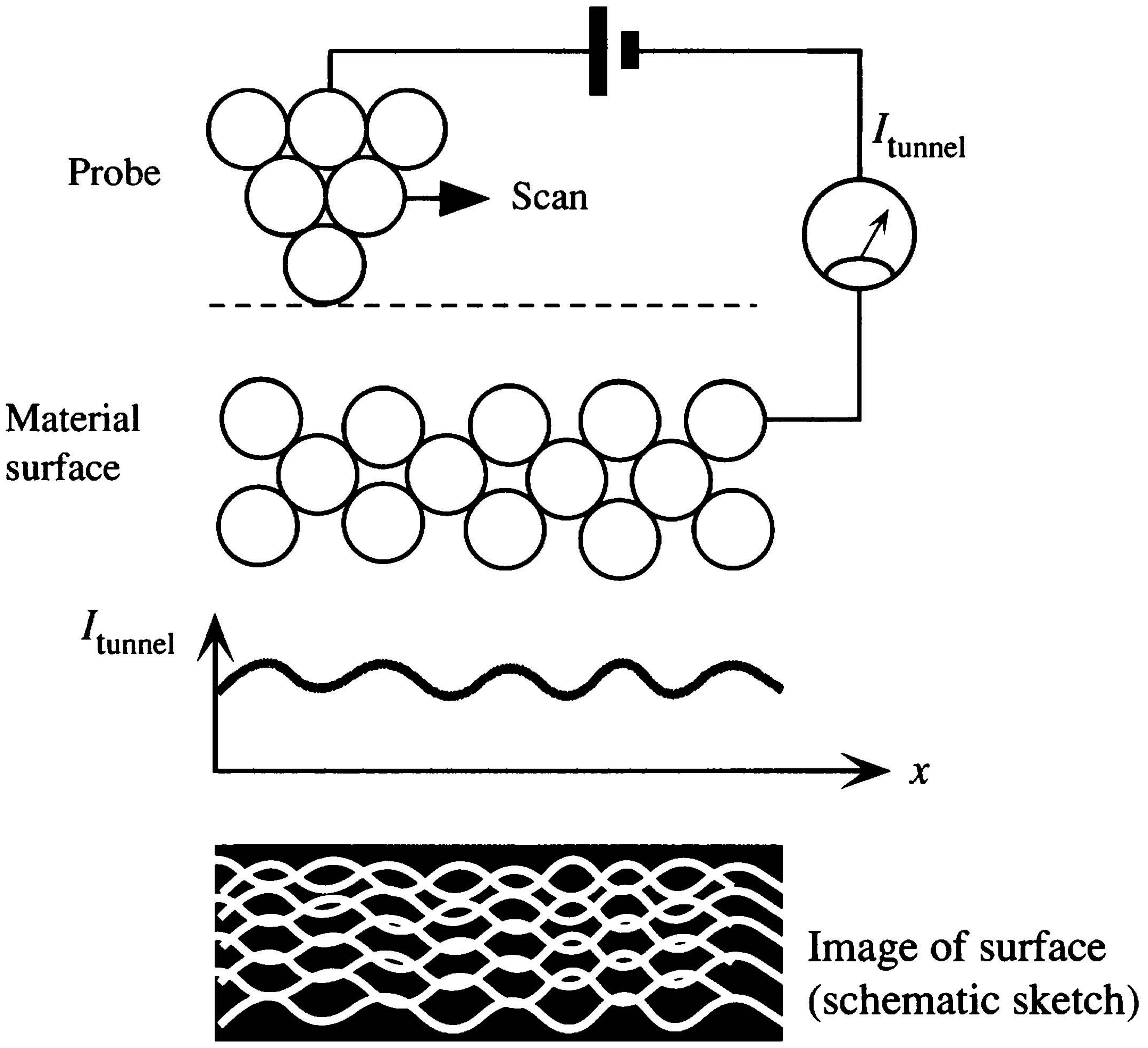
One of the most remarkable technological uses of the tunneling effect is in the scanning tunneling microscope (STM), which elegantly maps out the surfaces of solids. A conducting probe is brought so close to the surface of a solid that electrons can tunnel from the surface of the solid to the probe, as illustrated in Figure 3.17. When the probe is far removed, the wavefunction of an electron decays exponentially outside the material, by virtue of the potential energy barrier being finite (the work function is ~10 eV). When the probe is brought very close to the surface, the wavefunction penetrates into the probe and, as a result, the electron can tunnel from the material into the probe. Without an applied voltage, there will be as many electrons tunneling from the material to the probe as there are going in the opposite direction from the probe to the material, so the net current will be zero.

On the other hand, if a positive bias is applied to the probe with respect to the material, as shown in Figure 3.17, an electron tunneling from the material to the probe will see a lower potential barrier than one tunneling from the probe to the material. Consequently, there will be a net current from the probe to the material and this current



(a) The wavefunction decays exponentially as we move away from the surface because the *PE* outside the metal is V_o and the energy of the electron, $E < V_o$.

(b) If we bring a second metal close to the first metal, then the wavefunction can penetrate into the second metal. The electron can tunnel from the first metal to the second.



(c) The principle of the scanning tunneling microscope. The tunneling current depends on $\exp(-2\alpha a)$ where a is the distance of the probe from the surface of the specimen and α is a constant.

Figure 3.17

will depend very sensitively on the separation a of the probe from the surface, by virtue of Equation 3.31.

Because the tunneling current is extremely sensitive to the width of the potential barrier, the tunneling current is essentially dominated by electrons tunneling to the probe atom nearest to the surface. Thus, the probe tip has an atomic dimension. By scanning the surface of the material with the probe and recording the tunneling current

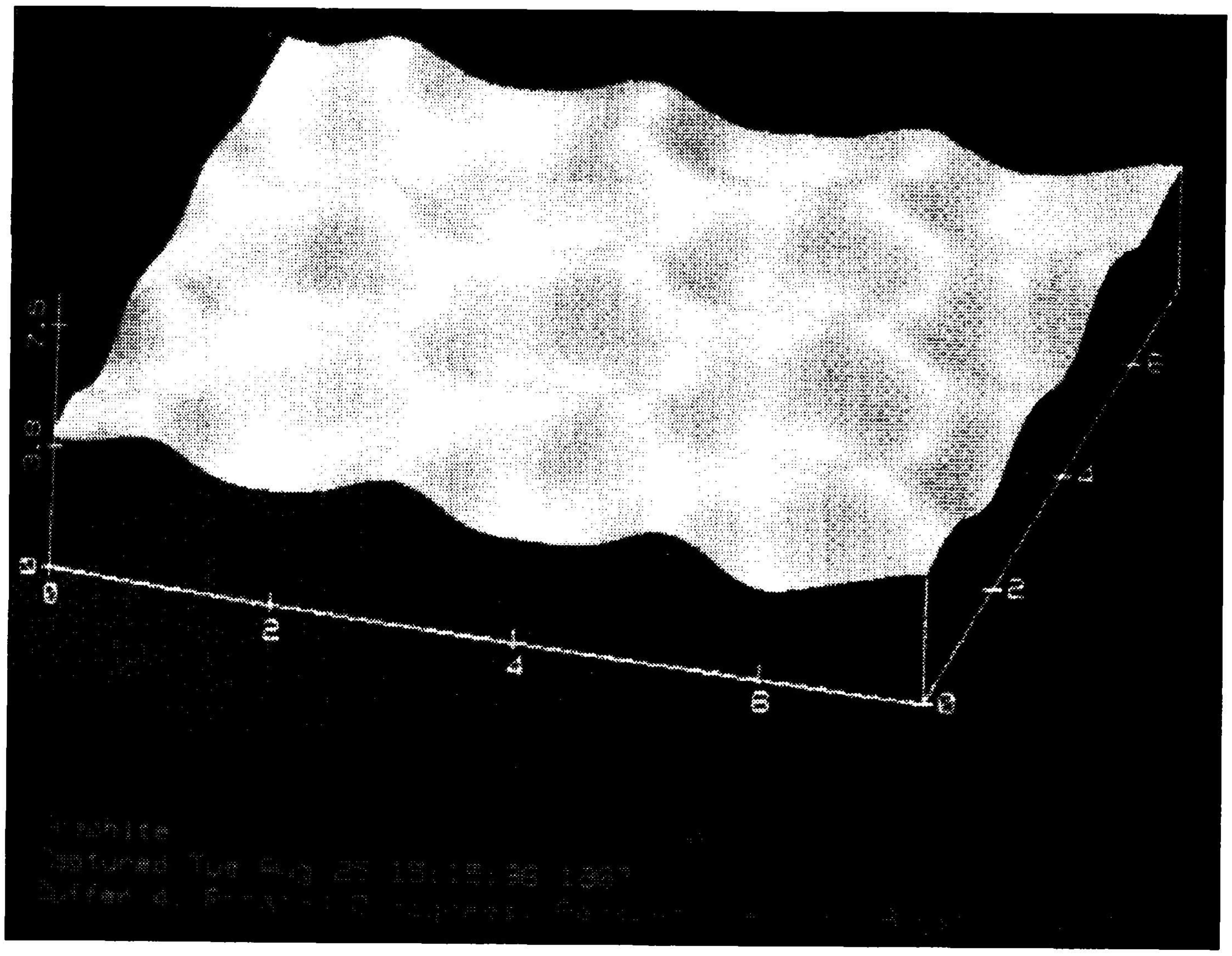


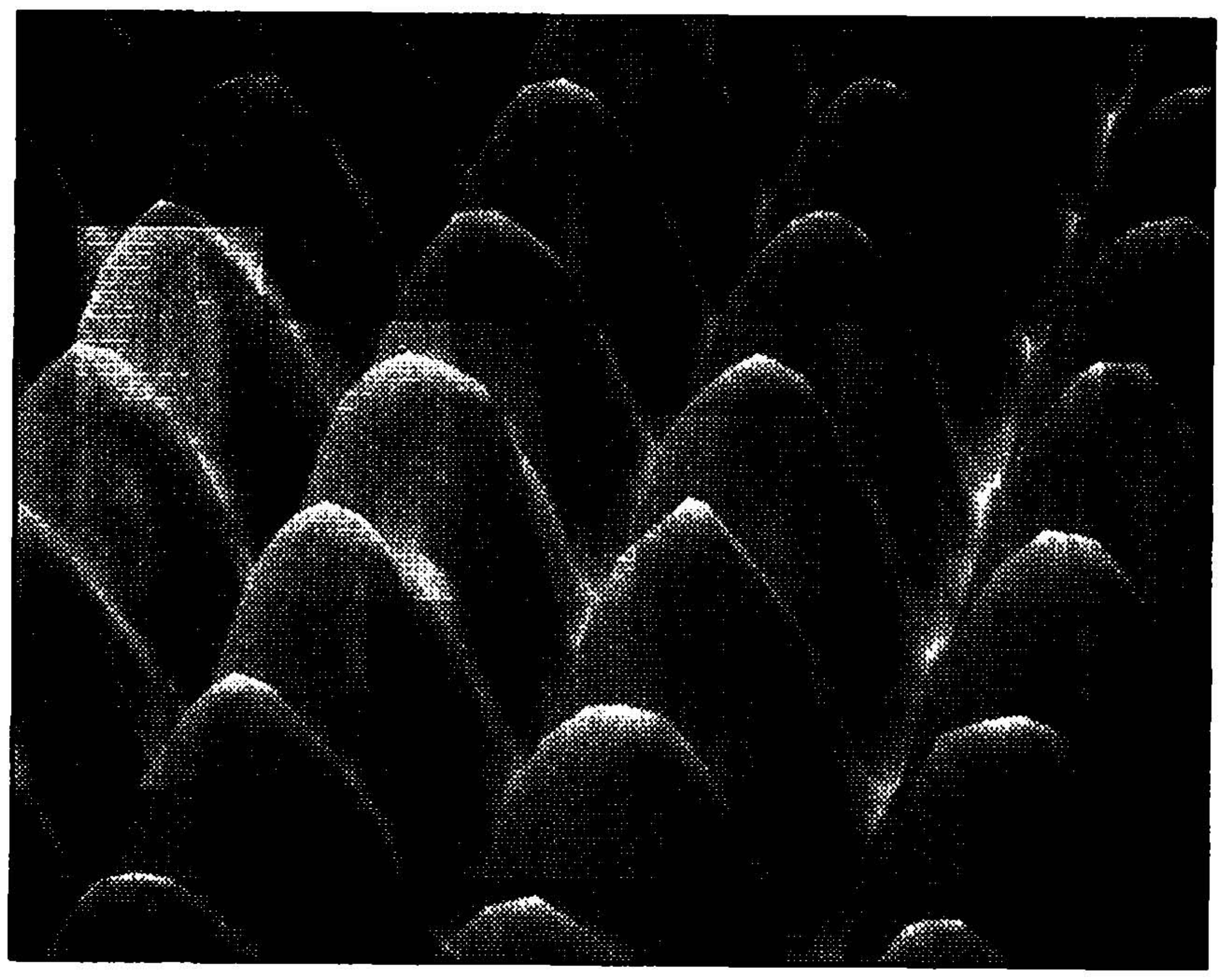
Figure 3.18 Scanning tunneling microscope (STM) image of a graphite surface where contours represent electron concentrations within the surface, and carbon rings are clearly visible. The scale is in 2 Å.

SOURCE: Courtesy of Veeco Instruments, Metrology Division, Santa Barbara, CA.

the user can map out the surface topology of the material with a resolution comparable to the atomic dimension. The probe motion along the surface, and also perpendicular to the surface, is controlled by piezoelectric transducers to provide sufficiently small and smooth displacements. Figure 3.18 shows an STM image of a graphite surface, on which the hexagonal carbon rings can be clearly seen. Notice that the scale is 0.2 nm (2 Å). The contours in the image actually represent electron concentrations within the surface since it is the electrons that tunnel from the graphite surface to the probe tip. The astute reader will notice that not all the carbon atoms in a hexagonal ring are at the same height; three are higher and three are lower. The reason is that the exact electron concentration on the surface is also influenced by the second layer of atoms underneath the top layer. The overall effect makes the electron concentration

STM's inventors Gerd Binning (right) and Heinrich Rohrer (left), at IBM Zurich Research Laboratory with one of their early devices. They won the 1986 Nobel prize for the STM.

SOURCE: Courtesy of IBM Zurich Research Laboratory.



An STM image of a Ni (110) surface.

SOURCE: Courtesy of IBM.

change (alternate) from one atomic site to a neighboring site within the hexagonal rings. STM was invented by Gerd Binning and Heinrich Rohrer at the IBM Research Laboratory in Zurich, for which they were awarded the 1986 Nobel prize.[5]

EXAMPLE 3.12 **TUNNELING CONDUCTION THROUGH METAL-TO-METAL CONTACTS** Consider two copper wires separated only by their surface oxide layer (CuO). Classically, since the oxide layer is an insulator, no current should be possible through the two copper wires. Suppose that for the conduction ("free") electrons in copper, the surface oxide layer looks like a square potential energy barrier of height 10 eV. Consider an oxide layer thickness of 5 nm and evaluate the transmission coefficient for conduction electrons in copper, which have a kinetic energy of about 7 eV. What will be the transmission coefficient if the oxide barrier is 1 nm?

SOLUTION

We can calculate α from

$$\begin{aligned}\alpha &= \left[\frac{2m(V_o - E)}{\hbar^2}\right]^{1/2}\\ &= \left[\frac{2(9.1\times10^{-31}\,\text{kg})(10\,\text{eV} - 7\,\text{eV})(1.6\times10^{-19}\,\text{J/eV})}{(1.05\times10^{-34}\,\text{J s})^2}\right]^{1/2}\\ &= 8.9\times10^{9}\,\text{m}^{-1}\end{aligned}$$

so that

$$\alpha a = (8.9\times10^{9}\,\text{m}^{-1})(5\times10^{-9}\,\text{m}) = 44.50$$

Since this is greater than unity, we use the wide-barrier transmission coefficient in Equation 3.31.

Now,

$$T_o = \frac{16E(V_o - E)}{V_o^2} = \frac{16(7\,\text{eV})(10\,\text{eV} - 7\,\text{eV})}{(10\,\text{eV})^2} = 3.36$$

Thus,

$$\begin{aligned}T &= T_o\exp(-2\alpha a)\\ &= 3.36\exp[-2(8.9\times10^{9}\,\text{m}^{-1})(5\times10^{-9}\,\text{m})] = 3.36\exp(-89)\\ &\approx 7.4\times10^{-39}\end{aligned}$$

an incredibly small number.

With $a = 1$ nm,

$$\begin{aligned}T &= 3.36\exp[-2(8.9\times10^{9}\,\text{m}^{-1})(1\times10^{-9}\,\text{m})]\\ &= 3.36\exp(-17.8) \approx 6.2\times10^{-8}\end{aligned}$$

Notice that reducing the layer thickness by five times increases the transmission probability by 10^{31}! Small changes in the barrier width lead to enormous changes in the transmission

---

[5] The IBM Research Laboratory in Zurich, Switzerland, received both the 1986 and the 1987 Nobel prizes. The first was for the scanning tunneling microscope by Gerd Binning and Heinrich Rohrer. The second was awarded to Georg Bednorz and Alex Müller for the discovery of high-temperature superconductors which we will examine in Chapter 8.

probability. We should note that when a voltage is applied across the two wires, the potential energy height is altered (PE = charge × voltage), which results in a large increase in the transmission probability and hence results in a current.

EXAMPLE 3.13

SIGNIFICANCE OF A SMALL $\hbar$ Estimate the probability that a roller coaster carriage that weighs 100 kg released from point A in Figure 3.16a from a height at 10 m can reach point E over a hump that is 15 m high and 10 m wide. What will this probability be in a universe where $\hbar \approx 10$ kJ s?

SOLUTION

The total energy of the carriage at height A is

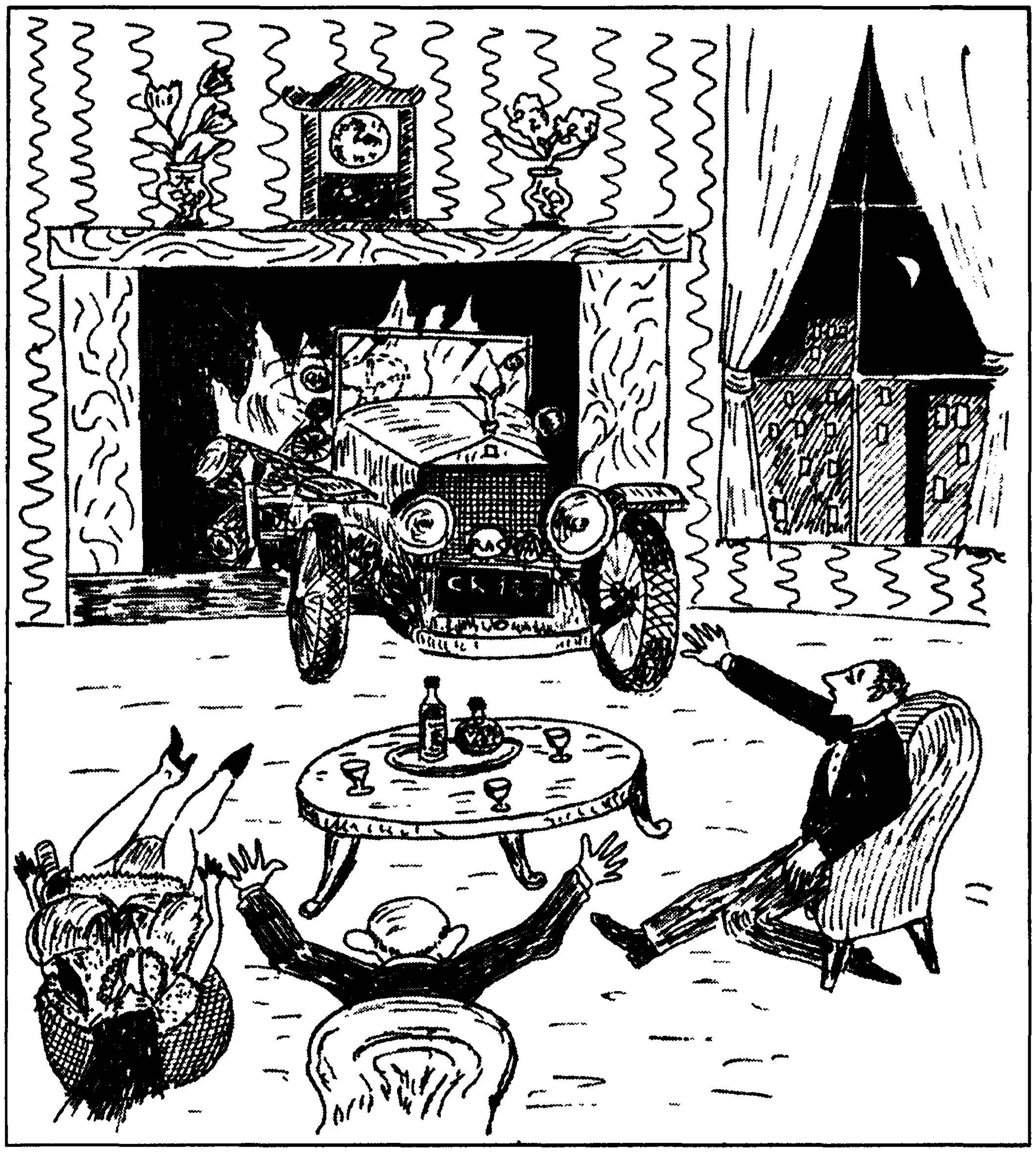
$$E = PE = mg(\text{height}) = (100\,\text{kg})(10\,\text{m s}^{-2})(10\,\text{m}) = 10^4\,\text{J}$$

Suppose that as a first approximation, we can approximate the hump as a square hill of height 15 m and width 10 m. The PE required to reach the peak would be

$$V_o = mg(\text{height}) = (100\,\text{kg})(10\,\text{m s}^{-2})(15\,\text{m}) = 1.5 \times 10^4\,\text{J}$$

Applying this, we have

$$\alpha^2 = \frac{2m(V_o - E)}{\hbar^2} = \frac{2(100\,\text{kg})(1.5 \times 10^4\,\text{J} - 10^4\,\text{J})}{(1.05 \times 10^{-34}\,\text{J s})^2} = 9.07 \times 10^{73}\,\text{m}^{-2}$$



"Just like the good old ghost of the middle ages." In a world where $\hbar$ is of the order of unity, one can expect tunneling surprises.

SOURCE: George Gamow, *Mr. Tompkins in Paperback*, Cambridge, England, University Press, 1965, p. 96. Used with permission.

and so

$$\alpha = 9.52 \times 10^{36}\ \text{m}^{-1}$$

With $a = 10$ m, we have $\alpha a \gg 1$, so we can use the wide-barrier tunneling equation,

$$T = T_o \exp(-2\alpha a)$$

where

$$T_o = \frac{16[E(V_o - E)]}{V_o^2} = 3.56$$

Thus,

$$T = 3.56 \exp[-2(9.52 \times 10^{36}\ \text{m}^{-1})(10\ \text{m})] = 3.56 \exp(-1.9 \times 10^{38})$$

which is a fantastically small number, indicating that it is impossible for the carriage to tunnel through the hump.

Suppose that $\hbar \approx 10$ kJ s. Then

$$\alpha^2 = \frac{2m(V_o - E)}{\hbar^2} = \frac{2(100\ \text{kg})(1.5 \times 10^4\ \text{J} - 10^4\ \text{J})}{(10^4\ \text{J s})^2} = 0.01\ \text{m}^{-2}$$

so that $\alpha = 0.1\ \text{m}^{-1}$. Clearly, $\alpha a = 1$, so we must use

$$T = [1 + D \sinh^2(\alpha a)]^{-1}$$

where

$$D = \frac{V_o^2}{[4E(V_o - E)]} = 1.125$$

Thus,

$$T = [1 + 1.125 \sinh^2(1)]^{-1} = 0.39$$

Thus, after three goes, the carriage would tunnel to the other side (giving the person standing at E the shock of his life).

3.6 POTENTIAL BOX: THREE QUANTUM NUMBERS

To examine the properties of a particle confined to a region of space, we take a three-dimensional space with a volume marked by a, b, c along the x, y, z axes. The *PE* is zero ($V = 0$) inside the space and is infinite on the outside, as illustrated in Figure 3.19. This is a three-dimensional potential energy well. The electron essentially lives in the "box." What will the behavior of the electron be in this box? In this case we need to solve the three-dimensional version of the Schrödinger equation,[6] which is

Schrödinger equation in three dimensions

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad [3.34]$$

---

[6] The term $\partial\psi/\partial x$ simply means differentiating $\psi(x, y, z)$ with respect to x while keeping y and z constant, just like $d\psi/dx$ in one dimension.

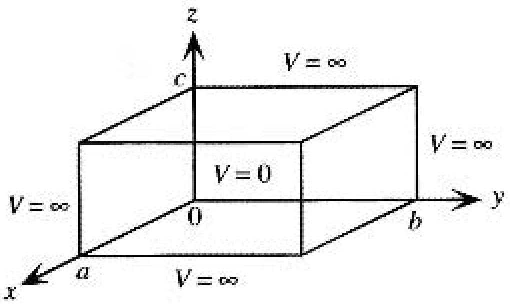


Figure 3.19 Electron confined in three dimensions by a three-dimensional infinite *PE* box.
Everywhere inside the box, $V = 0$, but outside, $V = \infty$. The electron cannot escape from the box.

with $V = 0$ in $0 < x < a, 0 < y < b$, and $0 < z < c$, and V infinite outside. We can try to solve this by separating the variables via $\psi(x, y, z) = \psi_x(x)\,\psi_y(y)\,\psi_z(z)$. Substituting this back into Equation 3.34, we can obtain three ordinary differential equations, each just like the one for the one-dimensional potential well. Having found $\psi_x(x)$, $\psi_y(y)$, and $\psi_z(z)$ we know that the total wavefunction is simply the product,

$$\psi(x, y, z) = A\sin(k_x x)\sin(k_y y)\sin(k_z z) \tag{3.35}$$

where k_x, k_y, k_z, and A are constants to be determined. We can then apply the boundary conditions at $x = a$, $y = b$, and $z = c$ to determine the constants k_x, k_y, and k_z in the same way we found k for the one-dimensional potential well. If $\psi(x, y, z) = 0$ at $x = a$, then k_x will be quantized via

$$k_x a = n_1 \pi$$

where n_1 is a quantum number, $n_1 = 1, 2, 3, \ldots$. Similarly, if $\psi(x, y, z) = 0$ at $y = b$ and $z = c$, then k_y and k_z will be quantized, so that, overall, we will have

$$k_x = \frac{n_1\pi}{a} \qquad k_y = \frac{n_2\pi}{b} \qquad k_z = \frac{n_3\pi}{c} \tag{3.36}$$

where n_1, n_2, and n_3 are quantum numbers, each of which can be any integer except zero.

We notice immediately that in three dimensions, we have three quantum numbers n_1, n_2, and n_3 associated with $\psi_x(x)$, $\psi_y(y)$, and $\psi_z(z)$. The eigenfunctions of the electron, denoted by the quantum numbers n_1, n_2, and n_3, are now given by

Electron wavefunction in infinite PE well

$$\psi_{n_1 n_2 n_3}(x, y, z) = A\sin\left(\frac{n_1\pi x}{a}\right)\sin\left(\frac{n_2\pi y}{b}\right)\sin\left(\frac{n_3\pi z}{c}\right) \tag{3.37}$$

Notice that these consist of the products of infinite one-dimensional *PE* well-type wavefunctions, one for each dimension, and each has its own quantum number n. Each possible eigenfunction can be labeled a **state** for the electron. Thus, ψ_{111} and ψ_{121} are two possible states.

To find the constant A in Equation 3.37, we need to use the normalization condition that $|\psi_{n_1 n_2 n_3}(x, y, z)|^2$ integrated over the volume of the box must be unity, since the electron is somewhere in the box. The result for a square box is $A = (2/a)^{3/2}$.

We can find the energy of the electron by substituting the wavefunction in Equation 3.35 into the Schrödinger Equation 3.34. The energy as a function of k_x, k_y, k_z is then found to be

$$E = E(k_x, k_y, k_z) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

which is quantized by virtue of k_x, k_y, and k_z being quantized. We can write this energy in terms of n_1^2, n_2^2, and n_3^2 by using Equation 3.36, as follows:

$$E_{n_1n_2n_3} = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

For a square box for which $a = b = c$, the energy is

Electron energy in infinite PE box

$$E_{n_1n_2n_3} = \frac{h^2\left(n_1^2 + n_2^2 + n_3^2\right)}{8ma^2} = \frac{h^2N^2}{8ma^2} \qquad [3.38]$$

where $N^2 = (n_1^2 + n_2^2 + n_3^2)$, which can only have certain integer values. It is apparent that the energy now depends on three quantum numbers. Our conclusion is that in three dimensions, we have three quantum numbers, each one arising from boundary conditions along one of the coordinates. They quantize the energy of the electron via Equation 3.38 and its momentum in a particular direction, such as, $p_x = \pm\hbar k_x = \pm(hn_1/2a)$, though the average momentum is zero.

The lowest energy for the electron is obviously equal to E_{111}, not zero. The next energy level corresponds to E_{211}, which is the same as E_{121} and E_{112}, so there are three states (*i.e.*, ψ_{211}, ψ_{121}, ψ_{112}) for this energy. The number of states that have the same energy is termed the **degeneracy** of that energy level. The second energy level E_{211} is thus **three-fold degenerate.**

EXAMPLE 3.14 **NUMBER OF STATES WITH THE SAME ENERGY** How many states (eigenfunctions) are there at energy level E_{443} for a square potential energy box?

SOLUTION

This energy level corresponds to $n_1 = 4$, $n_2 = 4$, and $n_3 = 3$, but the energy depends on

$$N^2 = n_1^2 + n_2^2 + n_3^2 = 4^2 + 4^2 + 3^2 = 41$$

via Equation 3.38. As long as $N^2 = 41$ for any choice of (n_1, n_2, n_3), not just (4, 4, 3), the energy will be the same.

The value $N^2 = 41$ can be obtained from (4, 4, 3), (4, 3, 4), and (3, 4, 4) as well as (6, 2, 1), (6, 1, 2), (2, 6, 1), (2, 1, 6), (1, 6, 2), and (1, 2, 6). There are thus three states from (4, 4, 3) combinations and six from (6, 2, 1) combinations, giving nine possible states, each with a distinct wavefunction, $\psi_{n_1n_2n_3}$. However, all these $\psi_{n_1n_2n_3}$ for the electron have the same energy E_{443}.

3.7 HYDROGENIC ATOM

3.7.1 ELECTRON WAVEFUNCTIONS

Consider the behavior of the electron in a hydrogenic (hydrogen-like) atom, which has a nuclear charge of $+Ze$, as depicted in Figure 3.20. For the hydrogen atom, $Z = 1$, whereas for an ionized helium atom He^+, $Z = 2$. For a doubly ionized lithium atom Li^{++}, $Z = 3$, and so on. The electron is attracted by a positive nuclear charge and therefore has a Coulombic *PE*,

$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_o r} \qquad [3.39]$$

Electron PE in hydrogenic atom

Since force $F = -dV/dr$, Equation 3.39 is simply a statement of Coulomb's force between the positive charge $+Ze$ of the nucleus and the negative charge $-e$ of the electron. The task of finding $\psi(x, y, z)$ and the energy E of the electron now involves putting $V(r)$ from Equation 3.39 into the Schrödinger equation with $r = \sqrt{x^2 + y^2 + z^2}$ and solving it.

Fortunately, the problem has a spherical symmetry, and we can solve the Schrödinger equation by transforming it into the r, θ, ϕ coordinates shown in Figure 3.20. Even then, obtaining a solution is not easy. We must then ensure that the solution for $\psi(r, \theta, \phi)$ satisfies all the boundary conditions, as well as being single-valued and continuous with a continuous derivative. For example, when we go 2π around the ϕ coordinate, $\psi(r, \theta, \phi)$ should come back to its original value, or $\psi(r, \theta, \phi) = \psi(r, \theta, \phi + 2\pi)$, as is apparent from an examination of Figure 3.20. Along the radial

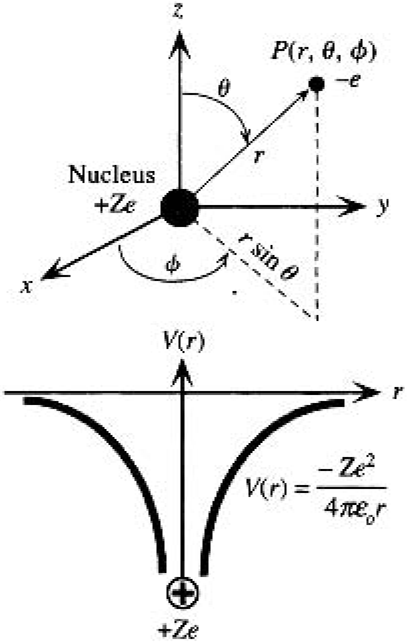


Figure 3.20 The electron in the hydrogenic atom is attracted by a central force that is always directed toward the positive nucleus.

Spherical coordinates centered at the nucleus are used to describe the position of the electron. The *PE* of the electron depends only on *r*.

coordinate, we need $\psi(r, \theta, \phi) \to 0$ as $r \to \infty$; otherwise, the total probability will diverge when $|\psi(r, \theta, \phi)|^2$ is integrated over all space. In an analogy with the three-dimensional potential well, there should be three quantum numbers to characterize the wavefunction, energy, and momentum of the electron. The three quantum numbers are called the **principal, orbital angular momentum,** and **magnetic quantum numbers** and are respectively denoted by n, ℓ, and m_ℓ. Unlike the three-dimensional potential well, however, not all the quantum numbers run as independent positive integers.

The solution to the Schrödinger equation $\psi(r, \theta, \phi)$ depends on three variables, r, θ, ϕ. The wavefunction $\psi(r, \theta, \phi)$ can be written as the product of two functions

$$\psi(r, \theta, \phi) = R(r)\, Y(\theta, \phi)$$

where $R(r)$ is a radial function depending only on r, and $Y(\theta, \phi)$ is called the **spherical harmonic,** which expresses the angular dependence of the wavefunction. These functions are characterized by the quantum numbers n, ℓ, m_ℓ. The radial part $R(r)$ depends on n and ℓ, whereas the spherical harmonic depends on ℓ and m_ℓ, so

$$\psi(r, \theta, \phi) = \psi_{n,\ell,m_\ell}(r, \theta, \phi) = R_{n,\ell}(r)\, Y_{\ell,m_\ell}(\theta, \phi) \qquad [3.40]$$

By solving the Schrödinger equation, these functions have already been evaluated. It turns out that we can only assign certain values to the quantum numbers n, ℓ, and m_ℓ to obtain acceptable solutions, that is, $\psi_{n,\ell,m_\ell}(r, \theta, \phi)$ that are well behaved: single-valued and with ψ and the gradient of ψ continuous. We can summarize the allowed values of n, ℓ, m_ℓ as follows:

Principal quantum number	$n = 1, 2, 3, \ldots$
Orbital angular momentum quantum number	$\ell = 0, 1, 2, \ldots, (n-1) < n$
Magnetic quantum number	$m_\ell = -\ell, -(\ell-1), \ldots, 0, \ldots, (\ell-1), \ell$ or $\lvert m_\ell \rvert \le \ell$

The ℓ values carry a special notation inherited from spectroscopic terms. The first four ℓ values are designated by the first letters of the terms *sharp, principal, diffuse,* and *fundamental,* whereas the higher ℓ values follow from *f* onwards, as *g*, *h*, *i*, etc. For example, any state ψ_{n,ℓ,m_ℓ} that has $\ell = 0$ is called an *s* state, whereas that which has $\ell = 1$ is termed a *p* state. We can also use n as a prefix to ℓ to identify n. Thus ψ_{n,ℓ,m_ℓ} with $n = 2$ and $\ell = 0$ corresponds to the 2*s* state. The notation for identifying the ℓ value and labeling a state is summarized in Table 3.1.

Table 3.1 Labeling of various $n\ell$ possibilities

	ℓ				
n	0	1	2	3	4
1	1*s*				
2	2*s*	2*p*			
3	3*s*	3*p*	3*d*		
4	4*s*	4*p*	4*d*	4*f*	
5	5*s*	5*p*	5*d*	5*f*	5*g*

Table 3.2 The radial and spherical harmonic parts of the wavefunction in the hydrogen atom ($a_o = 0.0529$ nm)

n	ℓ	$R(r)$	m_ℓ	$Y(\theta, \phi)$		
1	0	$\left(\frac{1}{a_o}\right)^{3/2} 2\exp\left(-\frac{r}{a_o}\right)$	0	$\frac{1}{2\sqrt{\pi}}$		
2	0	$\left(\frac{1}{2a_o}\right)^{3/2} \left(2-\frac{r}{a_o}\right) \exp\left(-\frac{r}{2a_o}\right)$	0	$\frac{1}{2\sqrt{\pi}}$		
2	1	$\left(\frac{1}{2a_o}\right)^{3/2} \left(\frac{r}{\sqrt{3}a_o}\right) \exp\left(-\frac{r}{2a_o}\right)$	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$		
			1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{j\phi}$	$\propto \sin\theta\cos\phi$	Correspond to $m_\ell = -1$ and $+1$.
			-1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-j\phi}$	$\propto \sin\theta\sin\phi$	

Table 3.2 summarizes the functional forms of $R_{n,\ell}(r)$ and $Y_{\ell,m_\ell}(\theta, \phi)$. For $\ell = 0$ (the s states), the angular dependence of $Y_{0,0}(\theta, \phi)$ is constant, which means that $\psi(r, \theta, \phi)$ is spherically symmetrical about the nucleus. For the $\ell = 1$ and higher states, there is a strong directionality to the wavefunctions with respect to each other. The radial part $R_{n,\ell}(r)$ is sketched in Figure 3.21a for two choices of n and ℓ. Notice that $R_{n,\ell}(r)$ is largest at $r = 0$, when $\ell = 0$. However, this does not mean that the electron will be mainly at $r = 0$, because the probability of finding the electron at a distance r actually depends on $r^2|R_{n,\ell}(r)|^2$, which vanishes as $r \rightarrow 0$.

Let us examine the probability of finding the electron at a distance r within a thin spherical shell of radius r and thickness δr (assumed to be very small). The directional dependence of the probability will be determined by the function $Y_{\ell,m_\ell}(\theta, \phi)$. We can average this over all directions (all angles θ and ϕ) to obtain $\overline{Y_{\ell,m_\ell}(\theta, \phi)}$, which turns out to be simply $1/4\pi$. The volume of the spherical shell is $\delta V = 4\pi r^2 \delta r$. The probability of finding the electron in this shell is then

$$|(\overline{Y_{\ell,m_\ell}(\theta, \phi)})(R_{n,\ell}(r))|^2 \times (4\pi r^2 \delta r)$$

If $\delta P(r)$ represents the probability that the electron is in this spherical shell of thickness δr, then

$$\delta P(r) = |R_{n,\ell}(r)|^2 r^2 \delta r \qquad [3.41]$$

The **radial probability density** $P_{n,\ell}(r)$ is defined as the probability per unit radial distance, that is, dP/dr which from Equation 3.41 is $|R_{n,\ell}(r)|^2 r^2$. The latter vanishes at the nucleus and peaks at certain locations, as shown in Figure 3.21b. This behavior implies that the probability of finding the electron within a thin spherical shell close to the nucleus also disappears. For $n = 1$, and $\ell = 0$, for example, the maximum probability is at $r = a_o = 0.0529$ nm, which is called the **Bohr radius.** Therefore, if the electron is in the 1s state, it spends most of its time at a distance a_o. Notice that the probability distribution does not depend on m_ℓ, but only on n and ℓ.

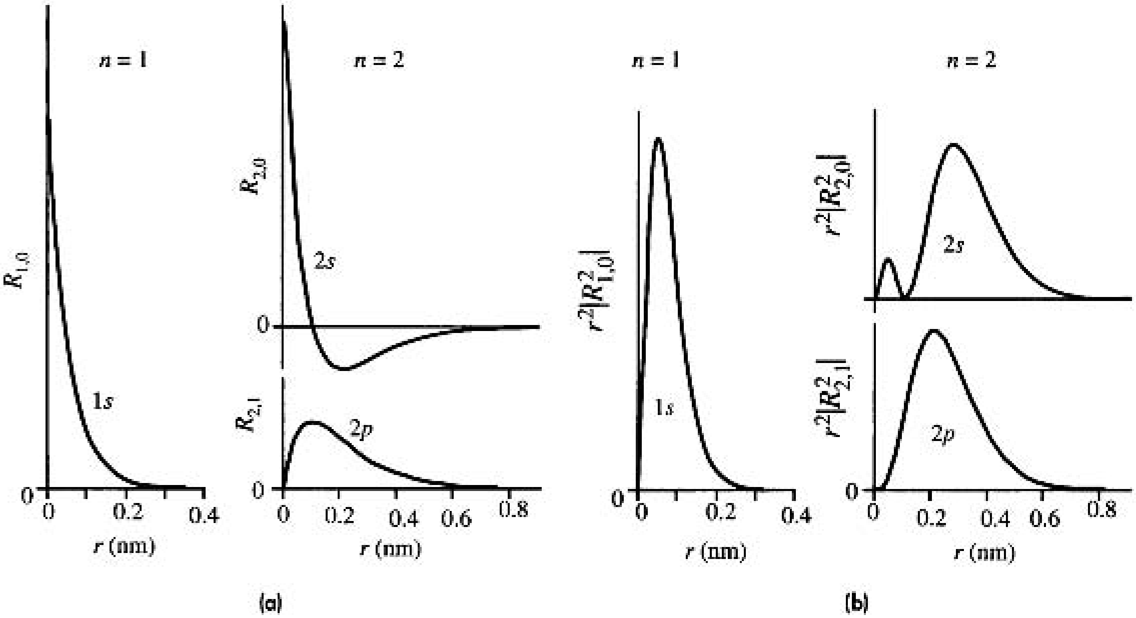


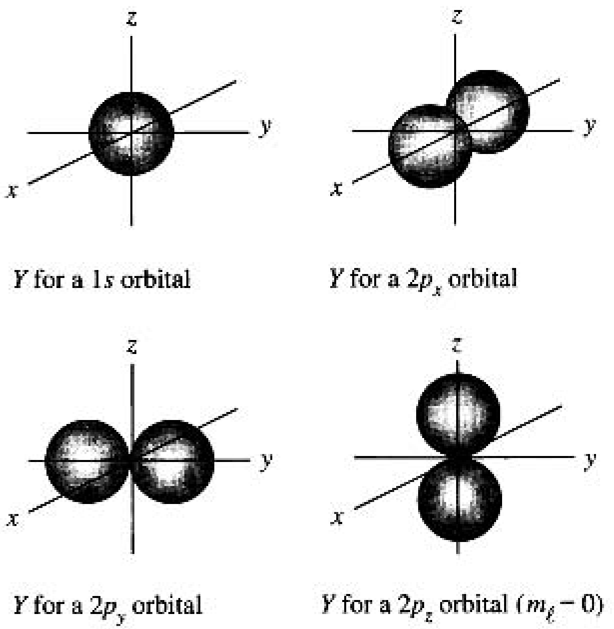
Figure 3.21

(a) Radial wavefunctions of the electron in a hydrogenic atom for various n and ℓ values.
(b) $r^2\,|R^2_{n,\ell}|$ gives the radial probability density. Vertical axis scales are linear in arbitrary units.

Table 3.2 summarizes the nature of the functions $R_{n,\ell}(r)$ and $Y_{\ell,m_\ell}(\theta,\phi)$ for various n,ℓ,m_ℓ values. Each possible wavefunction $\psi_{n,\ell,m_\ell}(r,\theta,\phi)$ with a particular choice of n,ℓ,m_ℓ constitutes a **quantum state** for the electron. The function $\psi_{n,\ell,m_\ell}(r,\theta,\phi)$ basically describes the behavior of the electron in the atom in probabilistic terms, as distinct from a well-defined line orbit for the electron, as one might expect from classical mechanics. For this reason, $\psi_{n,\ell,m_\ell}(r,\theta,\phi)$ is often referred to as an **orbital,** in contrast to the classical theory, which assigns an orbit to the electron.

Figure 3.22a shows the polar plots of $Y_{\ell,m_\ell}(\theta,\phi)$ for s and p orbitals. The radial distance from the origin in the polar plot represents the magnitude of $Y_{\ell,m_\ell}(\theta,\phi)$, which depends on the angles θ and ϕ. The polar plots of the probability distribution $|Y_{\ell,m_\ell}(\theta,\phi)|^2$ are shown in Figure 3.22b. Although for the s states, $Y_{1,0}(\theta,\phi)$ is spherically symmetric, resulting in a spherically symmetrical probability distribution around the nucleus, this is not so for $\ell = 1$ and higher states.

For example, each of the p states has a distinctly directional character, as illustrated in the polar plots in Figure 3.22. The angular dependence of $|\psi_{2,1,0}(r,\theta,\phi)|$, for which $m_\ell = 0$, is such that most of the probability is oriented along the z axis. This wavefunction is referred to as the $2p_z$ orbital. The two wavefunctions for $m_\ell = \pm 1$ are often represented by $\psi_{2p_x}(r,\theta,\phi)$ and $\psi_{2p_y}(r,\theta,\phi)$, or more simply, $2p_x$ and $2p_y$ orbitals, which do not possess a specific m_ℓ individually, but together represent the two $m_\ell = \pm 1$ wavefunctions. The angular dependence of $2p_x$ and $2p_y$ are essentially along the x and y directions. Thus, the three orbitals for $m_\ell = 0, \pm 1$ are all oriented perpendicular to each other, as depicted in Figure 3.22.



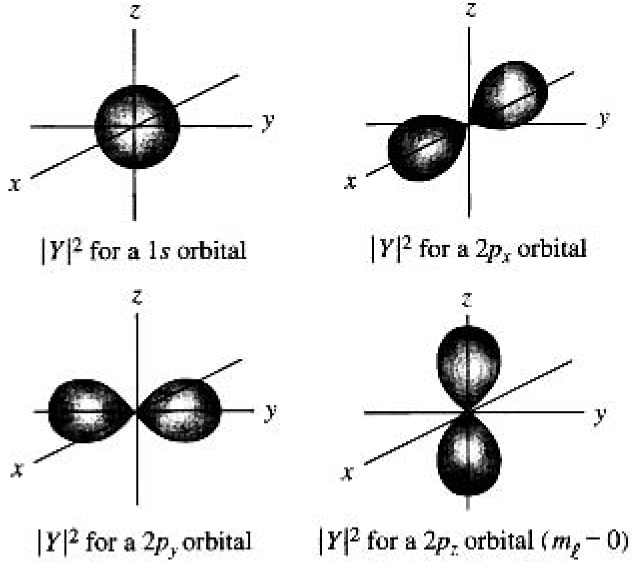
Y for a 1s orbital

Y for a 2p_x orbital

Y for a 2p_y orbital

Y for a 2p_z orbital (m_ℓ – 0)

(a)



$|Y|^2$ for a 1s orbital

$|Y|^2$ for a 2p_x orbital

$|Y|^2$ for a 2p_y orbital

$|Y|^2$ for a 2p_z orbital (m_ℓ – 0)

(b)

Figure 3.22

(a) The polar plots of $Y_{n,\ell}(\theta, \phi)$ for 1s and 2p states.

(b) The angular dependence of the probability distribution, which is proportional to $|Y_{n,\ell}(\theta, \phi)|^2$.

It should be noted that the probability distributions in Figures 3.21b and 3.22b do not depend on time. As previously mentioned, under steady-state conditions, the magnitude of the total wavefunction is

$$|\Psi(r,\theta,\phi,t)| = \left|\psi(r,\theta,\phi)\exp\left(-\frac{jEt}{\hbar}\right)\right| = |\psi(r,\theta,\phi)|$$

which is independent of time.

EXAMPLE 3.15 **PROBABILITY DENSITY FUNCTION** The quantity $|R_{n,\ell}(r)|^2 r^2$ in Equation 3.41 is called the **radial probability density function** and is simply written as $P_{n,\ell}(r)$. Thus, $dP(r) = P_{n,\ell}(r)\,dr$ is the probability of finding the electron between r and $r + dr$. We can use $P_{n,\ell}(r)$ to conveniently calculate the probability of finding the electron within a certain region of the atom, or to find the mean distance of the electron from the nucleus, and so on. For example, the electron in the 1*s* orbital has the wavefunction shown for $n = 1$, $\ell = 0$ in Table 3.2, which decays exponentially,

$$R_{n,\ell}(r) = 2a_o^{-3/2}\exp\left(-\frac{r}{a_o}\right)$$

The *total* probability of finding the electron inside the Bohr radius a_o can be found by summing (integrating) $P_{n,\ell}\,dr$ from $r = 0$ to $r = a_o$,

$$P_{\text{total}}(r < a_o) = \int_0^{a_o} P_{n,\ell}(r)\,dr = \int_0^{a_o} |R_{n,\ell}(r)|^2 r^2\,dr$$

$$= \int_0^{a_o} 4a_o^{-3}\exp\left(-\frac{2r}{a_o}\right) r^2\,dr = 0.32 \qquad \text{or} \qquad 32\%$$

The integration is not trivial but can nonetheless be done as indicated by the result 0.32 above. Thirty-two percent of the time the electron is therefore closer to the nucleus than the Bohr radius.

The mean distance $\bar{r}$ of the electron, from the definition of the mean, becomes

Average distance of electron from nucleus

$$\bar{r} = \int_0^{\infty} r P_{n,\ell}(r)\,dr = \frac{a_o n^2}{Z}\left[\frac{3}{2} - \frac{\ell(\ell+1)}{2n^2}\right] \qquad [3.42]$$

where we have simply inserted the result of the integration for various orbitals. (Again we take the mathematics as granted.) For the 1*s* orbital, in the hydrogen atom, $Z = 1$, $n = 1$, and $\ell = 0$, so $\bar{r} = \frac{3}{2}a_o$, further than the Bohr radius. Notice that the mean distance $\bar{r}$ of the electron increases as n^2.

3.7.2 QUANTIZED ELECTRON ENERGY

Once the wavefunctions $\psi_{n,\ell,m_\ell}(r,\theta,\phi)$ have been found, they can be substituted into or

$$E_n = -\frac{Z^2 E_I}{n^2} = -\frac{Z^2(13.6\ \text{eV})}{n^2} \tag{3.43b}$$

where

Ionization energy of hydrogen

$$E_I = \frac{me^4}{8\varepsilon_o^2 h^2} = 2.18 \times 10^{-18}\ \text{J} \qquad \text{or} \qquad 13.6\ \text{eV} \tag{3.43c}$$

This corresponds to the energy required to remove the electron in the hydrogen atom ($Z = 1$) from the lowest energy level E_1 (at $n = 1$) to infinity; hence, it represents the **ionization energy.** The energy E_n in Equation 3.43b is negative with respect to that for the electron completely isolated from the nucleus (at $r = \infty$, therefore $V = 0$). Thus, when the electron is in the vicinity of the nucleus, $+Ze$, it has a lower energy, which is a favorable situation (hence, formation of the hydrogenic atom is energetically favorable). In general, the energy required to remove an electron from the nth shell to $n = \infty$ (where the electron is free) is called the **ionization energy for the *n*th shell,** which from Equation 4.43b is simply $|E_n|$ or $(13.6\ \text{eV})Z^2/n^2$.

Since the energy is quantized, the lowest energy of the electron corresponds to $n = 1$, which is -13.6 eV. The next higher energy value it can have is $E_2 = -3.40$ eV when $n = 2$, and so on, as sketched in Figure 3.23. Normally, the electron will take up a state corresponding to $n = 1$, because this has the lowest energy, called the **ground energy.** Its wavefunction corresponds to $\psi_{100}(r, \theta, \phi)$, which has a probability peak at $r = a_o$ and no angular dependence, as indicated in Figures 3.21 and 3.22.

The electron can only become excited to the next energy level if it is supplied by the right amount of energy $E_2 - E_1$. A photon of energy $h\nu = E_2 - E_1$ can readily supply this energy when it strikes the electron. The electron then gets excited to the state with $n = 2$ by absorbing the photon, and its wavefunction changes to $\psi_{210}(r, \theta, \phi)$, which has the maximum probability at $r = 4a_o$. The electron thus spends most of its time in this excited state, at $r = 4a_o$. It can return from the excited state at E_2 to the ground state at E_1 by emitting a photon of energy $h\nu = E_2 - E_1$.

By virtue of the quantization of energy, we see that the emission of light from excited atoms can only have certain wavelengths: those corresponding to transitions from higher quantum-number states to lower ones. In fact, in spectroscopic analysis, these wavelengths can be used to identify the elements, since each element has its unique set of emission and absorption wavelengths arising from a unique set of energy levels. Figure 3.24 illustrates the origin of the emission and absorption spectra of atoms, which are a direct consequence of the quantization of the energy.

The electrons in atoms can also be excited by other means, for example, by collisions with other atoms as a result of heating a gas. Figure 3.25 depicts how collisions with other atoms can excite an electron to higher energies. If an impinging atom has sufficient kinetic energy, it can impart just the right energy to excite the electron to a higher energy level. Since the total energy must be conserved, the incoming atom will lose some of its kinetic energy in the process. The excited electron can later return to

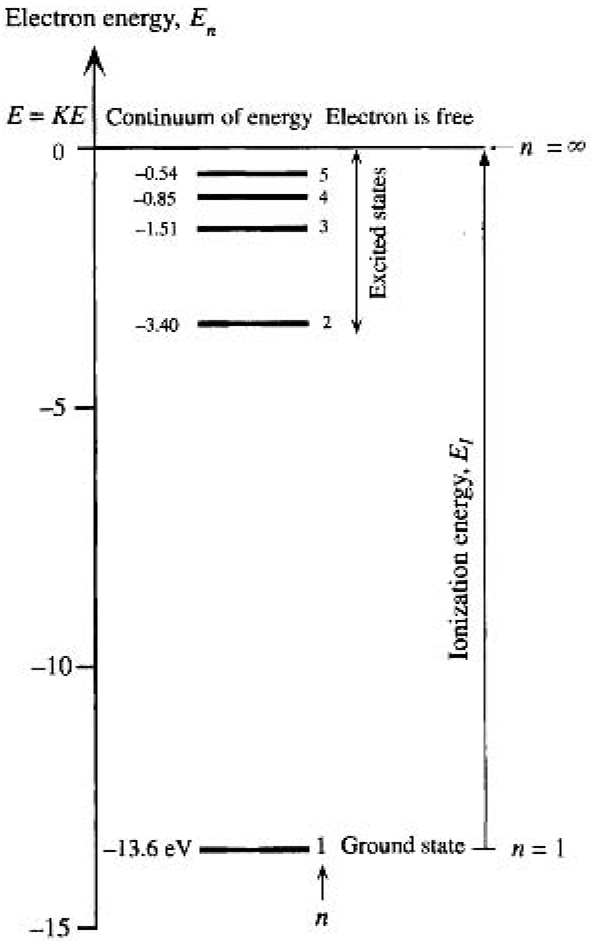
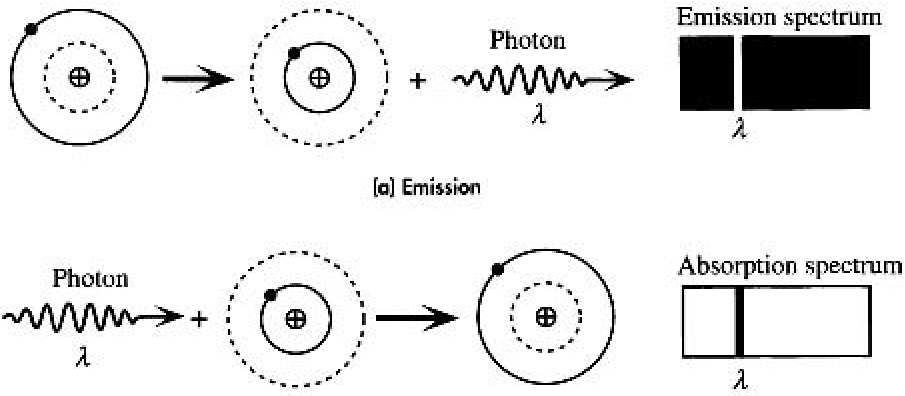


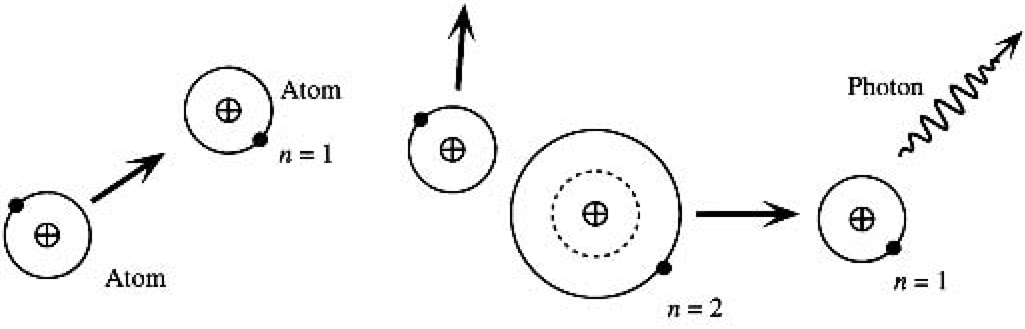
Figure 3.23 The energy of the electron in the hydrogen atom ($Z = 1$).



(a) Emission

(b) Absorption

Figure 3.24 The physical origin of spectra.



(a) Before collision (b) Just after collision (c) Photon emission

Figure 3.25 An atom can become excited by a collision with another atom. When it returns to its ground energy state, the atom emits a photon.

its ground state by emitting a photon. Excitation by atomic collisions is the process by which we obtain light from an electrical discharge in gases, a quantum phenomenon we experience every day as we read a neon sign. Indeed, this is exactly how the Ne atoms in the common laboratory HeNe laser are excited, via atomic collisions between Ne and He atoms.

Since the principal quantum number determines the energy of the electron and also the position of maximum probability, as we noticed in Figure 3.21, various n values define electron **shells,** within which we can most likely find the electron. These shells are customarily labeled $K, L, M, N, \ldots$, corresponding to $n = 1, 2, 3, \ldots$. For each n value, there are a number of ℓ values that determine the spatial distribution of the electron. For a given n, each ℓ value constitutes a **subshell.** For example, we often talk about $3s$, $3p$, $3d$ subshells within the M shell. From the radial dependence of the electron's wavefunction $\psi_{n,\ell,m_\ell}(r, \theta, \phi)$, shown in Figure 3.21, we see that for higher values of n, which correspond to more energetic states, the mean distance of the electron from the nucleus increases. In fact, we observe from Figure 3.21 that an orbital with $\ell = n - 1$ (*e.g.*, $1s$, $2p$) exhibits a single maximum in its radial probability distribution, and this maximum rapidly moves farther away from the nucleus as n increases. By examining the electron wavefunctions, we can show that the location of the maxima for these $\ell = n - 1$ states are at

Maximum probability for $\ell = n - 1$

$$r_{\max} = \frac{n^2 a_o}{Z} \qquad \text{for} \qquad \ell = n - 1 \tag{3.44}$$

where a_o is the radius of the ground state (0.0529 nm). The maximum probability radius $r_{\max}$ in Equation 3.44 is the Bohr radius. Note that $r_{\max}$ in Equation 3.44 is for $\ell = n - 1$ states only. For other ℓ values, there are multiple maxima, and we must think in terms of the average position of the electron from the nucleus. When we evaluate the average position from $\psi_{n,\ell,m_\ell}(r, \theta, \phi)$, we see that it depends on both n and ℓ; strongly on n and weakly on ℓ.

EXAMPLE 3.16 **THE IONIZATION ENERGY OF He$^+$** What is the energy required to further ionize He$^+$ ions to He^{++}?

SOLUTION

He$^+$ is a hydrogenic atom with one electron attracted by a nucleus with a $+2e$ charge. Thus $Z = 2$. The energy of the electron in a hydrogenic atom (in eV) is given by

$$E_n(\text{eV}) = -\frac{Z^2\,13.6}{n^2}$$

Since $Z = 2$, the energy required to ionize He$^+$ further is

$$|E_1| = |-(2^2)13.6| = 54.4\,\text{eV}$$

EXAMPLE 3.17 **IONIZATION ENERGY AND EFFECTIVE Z** The Li atom has a nucleus with a $+3e$ positive charge, which is surrounded by a full $1s$ orbital with two electrons, and a single valence electron in the outer $2s$ orbital as shown in Figure 3.26a. Intuitively we expect the valence electron to see the nuclear $+3e$ charge shielded by the two $1s$ electrons, that is, a net charge of $+1e$. It seems that we should be able to predict the ionization energy of the $2s$ electron by using the hydrogenic atom model and by taking $Z = 1$ and $n = 2$ as indicated in Figure 3.26b. However, according to quantum mechanics, the $2s$ electron has a probability distribution that has two peaks as shown in Figure 3.21; a major peak outside the $1s$ orbital, and a small peak around the $1s$ orbital. Thus, although the $2s$ electron spends a substantial time outside the $1s$ orbital, it does nonetheless penetrate the $1s$ shell and get close to the nucleus. Instead of experiencing a net $+1e$ of nuclear charge, it now experiences an effective nuclear charge that is greater than $+1e$, which we can represent as $+Z_{\text{effective}}e$, where we have used an *effective* Z. Thus, the ionization energy from Equation 3.43 is

Ionization and effective nuclear charge

$$E_{I,n} = \frac{Z^2_{\text{effective}}(13.6\,\text{eV})}{n^2} \qquad [3.45]$$

The experimental ionization energy of Li is 5.39 eV which corresponds to creating a Li$^+$ ion and an isolated electron. Calculate the effective nuclear charge seen by the $2s$ electron.

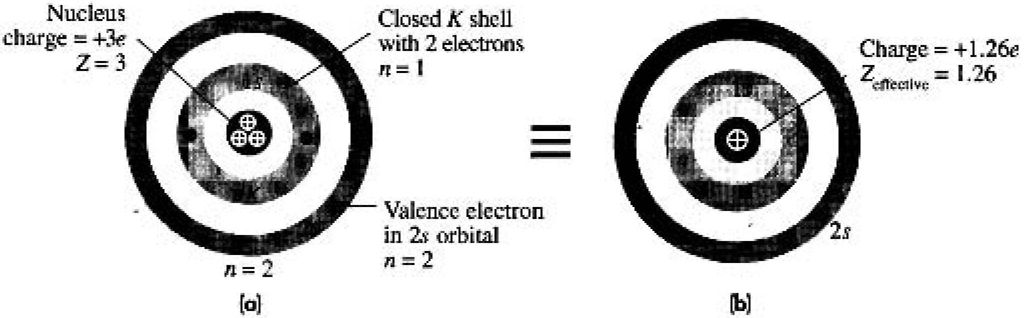


Figure 3.26

(a) The Li atom has a nucleus with charge $+3e$; two electrons in the K shell, which is closed; and one electron in the $2s$ orbital.

(b) A simple view of (a) would be one electron in the $2s$ orbital that sees a single positive charge, $Z = 1$.

SOLUTION

The most outer electron in the Li atom is in the 2s orbital, which is the electron that is removed in the ionization process. For this 2s electron, $n = 2$, and hence from Equation 3.45

$$5.39\text{ eV} = \frac{Z^2_{\text{effective}}(13.6\text{ eV})}{(2)^2}$$

Solving, we find $Z_{\text{effective}} = 1.26$. If we simply use $Z = 1$ in Equation 3.45, we would find $E_{I,n} = 3.4$ eV, too small compared with the experimental value because, according to its probability distribution, the electron spends some time close to the nucleus, and hence increases its binding energy (stronger attraction). Variables Z and $Z_{\text{effective}}$ should not be confused. Z is the integer number of protons in the nucleus of the simple hydrogenic atom that are attracting the electron, as in H, He$^+$, or Li^{++}. $Z_{\text{effective}}$ is a convenient way of describing what the outer electron experiences in an atom because we would like to continue to use the simple expression for $E_{I,n}$, Equation 3.45, which was originally derived for a hydrogenic atom.

3.7.3 ORBITAL ANGULAR MOMENTUM AND SPACE QUANTIZATION

The electron in the atom has an orbital angular momentum L. The electron is attracted to the nucleus by a central force, just like the Earth is attracted by the central gravitational force of the sun and thus possesses an orbital angular momentum. It is well known that in classical mechanics, under the action of a central force, both the total energy ($KE + PE$) and the orbital angular momentum (L) of an orbiting object are conserved. In quantum mechanics, the orbital angular momentum of the electron, like its energy, is also quantized, but by the quantum number ℓ. The magnitude of L is given by

Orbital angular momentum

$$L = \hbar[\ell(\ell+1)]^{1/2} \tag{3.46}$$

where $\ell = 0, 1, 2, \ldots < n$. Thus, for an electron in the ground state, $n = 1$ and $\ell = 0$, the angular momentum is zero, which is surprising since we always think of the electron as orbiting the nucleus. In the ground state, the spherical harmonic is a constant, independent of the angles θ and ϕ, so the electron has a spherically symmetrical probability distribution that depends only on r.

The quantum numbers n and ℓ quantize the energy and the magnitude of the orbital angular momentum. What is the significance of m_ℓ? In the presence of an external magnetic field B_z, taken arbitrarily in the z direction, the component of the angular momentum along the z axis, L_z, is also quantized and is given by

Orbital angular momentum along B_z

$$L_z = m_\ell \hbar \tag{3.47}$$

Therefore, the quantum number m_ℓ quantizes the component of the angular momentum along the direction of an external magnetic field B_z, which for reference purposes is taken along z, as illustrated in Figure 3.27. Therefore, m_ℓ, is appropriately called the **magnetic quantum number.** For any given ℓ, quantum mechanics requires that m_ℓ must have values in the range $-\ell, -(\ell-1), \ldots, -1, 0, 1, \ldots, (\ell-1), \ell$. We see that $|m_\ell| \le \ell$. Moreover, m_ℓ can be negative, since L_z can be negative or positive, depending on the orientation of the angular momentum vector **L**. Since $|m_\ell| \le \ell$, **L** can never align with the magnetic field along z; instead, it makes an angle with B_z, an

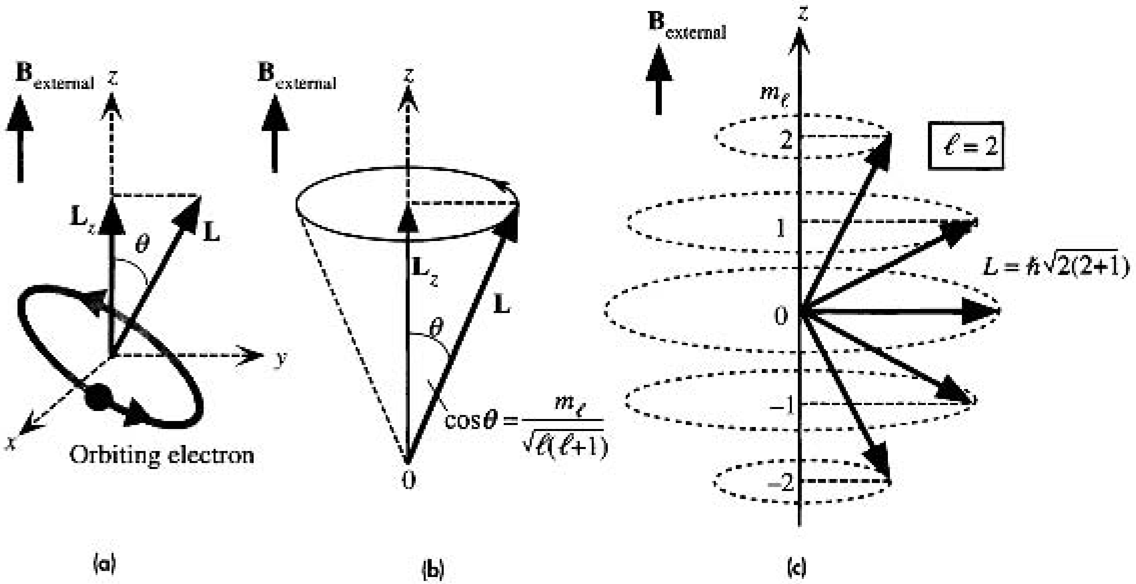


Figure 3.27

(a) The electron has an orbital angular momentum, which has a quantized component L along an external magnetic field B_{external}.

(b) The orbital angular momentum vector **L** rotates about the z axis. Its component L_z is quantized; therefore, the **L** orientation, which is the angle θ, is also quantized. **L** traces out a cone.

(c) According to quantum mechanics, only certain orientations (θ) for **L** are allowed, as determined by ℓ and m_ℓ.

angle that is determined by ℓ and m_ℓ. We say that **L is space quantized.** Space quantization is illustrated in Figure 3.27 for $\ell = 2$.

Since the energy of the electron does not depend on either ℓ or m_ℓ we can have a number of possible states for a given energy. For example, when the energy is E_2, then $n = 2$, which means that $\ell = 0$ or 1. For $\ell = 1$, we have $m_\ell = -1, 0, 1$, so there are a total of three different orbitals for the electron.

Since the electron has a quantized orbital angular momentum, when an electron interacts with a photon, the electron must obey the law of the conservation of angular momentum, much as an ice skater does sudden fast spins by pulling in her arms. All experiments indicate that the photon has an intrinsic angular momentum with a constant magnitude given by $\hbar$. Therefore, when a photon of energy $h\nu = E_2 - E_1$ is absorbed, the angular momentum of the electron must change. This means that following photon absorption or emission, both the principal quantum number n and the orbital angular momentum quantum number ℓ must change.

The rules that govern which transitions are allowed from one state to another as a consequence of photon absorption or emission are called **selection rules.** As a result of photon absorption or emission, we must have

Selection rules for EM radiation

$$\Delta\ell = \pm 1 \qquad \text{and} \qquad \Delta m_\ell = 0, \pm 1 \tag{3.48}$$

As an example, consider the excitation of the electron in the hydrogen atom from the ground energy E_1 to a higher energy level E_2. The photon energy $h\nu$ must be

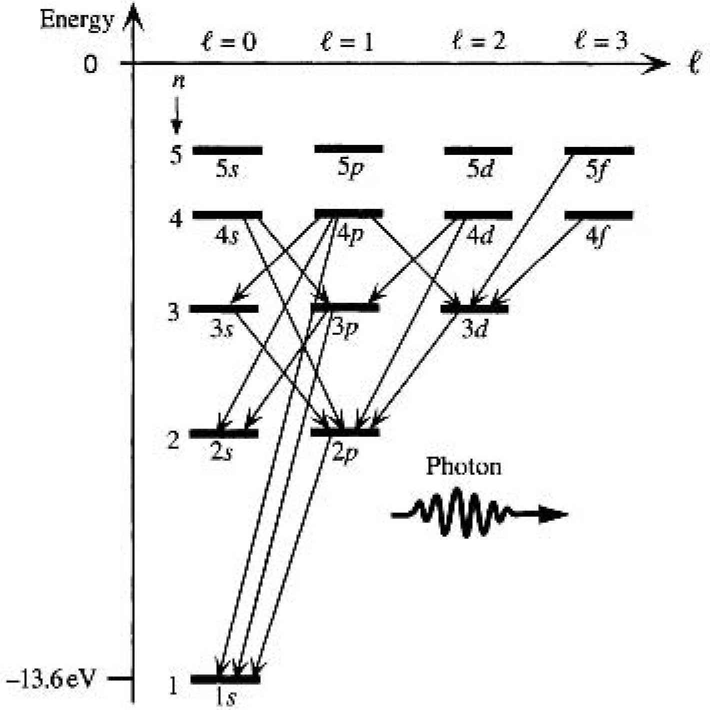


Figure 3.28 An illustration of the allowed photon emission processes.
Photon emission involves $\Delta\ell = \pm 1$.

exactly $E_2 - E_1$. The wavefunction of the 1*s* ground state is $\psi_{1,0,0}$, whereas there are four wavefunctions at E_2: one 2*s* state, $\psi_{2,0,0}$; and three 2*p* states, $\phi_{2,1,-1}$, $\psi_{2,1,0}$, and $\psi_{2,1,1}$. The excited electron cannot jump into the 2*s* state, because $\Delta\ell$ must be ± 1, so it enters a 2*p* state corresponding to one of the orbitals $\psi_{2,1,-1}$, $\psi_{2,1,0}$, or $\psi_{2,1,1}$. Various allowed transitions for photon emission in the hydrogen atom are indicated in Figure 3.28.

EXAMPLE 3.18

EXCITATION BY ELECTRON–ATOM COLLISIONS IN A GAS DISCHARGE TUBE A projectile electron with a velocity 2.1×10^6 m s^{-1} collides with a hydrogen atom in a gas discharge tube. Find the *n*th energy level to which the electron in the hydrogen atom gets excited. Calculate the possible wavelengths of radiation that will be emitted from the excited H atom as the electron returns to its ground state.

SOLUTION

The energy of the electron in the hydrogen atom is given by E_n (eV) $= -13.6/n^2$. The electron must be excited from its ground state $E_1 = -13.6$ eV to a quantized energy level $-(13.6/n^2)$ eV. The change in the energy is $\Delta E = (-13.6/n^2) - (-13.6)$ eV. This must be supplied by the incoming projectile electron, which has an energy of

$$E = \frac{1}{2}mv^2 = \frac{1}{2}(9.1 \times 10^{-31}\ \text{kg})(2.1 \times 10^6\ \text{m s}^{-1})^2$$

$$= 2.01 \times 10^{-18}\ \text{J} \qquad \text{or} \qquad 12.5\ \text{eV}$$

Therefore,

$$12.5\,\text{eV} = 13.6\,\text{eV} - \left[\frac{(13.6\,\text{eV})}{n^2}\right]$$

Solving this for n, we find

$$n^2 = \frac{13.6}{(13.6 - 12.5)} = 12.36$$

so $n = 3.51$. But n can only be an integer; thus, the electron gets excited to the level $n = 3$ where its energy is $E_3 = -13.6/3^2 = -1.51$ eV.

The energy of the incoming electron after the collision is less by

$$(E_3 - E_1) = 13.6 - 1.51 = 12.09\,\text{eV}$$

Since the initial energy of the incoming electron was 12.5 eV, it leaves the collision with a kinetic energy of $12.5 - 12.09 = 0.41$ eV. From the E_3 level, the electron can undergo a transition from $n = 3$ to $n = 1$,

$$\Delta E_{31} = -1.51\,\text{eV} - (-13.6\,\text{eV}) = 12.09\,\text{eV}$$

The emitted radiation will have a wavelength λ given by $hc/\lambda = \Delta E$, so that

$$\lambda_{31} = \frac{hc}{\Delta E_{31}} = \frac{(6.626 \times 10^{-34}\,\text{J s})(3 \times 10^8\,\text{m s}^{-1})}{12.09 \times 1.6 \times 10^{-19}\,\text{J}}$$

$$= 1.026 \times 10^{-7}\,\text{m} \qquad \text{or} \qquad 102.6\,\text{nm} \qquad \text{(in the ultraviolet region)}$$

Another possibility is the transition from $n = 3$ to $n = 2$, for which

$$\Delta E_{32} = -1.51\,\text{eV} - (-3.40\,\text{eV}) = 1.89\,\text{eV}$$

This will give a wavelength

$$\lambda_{32} = \frac{hc}{\Delta E_{32}} = 656\,\text{nm}$$

which is in the red region of the visible spectrum. For the transition from $n = 2$ to $n = 1$,

$$\Delta E_{21} = -3.40\,\text{eV} - (-13.6\,\text{eV}) = 10.2\,\text{eV}$$

which results in the emission of a photon of wavelength $\lambda_{21} = hc/\Delta E_{21} = 121.5$ nm. Note that each transition obeys $\Delta\ell = \pm 1$.

EXAMPLE 3.19

THE FRAUNHOFER LINES IN THE SUN'S SPECTRUM The light from the sun includes extremely sharp "dark lines" at certain wavelengths, superimposed on a bright continuum at all other wavelengths, as discovered by Josef von Fraunhofer in 1829. One of these dark lines occurs in the orange range and another in the blue. Fraunhofer measured their wavelengths to be 6563 Å and 4861 Å, respectively. With the aid of Figure 3.23, show that these are spectral lines from the hydrogen atom spectrum. (They are called the H_α and H_β Fraunhofer lines. Such lines provided us with the first clues to the chemical composition of the sun.)

SOLUTION

The energy of the electron in a hydrogenic atom is

$$E_n = -\frac{Z^2 E_I}{n^2}$$

where $E_I = me^4/(8\varepsilon_0^2 h^2)$. Photon emission resulting from a transition from quantum number n_2 to n_1 has an energy

$$\Delta E = E_{n_2} - E_{n_1} = -Z^2 E_I\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

From $h\nu = hc/\lambda = \Delta E$, we have

$$\frac{1}{\lambda} = \left(\frac{E_I}{hc}\right) Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R_\infty Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Emitted wavelengths for transitions in hydrogenic atom

where $R_\infty = E_I/hc = 1.0974 \times 10^7\ \text{m}^{-1}$. The equation for λ is called the **Balmer–Rydberg formula,** and R_∞ is called the **Rydberg constant.** We apply the Balmer–Rydberg formula with $n_1 = 2$ and $n_2 = 3$ to obtain

$$\frac{1}{\lambda} = (1.0974 \times 10^7\ \text{m}^{-1})(1^2)\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 1.524 \times 10^6\ \text{m}^{-1}$$

to get $\lambda = 6561$ Å. We can also apply the Balmer–Rydberg formula with $n_1 = 2$ and $n_2 = 4$ to get $\lambda = 4860$ Å.

EXAMPLE 3.20

GIANT ATOMS IN SPACE Radiotelescopic studies by B. Höglund and P. G. Mezger (*Science* vol. 150, p. 339, 1965) detected a 5009 MHz electromagnetic radiation in space. Show that this radiation comes from excited hydrogen atoms as they undergo transitions from $n = 110$ to 109. What is the size of such an excited hydrogen atom?

SOLUTION

Since the energy of the electron is $E_n = -(Z^2E_I/n^2)$, the energy of the emitted photon in the transition from n_2 to n_1 is

$$h\nu = E_{n_2} - E_{n_1} = Z^2E_I\left(n_1^{-2} - n_2^{-2}\right)$$

With $n_2 = 110$, $n_1 = 109$, and $Z = 1$, the frequency is

$$\begin{aligned}\nu &= \frac{Z^2E_I\left(n_1^{-2} - n_2^{-2}\right)}{h}\\ &= \frac{[(1.6 \times 10^{-19} \times 13.6)][(109^{-2} - 110^{-2})]}{(6.626 \times 10^{-34})}\\ &= 5 \times 10^9\ \text{s}^{-1} \qquad \text{or} \qquad 5000\ \text{MHz}\end{aligned}$$

The size of the atom from Equation 3.44 is on the order of

$$2r_{\max} = 2n^2a_o = 2(110^2)(52.918 \times 10^{-12}\ \text{m}) = 1.28 \times 10^{-6}\ \text{m} \qquad \text{or} \qquad 1.28\ \mu\text{m}$$

A giant atom!

3.7.4 ELECTRON SPIN AND INTRINSIC ANGULAR MOMENTUM S

One aspect of electron behavior does not come from the simple Schrödinger equation. That is the spin of the electron about its own axis, which is analogous to the 24-hour

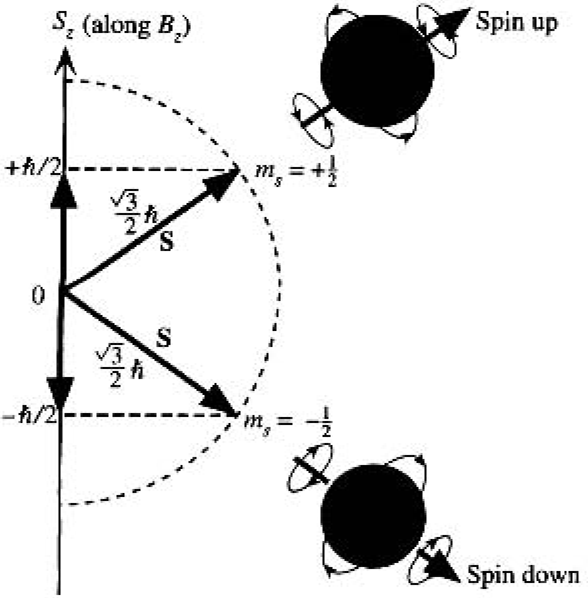


Figure 3.29 Spin angular momentum exhibits space quantization. Its magnitude along *z* is quantized, so the angle of **S** to the *z* axis is also quantized.

spin of Earth around its axis.[7] Earth has an orbital angular momentum due to its motion around the sun, and an intrinsic or spin angular momentum due to its rotation about its own axis. Similarly, the electron has a **spin** or **intrinsic angular momentum,** denoted by **S**. In classical mechanics, in the absence of external torques, spin angular momentum is conserved. In quantum mechanics, this spin angular momentum is quantized, in a manner similar to that of orbital angular momentum. The magnitude of the spin has been found to be constant, with a quantized component S_z in the z direction along a magnetic field:

Electron spin

$$S = \hbar[s(s+1)]^{1/2} \qquad s = \frac{1}{2} \tag{3.49}$$

Spin along magnetic field

$$S_z = m_s\hbar \qquad m_s = \pm\frac{1}{2} \tag{3.50}$$

where, in an analogy with ℓ and m_ℓ, we use the quantum numbers s and m_s, which are called the **spin** and **spin magnetic quantum numbers.** Contrary to our past experience with quantum numbers, s and m_s are not integers, but are $\frac{1}{2}$ and $\pm\frac{1}{2}$, respectively. The existence of electron spin was put forward by Goudsmit and Uhlenbeck in 1925 and derived by Dirac from relativistic quantum theory, which is beyond the scope of this book. Figure 3.29 illustrates the spin angular momentum of the electron and the two possibilities for S_z. When $S_z = +\frac{1}{2}\hbar$, using classical orbital motion as an analogy, we

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[7] Do not take the meaning of "spin" too literally, as in classical mechanics. Remember that the electron is assumed to have wave-like properties, which can have no classical spin.

Table 3.3 The four quantum numbers for the hydrogenic atom

n	Principal quantum number	$n = 1, 2, 3, \ldots$	Quantizes the electron energy
ℓ	Orbital angular momentum quantum number	$\ell = 0, 1, 2, \ldots (n-1)$	Quantizes the magnitude of orbital angular momentum L
m_ℓ	Magnetic quantum number	$m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell$	Quantizes the orbital angular momentum component along a magnetic field B_z
m_s	Spin magnetic quantum number	$m_s = \pm \dfrac{1}{2}$	Quantizes the spin angular momentum component along a magnetic field B_z

can label the spin of the electron as being in the clockwise direction, so $S_z = -\frac{1}{2}\hbar$ can be labeled as a counterclockwise spin. However, no such true clockwise or counterclockwise spinning of the electron can in reality[8] be identified. When $S_z = +\frac{1}{2}\hbar$, we could just as easily label the electron spin as "up," and call it "down" when $S_z = -\frac{1}{2}\hbar$. This terminology is used henceforth in this book.

Since the magnitude of the electron spin is constant, which is a remarkable fact, and is determined by $s = \frac{1}{2}$, we need not mention it further. It can simply be regarded as a fundamental property of the electron, in much the same way as its mass and charge. We do, however, need to specify whether $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$, since each of these selections gives the electron a different behavior. We therefore need four quantum numbers to specify what the electron is doing. Each state of the electron needs the spin magnetic quantum number m_s, in addition to n, ℓ, and m_ℓ. For each orbital $\psi_{n,\ell,m_\ell}(r, \theta, \phi)$, we therefore have two possibilities: $m_s = \pm\frac{1}{2}$. The quantum numbers n, ℓ, and m_ℓ determine the spatial extent of the electron by specifying the form of $\psi_{n,\ell,m_\ell}(r, \theta, \phi)$, whereas m_s determines the "direction" of the electron's spin. A full description of the behavior of the electron must therefore include all four quantum numbers n, ℓ, m_ℓ, and m_s.

An **electronic state** is a wavefunction that defines both the spatial (ψ_{n,ℓ,m_ℓ}) and spin (m_s) properties of an electron. Frequently, an electronic state is simply denoted ψ_{n,ℓ,m_ℓ,m_s}, which adds the spin quantum number to the orbital wavefunction.

The quantum numbers are extremely important, because they quantize the various properties of the electron: its total energy, orbital angular momentum, and the orbital and spin angular momenta along a magnetic field. Their significance is summarized in Table 3.3.

The spin angular momentum **S**, like the orbital angular momentum, is **space quantized.** $S_z = \pm(\frac{1}{2}\hbar)$ is smaller than $S = \hbar\sqrt{3}/2$, which means that S can never line up with z, or a magnetic field, and the angle θ between **S** and the z axis can only have two values corresponding to $m_\ell = +\frac{1}{2}$ and $-\frac{1}{2}$, which means that $\cos\theta = S_z/S = \pm 1/\sqrt{3}$. Classically, S_z of a spinning object, or the orientation of **S** to the z-axis, can be any value inasmuch as classical spin has no space quantization.

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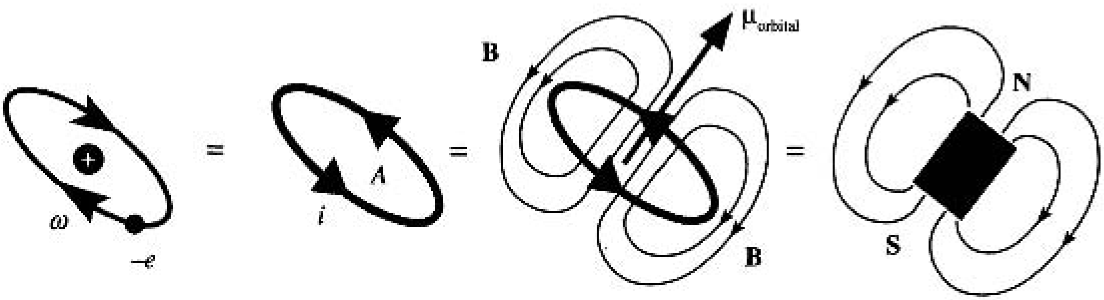
[8] The explanation in terms of spin and its two possible orientational directions ("clockwise" and "counterclockwise") serve as mental aids in visualizing a quantum mechanical phenomenon. One question, however, is, "If the electron is a wave, what is spinning?"

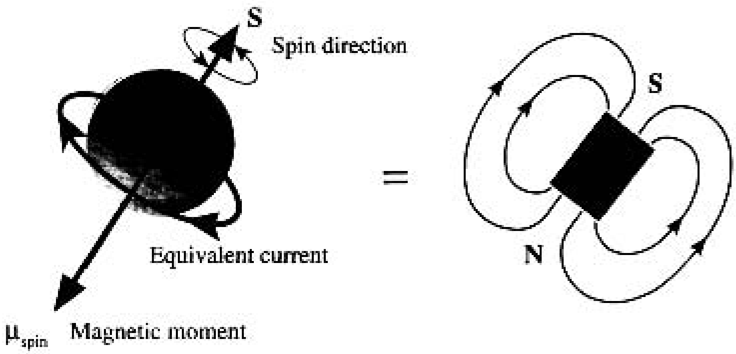
3.7.5 MAGNETIC DIPOLE MOMENT OF THE ELECTRON

Consider the electron orbiting the nucleus with an angular frequency ω as illustrated in Figure 3.30a. The orbiting electron is equivalent to a current loop. The equivalent current I due to the orbital motion of the electron is given by the charge flowing per unit time, $I = \text{charge/period} = -e(\omega/2\pi)$. The negative sign indicates that current I flows in the opposite direction to the electron motion. The magnetic field around the current loop is similar to that of a permanent magnet as depicted in Figure 3.30a. The magnetic moment is defined as $\mu = IA$, the product of the current and the area enclosed by the current loop. It is a vector normal to the surface A in a direction determined by the corkscrew rule applied to the circulation of the current I. If r is the radius of the orbit (current loop), then the magnetic moment is

$$\mu = IA = \left(-\frac{e\omega}{2\pi}\right)(\pi r^2) = -\frac{e\omega r^2}{2}$$



(a) The orbiting electron is equivalent to a current loop that behaves like a bar magnet.



(b) The spinning electron can be imagined to be equivalent to a current loop as shown. This current loop behaves like a bar magnet, just as in the orbital case.

Figure 3.30

Consider now the orbital angular momentum L, which is the linear momentum p multiplied by the radius r, or

$$L = pr = m_e vr = m_e \omega r^2$$

Using this, we can substitute for ωr^2 in $\mu = -e\omega r^2/2$ to obtain

$$\mu = -\frac{e}{2m_e}L$$

In vector notation, using the subscript "orbital" to identify the origin of the magnetic moment,

Orbital magnetic moment

$$\boldsymbol{\mu}_{\text{orbital}} = -\frac{e}{2m_e}\mathbf{L} \qquad [3.51]$$

This means that the orbital magnetic moment $\boldsymbol{\mu}_{\text{orbital}}$ is in the opposite direction to that of the orbital angular momentum **L** and is related to it by a constant $(e/2m_e)$.

Similarly, the spin angular momentum of the electron **S** leads to a **spin magnetic moment** $\boldsymbol{\mu}_{\text{spin}}$, which is in the opposite direction to **S** and given by

Spin magnetic moment

$$\boldsymbol{\mu}_{\text{spin}} = -\frac{e}{m_e}\mathbf{S} \qquad [3.52]$$

which is shown in Figure 3.30b. Notice that there is no factor of 2 in the denominator. We see that, as a consequence of the orbital motion and also of spin, the electron has two distinct magnetic moments. These moments act on each other, just like two magnets interact with each other. The result is a coupling of the orbital and the spin angular momenta **L** and **S** and their precession about the total angular momentum **J** = **L** + **S**, which is discussed in Section 3.7.6.

Since both **L** and **S** are quantized, so are the orbital and spin magnetic moments $\boldsymbol{\mu}_{\text{orbital}}$ and $\boldsymbol{\mu}_{\text{spin}}$. In the presence of an external magnetic field **B**, the electron has an additional energy term that arises from the interaction of these magnetic moments with **B**. We know from electromagnetism that a magnetic dipole (equivalent to a magnet) placed in a magnetic field **B** will have a potential energy PE. (A free magnet will rotate to align with the magnetic field, as in a compass, and thereby reduce the PE.) The *potential energy* E_{BL} due to μ_{orbital} and B interacting is given by

Potential energy of a magnetic moment

$$E_{BL} = -\mu_{\text{orbital}} B\cos\theta$$

where θ is the angle between μ_{orbital} and B. The potential energy E_{BL} is minimum when μ_{orbital} (the magnet) and B are parallel, $\theta = 0$. We know that, by definition, the z axis is always along an external field **B**, and L_z is the component of L along z (along B), and is quantized, so that $L_z = L\cos\theta = m_\ell\hbar$. We can substitute for μ_{orbital} to find

Potential energy of orbital angular momentum in B

$$E_{BL} = -\left(\frac{e}{2m_e}\right)LB\cos\theta = -\left(\frac{e}{2m_e}\right)L_zB = -\left(\frac{e\hbar}{2m_e}\right)m_\ell B$$

which depends on m_ℓ, and it is minimum for the largest m_ℓ. Since $m_\ell = -\ell, \ldots, 0, \ldots, +\ell$, negative and positive values through zero, the electron's energy splits into a number of levels determined by m_ℓ. Similarly, the spin magnetic moment $\boldsymbol{\mu}_{\text{spin}}$ and

Potential energy of orbital angular momentum in B

B interact to give the electron a potential energy E_{SL},

$$E_{SL} = -\left(\frac{e\hbar}{m_e}\right)m_s B$$

which depends on m_s. Since $m_s = \pm\frac{1}{2}$, E_{SL} has only two values, positive ($m_s = -\frac{1}{2}$) and negative ($m_s = +\frac{1}{2}$), which add and subtract from the electron's energy depending on whether the spin is down or up. Thus, in an external magnetic field, the electron's spin splits the energy level into two levels. The separation ΔE_{SL} of the split levels is $(e\hbar/m_e)B$, which is 0.12 meV T^{-1}, very small compared with the energy E_n in the absence of the field. It should also be apparent that a single wavelength emission λ_o corresponding to a particular transition from $E_{n'}$ to E_n will now be split into a number of closely spaced wavelengths around λ_o. Although the separation ΔE_{SL} is small, it is still more than sufficient even at moderate fields to be easily detected and used in various applications. As it turns out, spin splitting of the energy in a field can be fruitfully used to study the electronic structures of not only atoms and molecules, but also various defects in semiconductors in what is called *electron spin resonance*.

EXAMPLE 3.21

STERN–GERLACH EXPERIMENT AND SPIN The Stern–Gerlach experiment is quite famous for demonstrating the spin of the electron and its space quantization. A neutral silver atom has one outer valence electron in a 4*s* orbital and looks much like the hydrogenic atom. (We can simply ignore the inner filled subshells in the Ag atom.). The 4*s* electron has no orbital angular momentum. Because of the *spin* of this one outer 4*s* electron, the whole Ag atom has a spin magnetic moment $\boldsymbol{\mu}_{\text{spin}}$. When Otto Stern and Walther Gerlach (1921–1922) passed a beam of Ag atoms through a nonuniform magnetic field, they found that the narrow beam split into two distinct beams as depicted in Figure 3.31a. The interpretation of the experiment was that the Ag atom's magnetic moment along the field direction can have only two values, hence the split beam. This observation agrees with the quantum mechanical fact that in a field along z, $\mu_{\text{spin},z} = -(e/m_e)m_s\hbar$ where $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$; that is, the electron's spin can have only two values parallel to the field, or in other words, the electron spin is *space quantized.*

In the Stern–Gerlach experiment, the nonuniform magnetic field is generated by using a big magnet with shaped poles as in Figure 3.31a. The N-pole is sharp and the S-pole is wide, so the magnetic field lines get closer toward the N-pole and hence the magnetic field increases towards the N-pole. (This is much like a sharp point having a large electric field.) Whenever a magnetic moment, which we take to be a simple bar magnet, is in a nonuniform field, its poles experience different forces, say $\mathbf{F}_{\text{large}}$ and $\mathbf{F}_{\text{small}}$, and hence the magnet, overall, experiences a net force. The direction of the net force depends on the orientation of the magnet with respect to the z axis as illustrated in Figure 3.31b for two differently oriented magnets representing magnetic moments labeled as 1 and 2. The S-pole of magnet 1 is in the high field region and experiences a bigger pull ($\mathbf{F}_{\text{large}}$) from the big magnet's N-pole than the small force ($\mathbf{F}_{\text{small}}$) pulling the N-pole of 1 to the big magnet's S-pole. Hence magnet 1 is pulled toward the N-pole and is deflected up. The overall force on a magnetic moment is the difference between $\mathbf{F}_{\text{large}}$ and $\mathbf{F}_{\text{small}}$, and its direction here is determined by the force on whichever pole is in the high field region. Magnet 2 on the other hand has its N-pole in the high field region, and hence is pushed away from the big magnet's N-pole and is deflected down. If the magnet is at right angles to the z axis ($\theta = \pi/2$), it would experience no net force as both of its poles would be in the same field. This magnetic moment would pass through undeflected.

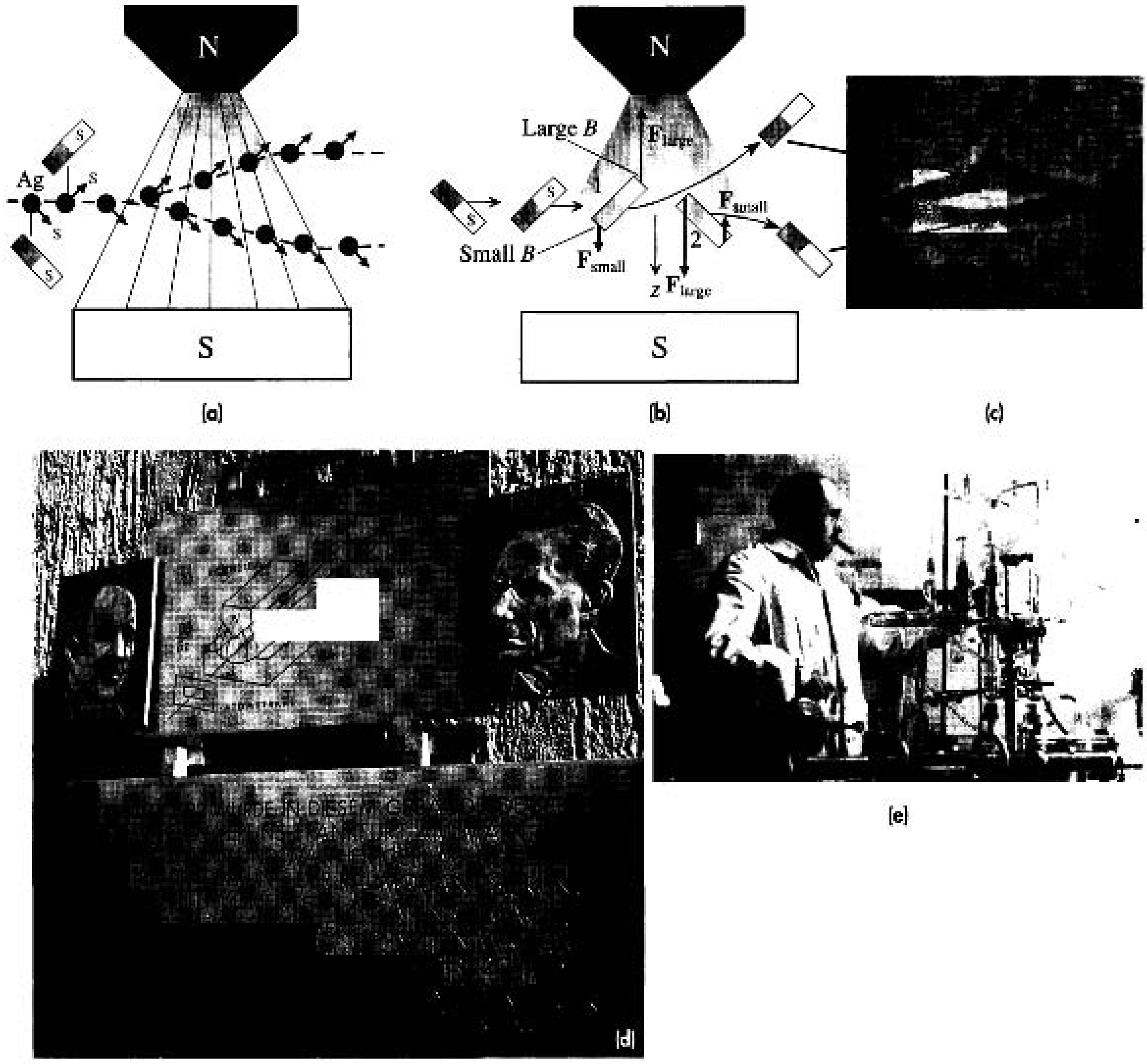


Figure 3.31

(a) Schematic illustration of the Stern–Gerlach experiment. A stream of Ag atoms passing through a nonuniform magnetic field splits into two.

(b) Explanation of the Stern–Gerlach experiment.

(c) Actual experimental result recorded on a photographic plate by Stern and Gerlach (O. Stern and W. Gerlach, *Zeitschr. fur. Physik*, **9**, 349, 1922.) When the field is turned off, there is only a single line on the photographic plate. Their experiment is somewhat different than the simple sketches in (a) and (b) as shown in (d).

(d) Stern–Gerlach memorial plaque at the University of Frankfurt. The drawing shows the original Stern–Gerlach experiment in which the Ag atom beam is passed along the long-length of the external magnet to increase the time spent in the nonuniform field, and hence increase the splitting.

(e) The photo on the lower right is Otto Stern (1888–1969), standing and enjoying a cigar while carrying out an experiment. Otto Stern won the Nobel prize in 1943 for development of the molecular beam technique.

SOURCES: (d) Courtesy of Horst Schmidt-Böcking from B. Friedrich and D. Herschbach, "Stern and Gerlach: How a Bad Cigar Helped Reorient Atomic Physics," *Physics Today*, December 2003, pp. 53–59. (e) AIP Emilio Segrè Visual Archives, Segrè Collection.

When we pass a stream of classical magnetic moments through a nonuniform field, there will be all possible orientations of the magnetic moment, from $-\pi$ to $+\pi$, with the field because there is no space quantization. Classically, the Ag atoms passing through a nonuniform field would be deflected through a distribution of angles and would not split into two distinct beams. The actual result of Stern and Gerlach's experiment is shown in Figure 3.31c, which is their photographic recording of a flat line-beam of Ag atoms passing through a long nonuniform field. In the absence of the field, the image is a simple horizontal line, the cross section of the beam. With the field turned on, the line splits into two. The edges of the line do not experience splitting because the field is very weak in the edge region. In the actual experiment, as shown in Figure 3.31c, an Ag atomic beam is passed along the long-length of the external magnet to increase the time spent in the nonuniform field, and hence increase the splitting. The physics remains the same.

3.7.6 TOTAL ANGULAR MOMENTUM J

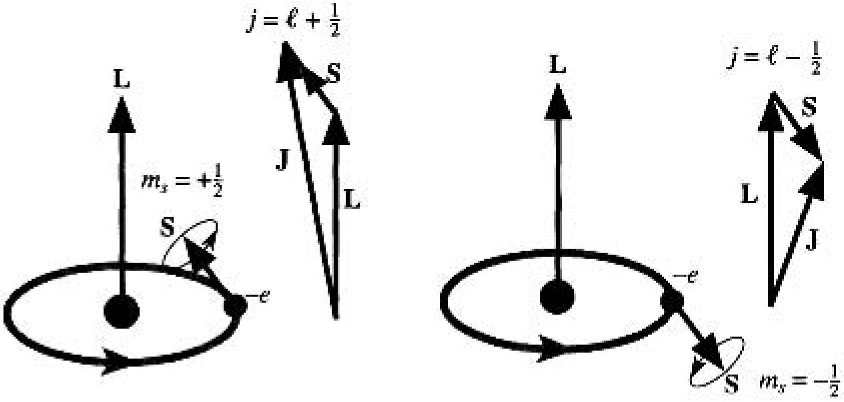
The orbital angular momentum **L** and the spin angular momentum **S** add to give the electron a total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, as illustrated in Figure 3.32. There are a number of possibilities for the total angular momentum **J**, based on the relative orientations of **L** and **S**. For example, for a given **L**, we can add **S** either in parallel or antiparallel, as depicted in Figure 3.32a and b, respectively.

Since in classical physics the total angular momentum of a body (not experiencing an external torque) must be conserved, we can expect J (the magnitude of **J**) to be quantized. This turns out to be true. The magnitude of **J** and its z component along an external magnetic field are quantized via

Total angular momentum

$$J = \hbar[j(j+1)]^{1/2} \tag{3.53}$$

$$J_z = m_j\hbar \tag{3.54}$$



(a) Parallel **(b) Antiparallel**

Figure 3.32 Orbital angular momentum vector **L** and spin angular momentum vector **S** can add either in parallel as in (a) or antiparallel, as in (b).
The total angular momentum vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$, has a magnitude $J = \sqrt{[j[j+1]]}$, where in (a) $j = \ell + \frac{1}{2}$ and in (b) $j = \ell - \frac{1}{2}$.

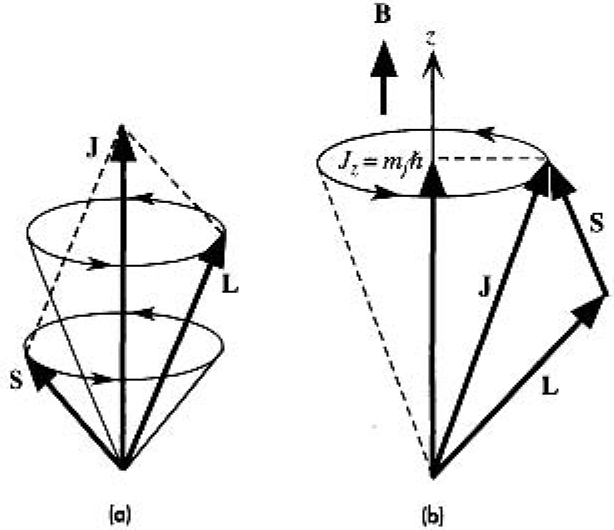


Figure 3.33
(a) The angular momentum vectors **L** and **S** precess around their resultant total angular momentum vector J.
(b) The total angular momentum vector is space quantized. Vector **J** precesses about the z axis, along which its component must be $m_j\hbar$.

where both j and m_j are quantum numbers[9] like ℓ and m_ℓ, but j and m_j can have fractional values. A rigorous theory of quantum mechanics shows that when $\ell > s$, the quantum numbers for the total angular momentum are given by $j = \ell + s$ and $\ell - s$ and $m_j = \pm j, \pm(j-1)$. For example, for an electron in a p orbital, where $\ell = 1$, we have $j = \frac{3}{2}$ and $\frac{1}{2}$, and $m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$, and $-\frac{3}{2}$. However, when $\ell = 0$ (as for all s orbitals), we have $j = s = \frac{1}{2}$ and $m_j = m_s = \pm\frac{1}{2}$, which are the only possibilities. We note from Equations 3.53 and 3.54 that $|J_z| < J$ and both are quantized, which means that **J** is space quantized; its orientation (or angle) with respect to the z axis is determined by j and m_j.

The spinning electron actually experiences a magnetic field $\mathbf{B}_{\text{int}}$ due to its orbital motion around the nucleus. If we were sitting on the electron, then in our reference frame, the positively charged nucleus would be orbiting around us, which would be equivalent to a current loop. At the center of this current loop, there would be an "internal" magnetic field $\mathbf{B}_{\text{int}}$, which would act on the magnetic moment of the spinning electron to produce a torque. Since **L** and **S** add to give **J**, and since the latter quantity is space quantized (or conserved), then as a result of the internal torque on the electron, we must have **L** and **S** synchronously precessing about **J**, as illustrated in Figure 3.33a. If there is an external magnetic field **B** taken to be along z, this torque will act on the net magnetic moment due to **J** to cause this quantity to precess about **B**, as depicted in Figure 3.33b. Remember that the component along the z axis must be quantized and equal to $m_j\hbar$, so the torque can only cause precession. To understand the precession of the electron's angular momentum about the magnetic field **B**, think of a spinning top that precesses about the gravitational field of Earth.

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[9] The quantum number j as used here should not be confused with j for $\sqrt{-1}$.

3.8 THE HELIUM ATOM AND THE PERIODIC TABLE

3.8.1 He ATOM AND PAULI EXCLUSION PRINCIPLE

In the He atom, there are two electrons in the presence of a nucleus of charge $+2e$, as depicted in Figure 3.34. (Obviously, in higher-atomic-number elements, there will be Z electrons around a nucleus of charge $+Ze$.) The *PE* of an electron in the He atom consists of two interactions. The first is due to the Coulombic attraction between itself and the positive nucleus; the second is due to the mutual repulsion between the two electrons. The *PE* function V of any one of the electrons, for example, that labeled as 1, therefore depends on both its distance from the nucleus r_1 and the separation of the two electrons r_{12}. The *PE* of electron 1 thus depends on the locations of both the electrons, or

PE of one electron in He atom

$$V(r_1, r_{12}) = -\frac{2e^2}{4\pi\varepsilon_o r_1} + \frac{e^2}{4\pi\varepsilon_o r_{12}} \qquad [3.55]$$

When we use this *PE* in the Schrödinger equation for a single electron, we find the wavefunction and energy of one of the electrons in the He atom. We thus obtain the **one-electron wavefunction** and the **energy of one electron** within a many-electron atom.

One immediate and obvious result is that the energy of an electron now depends not only on n but also on ℓ, because the electron–electron potential energy term (the second term in Equation 3.55, which contains r_{12}) depends on the relative orientations of the electron orbitals, which change r_{12}. We therefore denote the electron energy by $E_{n,\ell}$. The dependence on ℓ is weaker than on n, as shown in Figure 3.35. As n and ℓ increase, $E_{n,\ell}$ also increases. Notice, however, that the energy of a 4*s* state is lower than that of a 3*d* state, and the same pattern also occurs at 4*s* and 5*s*.

One of the most important theorems in quantum physics is the **Pauli exclusion principle,** which is based on experimental observations. This principle states that *no two electrons within a given system (e.g., an atom) may have all four identical quantum numbers,* n, ℓ, m_ℓ, and m_s. Each set of values for n, ℓ, m_ℓ, and m_s represents a possible electronic state, that is, a wavefunction denoted by ψ_{n,ℓ,m_ℓ,m_s}, that the electron may (or may not) acquire. For example, an electron with the quantum numbers given by $2, 1, 1, \frac{1}{2}$ will have a definite wavefunction $\psi_{n,\ell,m_\ell,m_s} = \psi_{2,1,1,1/2}$, and it is said to be

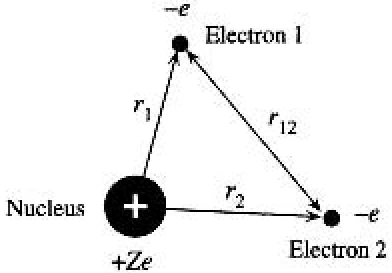

Figure 3.34 A helium-like atom.
The nucleus has a charge of $+Ze$, where $Z = 2$ for He. If one electron is removed, we have the He^+ ion, which is equivalent to the hydrogenic atom with $Z = 2$.

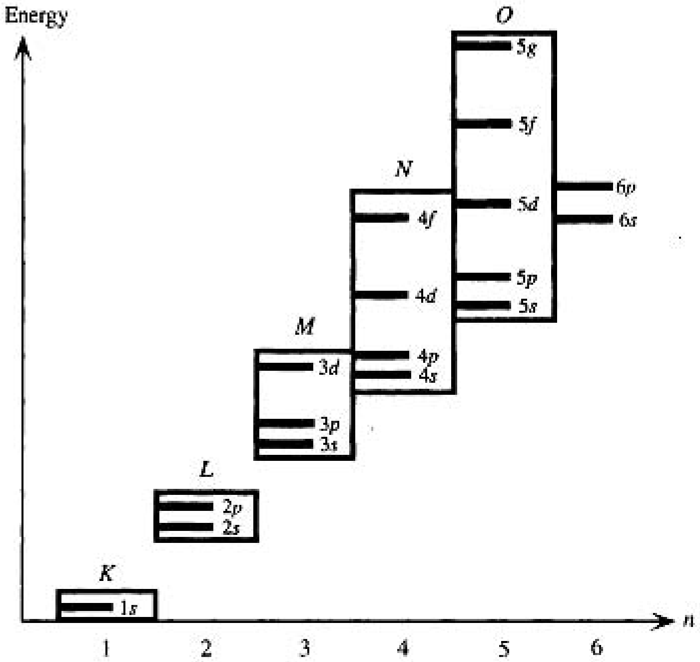

Figure 3.35 Energy of various one-electron states. The energy depends on both n and ℓ.

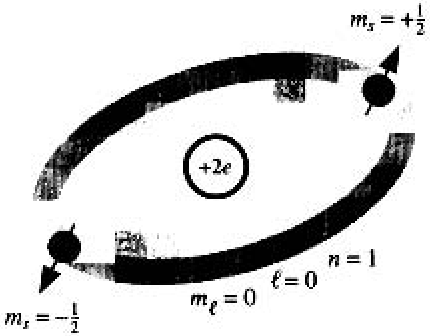

Figure 3.36 Paired spins in an orbital.

in the state $2p$, $m_\ell = 1$ and spin up. Its energy will be E_{2p}. The Pauli exclusion principle requires that no other electron be in this same state.

The orbital motion of an electron is determined by n, ℓ, and m_ℓ, whereas m_s determines the spin direction (up or down). Suppose two electrons are in the same orbital state, with identical n, ℓ, m_ℓ. By the Pauli exclusion principle, they would have to spin in opposite directions, as shown in Figure 3.36. One would have to spin "up" and the other "down." In this case we say that the electrons are **spin paired.** Two electrons can thus have the same orbitals (occupy the same region of space) if they pair their spins. However, the Pauli exclusion principle prevents a third electron from entering this orbital, since m_s can only have two values.

Using the Pauli exclusion principle, we can determine the electronic structure of many-electron atoms. For simplicity, we will use a box to represent an orbital state defined by a set of n, ℓ, m_ℓ values. Each box can take two electrons at most, with their spins paired. When we put an electron into a box, we are essentially assigning a wavefunction to that electron; that is, we are defining its orbital n, ℓ, m_ℓ. We use an arrow to show whether the electron is spinning up or down. As depicted in Figure 3.37, we arrange all the boxes to correspond to the electronic subshells. As an example, consider boron, which has five electrons. The first electron enters the $1s$ orbital at the lowest energy. The second also enters this orbital by spinning in the opposite direction. The third goes into the $n = 2$ orbital. The lowest energy there is in the s orbitals corresponding to $\ell = 0$ and $m_\ell = 0$. The fourth electron can also enter the $2s$

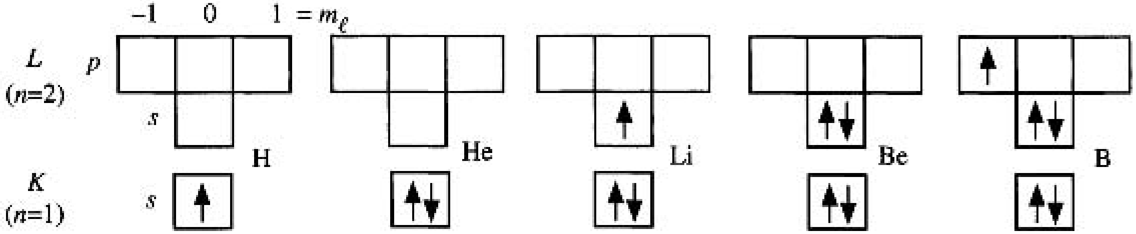

Figure 3.37 Electronic configurations for the first five elements. Each box represents an orbital $\psi(n, \ell, m_\ell)$.

orbital, provided that it spins in the opposite direction. Similarly, the fifth must go into another orbital, and the next nearest low-energy orbitals are those having $\ell = 1$ (p states) and $m_\ell = -1, 0, +1$. The final electronic structure of the B atom is shown in Figure 3.37.

We see that because the electron energy depends on n and ℓ, there are a number of states for a given energy $E_{n,\ell}$. Each of these states corresponds to different sets of m_ℓ and m_s. For example, the energy $E_{2,1}$ (or E_{2p}) corresponding to $n = 2$, $\ell = 1$ has six possible states, arising from $m_\ell = -1, 0, 1$ and $m_s = +\frac{1}{2}, -\frac{1}{2}$. Each m_ℓ state can have an electron spinning up or down, $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$, respectively.

EXAMPLE 3.22 **THE NUMBER OF STATES AT AN ENERGY LEVEL** Enumerate and identify the states corresponding to the energy level E_{3d}, or $n = 3$, $\ell = 2$.

SOLUTION

When $n = 3$ and $\ell = 2$, m_ℓ and m_s can have these following values: $m_\ell = -2, -1, 0, 1, 2$, and $m_s = +\frac{1}{2}, -\frac{1}{2}$. This means there are 10 combinations. The possible wavefunctions (electron states) are

- $\psi_{3,2,2,1/2}$; $\psi_{3,2,1,1/2}$; $\psi_{3,2,0,1/2}$; $\psi_{3,2,-1,1/2}$; $\psi_{3,2,-2,1/2}$, all of which have spins up ($m_s = +\frac{1}{2}$)
- $\psi_{3,2,2,-1/2}$; $\psi_{3,2,1,-1/2}$; $\psi_{3,2,0,-1/2}$; $\psi_{3,2,-1,-1/2}$; $\psi_{3,2,-2,-1/2}$, all of which have spins down ($m_s = -\frac{1}{2}$)

3.8.2 HUND'S RULE

In the many-electron atom, the electrons take up the lowest-energy orbitals and obey the Pauli exclusion principle. However, the Pauli exclusion principle does not determine how any two electrons distribute themselves among the many states of a given n and ℓ. For example, there are six $2p$ states corresponding to $m_\ell = -1, 0, +1$, with each m_ℓ having $m_s = \pm\frac{1}{2}$. The two electrons could pair their spins and enter a given m_ℓ state, or they could align their spins (same m_s) and enter different m_ℓ states. An experimental fact deducted from spectroscopic studies shows that *electrons in the same* n, ℓ *orbitals prefer their spins to be parallel* (same m_s). This is known as **Hund's rule.**

The origin of Hund's rule can be readily understood. If electrons enter the same m_ℓ state by pairing their spins (different m_s), their quantum numbers n, ℓ, m_ℓ will be the same and they will both occupy the same region of space (same ψ_{n,ℓ,m_ℓ} orbital). They will then experience a large Coulombic repulsion and will have a large Coulombic potential energy. On the other hand, if they parallel their spins (same m_s), they will each have a different m_ℓ and will therefore occupy different regions of space (different ψ_{n,ℓ,m_ℓ} orbitals), thereby reducing their Coulombic repulsion.

The oxygen atom has eight electrons and its electronic structure is shown in Figure 3.38. The first two electrons enter the $1s$ box (orbital). The next two enter the $2s$ box. But p states can accommodate six electrons, so the remaining four electrons have a choice. Hund's rule forces three of the four electrons to enter the boxes corresponding to $m_\ell = -1, 0, +1$, all with their spins parallel. The last electron can go into any of the $2p$ boxes, but it has no choice for spin. It must pair its spin with the electron already in the box. Thus, the oxygen atom has two unpaired electrons in half-occupied orbitals, as indicated in Figure 3.38. Since these two unpaired electrons spin in the same direction, they give the O atom a net angular momentum. An angular momentum due to charge rotation (*i.e.*, spin) gives rise to a magnetic moment $\boldsymbol{\mu}$. If there is an external magnetic field present, then $\boldsymbol{\mu}$ experiences a force given by $\boldsymbol{\mu} \cdot d\mathbf{B}/dx$. Oxygen atoms will therefore be deflected by a nonuniform magnetic field, as experimentally observed.

Following the Pauli exclusion principle and Hund's rule, it is not difficult to build the electronic structure of various elements in the Periodic Table. There are only a few instances of unusual behavior in the energy levels of the electronic states. The $4s$ state happens to be energetically lower than the $3d$ states, so the $4s$ state fills up first. Similarly, the $5s$ state is at a lower energy than the $4d$ states. These features are summarized in the energy diagram of Figure 3.35. There is a neat shorthand way of writing the electronic structure of any atom. To each $n\ell$ state, we attach a superscript to represent the number of electrons in those $n\ell$ states. For example, for oxygen, we write $1s^2 2s^2 2p^4$, or simply $[\mathrm{He}]2s^2 2p^4$, since $1s^2$ is a full (closed) shell corresponding to He.

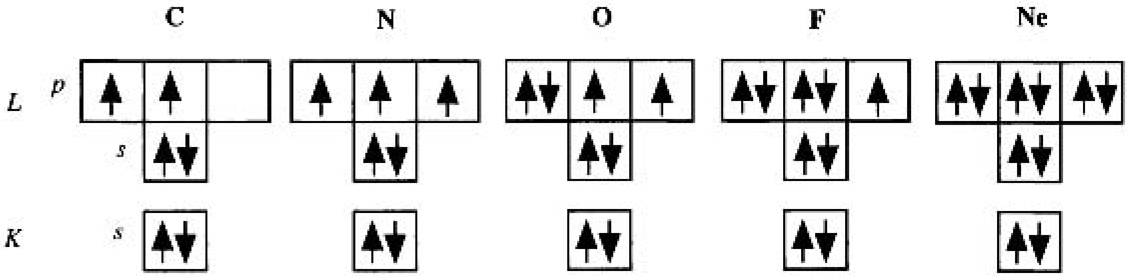

Figure 3.38 Electronic configurations for C, N, O, F, and Ne atoms.
Notice that in C, N, and O, Hund's rule forces electrons to align their spins. For the Ne atom, all the K and L orbitals are full.

EXAMPLE 3.23 **HUND'S RULE** The Fe atom has the electronic structure $[\mathrm{Ar}]3d^6 4s^2$. Show that the Fe atom has four unpaired electrons and therefore a net angular momentum and a magnetic moment due to spin.

SOLUTION

In a closed subshell, for example, $2p$ subshell with six states given by $m_\ell = -1, 0, +1$ and $m_s = \pm\frac{1}{2}$, all m_ℓ and m_s values have been taken up by electrons, so each m_ℓ orbital is occupied and has paired electrons. Each positive m_ℓ (or m_s) value assigned to an electron is canceled by the negative m_ℓ (or m_s) value assigned to another electron in the subshell. Therefore, *there is no net angular momentum from a closed subshell.* Only unfilled subshells contribute to the overall angular momentum. Thus, only the six electrons in the $3d$ subshell need be considered.

There are five d orbitals, corresponding to $m_\ell = -2, -1, 0, 1, 2$. Five of the six electrons obey Hund's rule and align their spins, with each taking one of the m_ℓ values.

$m_\ell = -2$	-1	0	1	2
↑ ↓	↑	↑	↑	↑

The sixth must take the same m_ℓ as another electron. This is only possible if they pair their spins. Consequently, there are four electrons with unpaired spins in the Fe atom, which gives the Fe atom a net angular momentum. The Fe atom therefore possesses a magnetic moment as a result of four electrons having their charges spinning in the same direction.

Many *isolated* atoms possess unpaired spins and hence also possess a magnetic moment. For example, the isolated Ag atom has one outer $5s$ electron with an unpaired spin and hence it is magnetic; it can be deflected in a magnetic field. The silver crystal, however, is nonmagnetic. In the crystal, the $5s$ electrons become detached to form the electron gas (metallic bonding) where they pair their spins, and the silver crystal has no net magnetic moment. The iron crystal is magnetic because the constituent Fe atoms retain at least two of the unpaired electron spins which then all align in the same direction to give the crystal an overall magnetic moment; iron is a magnetic metal.[10]

3.9 STIMULATED EMISSION AND LASERS

3.9.1 STIMULATED EMISSION AND PHOTON AMPLIFICATION

An electron can be excited from an energy level E_1 to a higher energy level E_2 by the absorption of a photon of energy $h\nu = E_2 - E_1$, as show in Figure 3.39a. When an electron at a higher energy level transits down in energy to an unoccupied energy level,

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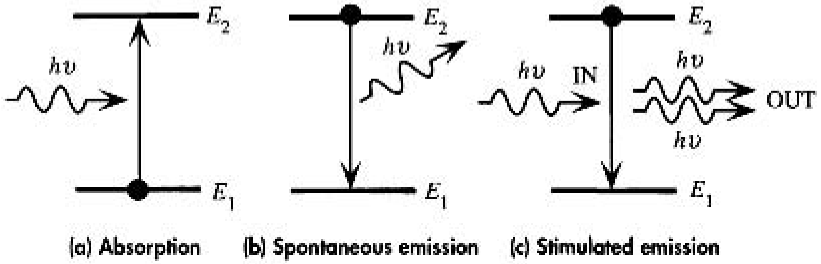
[10] This qualitative explanation is discussed in Chapter 8.



(a) Absorption (b) Spontaneous emission (c) Stimulated emission

Figure 3.39 Absorption, spontaneous emission, and stimulated emission.

it emits a photon. There are essentially two possibilities for the emission process. The electron can spontaneously undergo the downward transition by itself, or it can be induced to do so by another photon.

In **spontaneous emission,** the electron falls in energy from level E_2 to E_1 and emits a photon of energy $h\nu = E_2 - E_1$, as indicated in Figure 3.39b. The transition is only spontaneous if the state with energy E_1 is not already occupied by another electron. In classical physics, when a charge accelerates and decelerates, as in an oscillatory motion, with a frequency ν, it emits an electromagnetic radiation also of frequency ν. The emission process during the transition of the electron from E_2 to E_1 appears as if the electron is oscillating with a frequency ν.

In **stimulated emission,** an incoming photon of energy $h\nu = E_2 - E_1$ stimulates the emission process by inducing the electron at E_2 to transit down to E_1. The emitted photon is in phase with the incoming photon, it is going in the same direction, and it has the same frequency, since it must also have the energy $E_2 - E_1$, as shown in Figure 3.39c. To get a feel for what is happening during stimulated emission, imagine the electric field of the incoming photon coupling to the electron and thereby driving it with the same frequency as the photon. The forced oscillation of the electron at a frequency $\nu = (E_2 - E_1)/h$ causes the electron to emit electromagnetic radiation, for which the electric field is totally in phase with that of the stimulating photon. When the incoming photon leaves the site, the electron can return to E_1, because it has emitted a photon of energy $h\nu = E_2 - E_1$.

Stimulated emission is the basis for photon amplification, since one incoming photon results in two outgoing photons, which are in phase. It is possible to achieve a practical light amplifying device based on this phenomenon. From Figure 3.39c, we see that to obtain stimulated emission, the incoming photon should not be absorbed by another electron at E_1. When we are considering using a collection of atoms to amplify light, we must therefore require that the majority of the atoms be at the energy level E_2. If this were not the case, the incoming photons would be absorbed by the atoms at E_1. When there are more atoms at E_2 than at E_1, we have what is called a **population inversion.** It should be apparent that with two energy levels, we can never achieve a population at E_2 greater than that at E_1, because, in the steady state, the incoming photon flux will cause as many upward excitations as downward stimulated emissions.

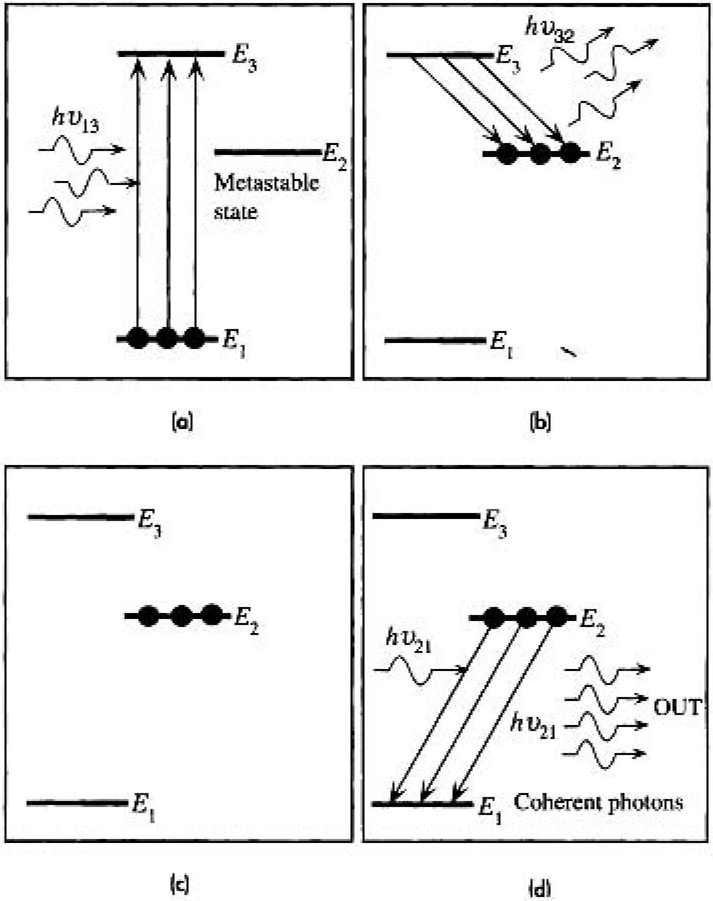


Figure 3.40 The principle of the LASER.

(a) Atoms in the ground state are pumped up to energy level E_3 by incoming photons of energy $h\nu_{13} = E_3 - E_1$.

(b) Atoms at E_3 rapidly decay to the metastable state at energy level E_2 by emitting photons or emitting lattice vibrations: $h\nu_{32} = E_3 - E_2$.

(c) Since the states at E_2 are metastable, they quickly become populated, and there is a population inversion between E_2 and E_1.

(d) A random photon of energy $h\nu_{21} = E_2 - E_1$ can initiate stimulated emission. Photons from this stimulated emission can themselves further stimulate emissions, leading to an avalanche of stimulated emissions and coherent photons being emitted.

Let us consider the three-energy-level system shown in Figure 3.40. Suppose an external excitation causes the atoms[11] in this system to become excited to energy level E_3. This is called the **pump energy level,** and the process of exciting the atoms to E_3 is called **pumping.** In the present case, **optical pumping** is used, although this is not the only means of taking the atoms to E_3. Suppose further that the atoms in E_3 decay rapidly to energy level E_2, which happens to correspond to a state that does not rapidly and spontaneously decay to a lower energy state. In other words, the state at E_2 is a **long-lived state.**[12] Quite often, the long-lived states are referred to as **metastable states.** Since the atoms cannot decay rapidly from E_2 to E_1, they accumulate at this energy level, causing a population inversion between E_2 and E_1 as pumping takes more and more atoms to E_3 and hence to E_2.

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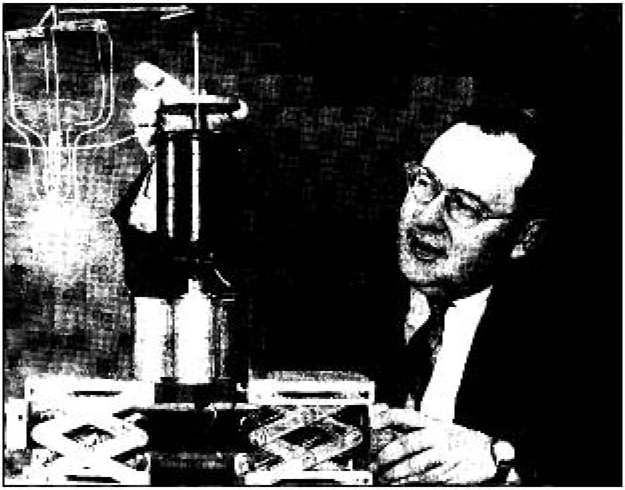
[11] An atom is in an excited state when one (or more) of its electrons is excited from the ground energy to a higher energy level. The ground state of an atom has all the electrons in their lowest energy states consistent with the Pauli exclusion principle and Hund's rule.

[12] We will not examine what causes certain states to be long lived; we will simply accept that these states do not decay rapidly and spontaneously to lower energy states.



Arthur L. Schawlow in 1961 with a ruby laser built by his Stanford group. The solid state laser was a dark ruby crystal containing Cr^{3+} ions. Lasing is obtained by stimulated emission from the Cr^{3+} ions. Arthur Schawlow won the Nobel prize in Physics in 1981 for his contribution to the development of laser spectroscopy.

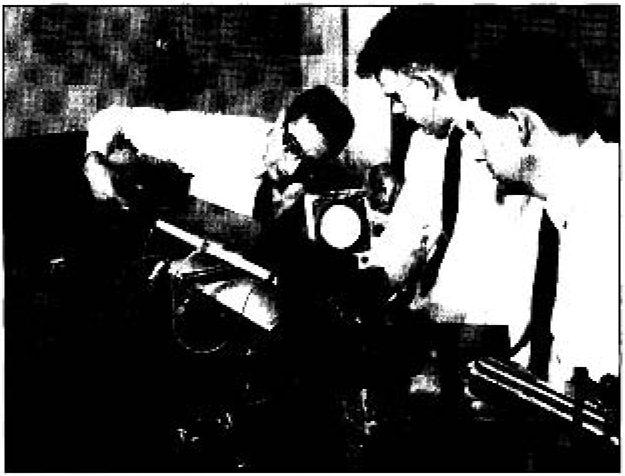
SOURCE: Stanford University, courtesy of AIP Emilio Segrè Visual Archives.

When one atom at E_2 decays spontaneously, it emits a photon, which can go on to a neighboring atom and cause that to execute stimulated emission. The photons from the latter can then go on to the next atom at E_2 and cause that atom to emit by stimulated emission, and so on. The result is an avalanche effect of stimulated emission processes with all the photons in phase, so the light output is a large collection of coherent photons. This is the principle of the ruby laser in which the energy levels E_1, E_2, and E_3 are those of the Cr^{+3} ion in the Al_2O_3 crystal. At the end of the avalanche of stimulated emission processes, the atoms at E_2 will have returned to E_1 and can be pumped again to repeat the stimulated emission cycle again. The emission from E_2 to E_1 is called the **lasing emission.**

The system we have just described for photon amplification is a **LASER,** an acronym for light amplification by stimulated emission of radiation. In the ruby laser, pumping is achieved by using a xenon flashlight. The lasing atoms are chromium ions (Cr^{3+}) in a crystal of alumina Al_2O_3 (sapphire). The ends of the ruby crystal are silvered to reflect the stimulated radiation back and forth so that its intensity builds up, in much the same way we build up voltage oscillations in an electric oscillator circuit. One of the mirrors is partially silvered to allow some of this radiation to be tapped out. What comes out is a highly coherent radiation with a high intensity. The coherency and the well-defined wavelength of this radiation are what make it distinctly different from a random stream of different-wavelength photons emitted from a tungsten bulb.

3.9.2 HELIUM–NEON LASER

With the helium–neon (HeNe) laser, the actual operation is not simple, since we need to know such things as the energy states of the whole atom. We will therefore only consider the lasing emission at 632.8 nm, which gives the well-known red color to the laser light. The actual stimulated emission occurs from the Ne atoms; He atoms are used to excite the Ne atoms by atomic collisions.



Ali Javan and his associates William Bennett Jr. and Donald Herriott at Bell Labs were first to successfully demonstrate a continuous wave (cw) helium-neon laser operation (1960).
SOURCE: Courtesy of Bell Labs, Lucent Technologies.

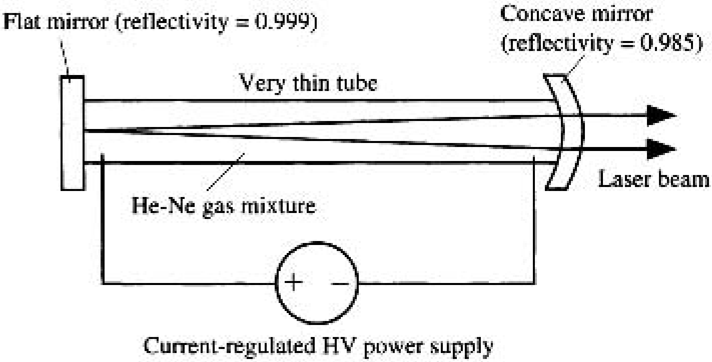


Figure 3.41 Schematic illustration of the HeNe laser.

A modern stabilized HeNe laser.
SOURCE: Courtesy of Melles Griot.

Ne is an inert gas with a ground state $(1s^2 2s^2 2p^6)$, which is represented as $(2p^6)$ when the inner closed $1s$ and $2s$ subshells are ignored. If one of the electrons from the $2p$ orbital is excited to a $5s$ orbital, the excited configuration $(2p^5 5s^1)$ is a state of the Ne atom that has higher energy. Similarly, He is an inert gas with the ground-state configuration of $(1s^2)$. The state of He when one electron is excited to a $2s$ orbital can be represented as $(1s^1 2s^1)$, which has higher energy.

The HeNe laser consists of a gaseous mixture of He and Ne atoms in a gas discharge tube, as shown schematically in Figure 3.41. The ends of the tube are mirrored to reflect the stimulated radiation and to build up the intensity within the cavity. If sufficient dc high voltage is used, electrical discharge is obtained within the tube, causing the He atoms to become excited by collisions with the drifting electrons. Thus,

$$\text{He} + e^- \rightarrow \text{He}^* + e^-$$

where He* is an excited He atom.

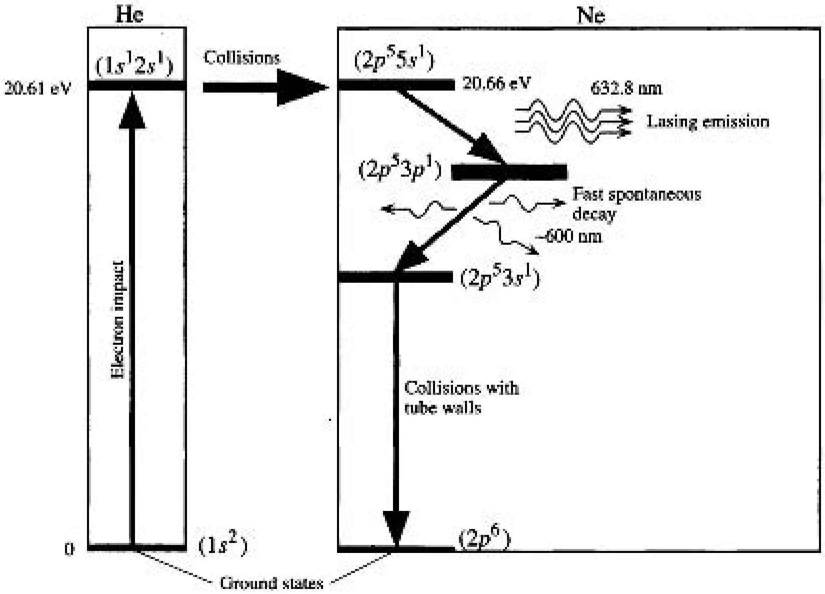


Figure 3.42 The principle of operation of the HeNe laser. Important HeNe laser energy levels (for 632.8 nm emission).

The excitation of the He atom by an electron collision puts the second electron in He into a $2s$ state, so the excited He atom, He*, has the configuration $(1s^1 2s^1)$. This atom is metastable (long lasting) with respect to the $(1s^2)$ state, as shown schematically in Figure 3.42. He* cannot spontaneously emit a photon and decay down to the $(1s^2)$ ground state because $\Delta\ell$ must be ± 1. Thus, a large number of He* atoms build up during the electrical discharge.

When an excited He atom collides with a Ne atom, it transfers its energy to the Ne atom by resonance energy exchange. This happens because, by good fortune, Ne has an empty energy level, corresponding to the $(2p^5 5s^1)$ configuration, which matches that of $(1s^1 2s^1)$ of He*. The collision process excites the Ne atom and de-excites He* down to its ground energy, that is,

$$\mathrm{He}^* + \mathrm{Ne} \rightarrow \mathrm{He} + \mathrm{Ne}^*$$

With many He*–Ne collisions in the gaseous discharge, we end up with a large number of Ne* atoms and a population inversion between the $(2p^5 5s^1)$ and $(2p^5 3p^1)$ states of the Ne atom, as indicated in Figure 3.42. The spontaneous emission of a photon from one Ne* atom falling from $5s$ to $3p$ gives rise to an avalanche of stimulated emission processes, which leads to a lasing emission with a wavelength of 632.8 nm, in the red.

There are a few interesting facts about the HeNe laser, some of which are quite subtle. First, the $(2p^5 5s^1)$ and $(2p^5 3p^1)$ electronic configurations of the Ne atom actually have a spread of energies. For example for Ne$(2p^5 5s^1)$, there are four closely spaced energy levels. Similarly, for Ne$(2p^5 3p^1)$, there are 10 closely separated energies. We can therefore achieve population inversion with respect to a number of energy levels. As a result, the lasing emissions from the HeNe laser contain a variety of wavelengths. The two lasing emissions in the visible spectrum, at 632.8 nm and 543 nm, can be used to build a red or green HeNe laser. Further, we should note that the energy of the Ne($2p^54p^1$) state (not shown) is above that of Ne($2p^53p^1$) but below that of Ne($2p^55s^1$). Consequently, there will also be stimulated transitions from Ne($2p^55s^1$) to Ne($2p^54p^1$), and hence a lasing emission at a wavelength of ~3.39 μm infrared. To suppress lasing emissions at the unwanted wavelengths (*e.g.*, the infrared) and to obtain lasing only at the wavelength of interest, we can make the reflecting mirrors wavelength selective. This way the optical cavity builds up optical oscillations at the selected wavelength.

From ($2p^53p^1$) energy levels, the Ne atoms decay rapidly to the ($2p^53s^1$) energy levels by spontaneous emission. Most of the Ne atoms with the ($2p^53s^1$) configuration, however, cannot simply return to the ground state $2p^6$, because the return of the electron in $3s$ requires that its spin be flipped to close the $2p$ subshell. An electromagnetic radiation cannot change the electron spin. Thus, the Ne($2p^53s^1$) energy levels are metastable. The only possible means of returning to the ground state (and for the next repumping act) is collisions with the walls of the laser tube. Therefore, we cannot increase the power obtainable from a HeNe laser simply by increasing the laser tube diameter, because that will accumulate more Ne atoms at the metastable ($2p^53s^1$) states.

A typical HeNe laser, illustrated in Figure 3.41, consists of a narrow glass tube that contains the He and Ne gas mixture (typically, the He to Ne ratio is 10:1). The lasing emission intensity increases with tube length, since more Ne atoms are then used in stimulated emission. The intensity decreases with increasing tube diameter, since Ne atoms in the ($2p^53s^1$) states can only return to the ground state by collisions with the walls of the tube. The ends of the tube are generally sealed with a flat mirror (99.9 percent reflecting) at one end and, for easy alignment, a concave mirror (98.5 percent reflecting) at the other end, to obtain an optical cavity within the tube. The outer surface of the concave mirror is ground to behave like a convergent lens, to compensate for the divergence in the beam arising from reflections from the concave mirror. The output radiation from the tube is typically a beam of diameter 0.5–2 mm and a divergence of 1 milliradians at a power of a few milliwatts. In high-power HeNe lasers, the mirrors are external to the tube. In addition, Brewster windows are fused at the ends of the laser tube, to allow only polarized light to be transmitted and amplified within the cavity, so that the output radiation is polarized (that is, has electric field oscillations in one plane).

EXAMPLE 3.24 **EFFICIENCY OF THE HeNe LASER** A typical low-power 2.5 mW HeNe laser tube operates at a dc voltage of 2 kV and carries a current of 5 mA. What is the efficiency of the laser?

SOLUTION

From the definition of efficiency,

$$\text{Efficiency} = \frac{\text{Output power}}{\text{Input power}}$$

$$= \frac{(2.5 \times 10^{-3}\ \text{W})}{(5 \times 10^{-3}\ \text{A})(2000\ \text{V})} = 0.00025 \qquad \text{or} \qquad 0.025\%$$

3.9.3 LASER OUTPUT SPECTRUM

The output radiation from a laser is not actually at one single well-defined wavelength corresponding to the lasing transition. Instead, the output covers a spectrum of wavelengths with a central peak. This is not a simple consequence of the Heisenberg uncertainty principle (which does broaden the output). Predominantly, it is a result of the broadening of the emitted spectrum by the **Doppler effect.** We recall from the kinetic molecular theory that gas atoms are in random motion, with an average translational kinetic energy of $\frac{3}{2}kT$. Suppose that these gas atoms emit radiation of frequency ν_0 which we label as the source frequency. Then, due to the Doppler effect, when a gas atom moves toward an observer, the latter detects a higher frequency ν_2, given by

$$\nu_2 = \nu_0\left(1 + \frac{v_x}{c}\right)$$

Doppler effect

where v_x is the relative velocity of the atom with respect to the observer and c is the speed of light. When the atom moves away, the observer detects a smaller frequency, which corresponds to

$$\nu_1 = \nu_0\left(1 - \frac{v_x}{c}\right)$$

Doppler effect

Since the atoms are in random motion, the observer will detect a range of frequencies, due to this Doppler effect. As a result, the frequency or wavelength of the output radiation from a gas laser will have a "linewidth" of $\Delta\nu = \nu_2 - \nu_1$, called a Doppler-broadened **linewidth** of a laser radiation. Other mechanisms also broaden the output spectrum, but we will ignore these at present.

The reflections from the laser end mirrors give rise to traveling waves in opposite directions within the cavity. Since the waves are in phase, they interfere constructively, to set up a standing wave—in other words, stationary oscillations. Some of the energy in this wave is tapped by the 99 percent reflecting mirror to get an output, in much the same way that we tap the energy from an oscillating field in an LC circuit by attaching an antenna to it.

Only standing waves with certain wavelengths can be maintained within the optical cavity, just as only certain acoustic wavelengths can be obtained from musical instruments. Any standing wave in the cavity must have a half-wavelength $\lambda/2$ that fits into the cavity length L, or

$$n\left(\frac{\lambda}{2}\right) = L \qquad [3.56]$$

Laser cavity modes

where n is an integer called the **mode number** of the standing wave. Each possible standing wave within the laser tube (cavity) satisfying Equation 3.56 is called a **cavity mode.** The laser output thus has a broad spectrum with peaks at certain wavelengths corresponding to various cavity modes existing within the Doppler-broadened emission curve. Figure 3.43 shows the expected output from a typical gas laser. At wavelengths satisfying Equation 3.56, that is, representing certain cavity modes, we have intensity spikes in the output. The net envelope of the output

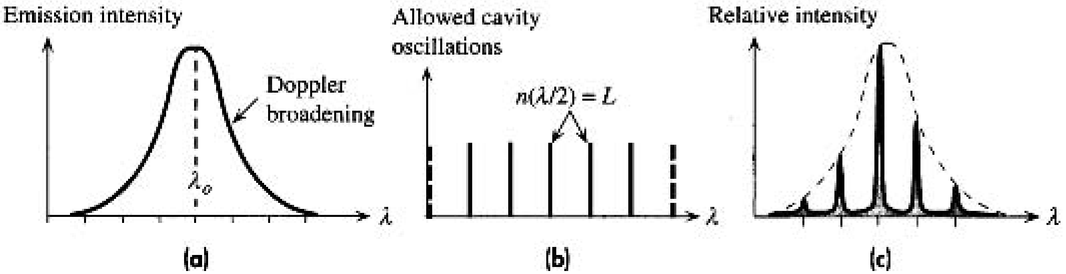


Figure 3.43
(a) Doppler-broadened emission versus wavelength characteristics of the lasing medium.
(b) Allowed oscillations and their wavelengths within the optical cavity.
(c) The output spectrum is determined by satisfying (a) and (b) simultaneously.

radiation is a Gaussian distribution, which is essentially due to the Doppler-broadened linewidth.

Even though we can try to get as parallel a beam as possible by lining the mirrors up perfectly, we will still be faced with diffraction effects at the output. When the output laser beam hits the end of the laser tube, it becomes diffracted, so the emerging beam is necessarily divergent. Simple diffraction theory can readily predict the divergence angle.

EXAMPLE 3.25

DOPPLER-BROADENED LINEWIDTH Calculate the Doppler-broadened linewidths $\Delta\nu$ and $\Delta\lambda$ for the HeNe laser transition $\lambda = 632.8$ nm, if the gas discharge temperature is about 127 °C. The atomic mass of Ne is 20.2 g mol^{-1}.

SOLUTION

Due to the Doppler effect, the laser radiation from gas lasers is broadened around a central frequency ν_o, which corresponds to the source frequency. Higher frequencies detected will be due to radiations emitted from atoms moving toward the observer, and lower frequencies detected will be the result of emissions from atoms moving away from the observer. Therefore, the width of the observed frequencies will be approximately

Doppler-broadened frequency width

$$\Delta\nu = \nu_o\left(1 + \frac{v_x}{c}\right) - \nu_o\left(1 - \frac{v_x}{c}\right) = \frac{2\nu_o v_x}{c}$$

From $\lambda = c/\nu$, we obtain the following by differentiation:

$$\frac{d\lambda}{d\nu} = -\frac{c}{\nu^2} = -\frac{\lambda}{\nu} = -\frac{\lambda^2}{c}$$

We need to know v_x, which is given by kinetic theory as $v_x^2 = kT/m$. For the HeNe laser, the Ne atoms lase, so

$$m = \frac{20.2 \times 10^{-3}\ \text{kg mol}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}} = 3.35 \times 10^{-26}\ \text{kg}$$

Thus

$$v_x = \left[\frac{(1.38 \times 10^{-23}\text{J K}^{-1})(127 + 273\ \text{K})}{(3.35 \times 10^{-26}\ \text{kg})}\right]^{1/2} = 406\ \text{m s}^{-1}$$

The central frequency is

$$\nu_o = \frac{c}{\lambda_o} = \frac{3 \times 10^8 \text{ m s}^{-1}}{632.8 \times 10^{-9} \text{ m}} = 4.74 \times 10^{14} \text{ s}^{-1}$$

The frequency linewidth is

$$\Delta\nu = \frac{(2\nu_o v_x)}{c} = \frac{2(4.74 \times 10^{14} \text{ s}^{-1})(406 \text{ m s}^{-1})}{3 \times 10^8 \text{ m s}^{-1}} = 1.283 \text{ GHz}$$

To get $\Delta\lambda$, we use $d\lambda/d\nu = -\lambda/\nu$, so that

$$\Delta\lambda = \Delta\nu\left|-\frac{\lambda_o}{\nu_o}\right| = \frac{(1.283 \times 10^9 \text{ Hz})(632.8 \times 10^{-9} \text{ m})}{4.74 \times 10^{14} \text{ s}^{-1}}$$

$$= 1.71 \times 10^{-12} \text{ m} \qquad \text{or} \qquad 0.0017 \text{ nm}$$

ADDITIONAL TOPICS

3.10 OPTICAL FIBER AMPLIFIERS

A light signal that is traveling along an optical fiber communications link over a long distance suffers marked attenuation. It becomes necessary to regenerate the light signal at certain intervals for long-haul communications over several thousand kilometers. Instead of regenerating the optical signal by photodetection, conversion to an electrical signal, amplification, and then conversion back from electrical to light energy by a laser diode, it becomes practical to amplify the signal directly by using an optical amplifier. The photons in an optical signal have a wavelength of 1550 nm, and optical amplifiers have to amplify signal photons at this wavelength.

One practical **optical amplifier** is based on the **erbium (Er^{3+} ion) doped fiber amplifier (EDFA).**[13] The core region of an optical fiber is doped with Er^{3+} ions. The host fiber core material is a glass based on SiO_3–GeO_2 and perhaps some other glass-forming oxides such as Al_2O_3. It is easily fused to a long-distance optical fiber by a technique called splicing.

When the Er^{3+} ion is implanted in the host glass material, it has the energy levels indicated in Figure 3.44 where E_1 corresponds to the lowest energy possible consistent with the Pauli exclusion principle and Hund's rule. One of the convenient energy levels for optically pumping the Er^{3+} ion is at E_3, approximately 1.27 eV above the ground energy level. The Er^{3+} ions are optically pumped, usually from a laser diode, to excite them to E_3. The wavelength for this pumping is about 980 nm. The Er^{3+} ions decay rapidly from E_3 to a **long-lived** energy level at E_2 which has a long lifetime of ~10 ms (very long on the atomic scale). The decay E_3 to E_2 involves energy losses by radiationless transitions (generation of crystal vibrations) and are very rapid. Thus, more and more Er^{3+} ions accumulate at E_2 which is 0.80 eV above the ground energy. The accumulation of Er^{3+} ions at E_2 leads to a population inversion between E_2 and E_1. Signal photons at 1550 nm have an energy of 0.80 eV, or $E_2 - E_1$, and give rise to *stimulated transitions* of Er^{3+} ions from E_2 to E_1. Any Er^{3+} ions left at E_1, however, will

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[13] EDFA was first reported in 1987 by E. Desurvire, J. R. Simpson, and P. C. Becker and, within a short period, AT&T began deploying EDFA repeaters in long-haul fiber communications in 1994.

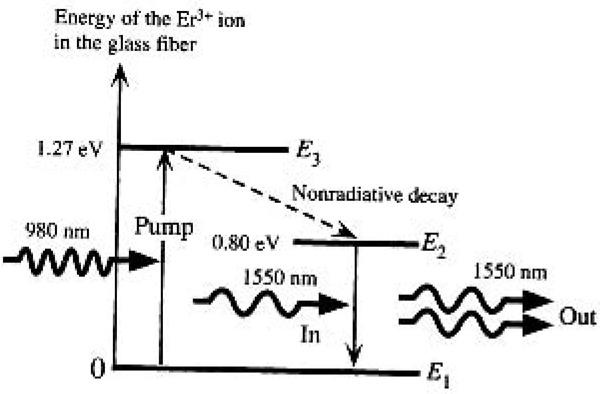

Figure 3.44 Energy diagram for the Er^{3+} ion in the glass fiber medium and light amplification by stimulated emission from E_2 to E_1.
Dashed arrows indicate radiationless transitions (energy emission by lattice vibrations).

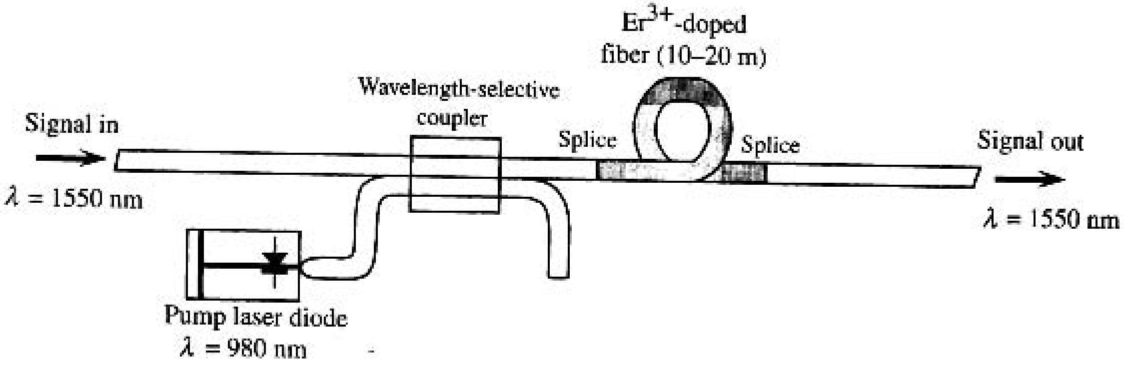

Figure 3.45 A simplified schematic illustration of an EDFA (optical amplifier).
The erbium-ion doped fiber is pumped by feeding the light from a laser pump diode, through a coupler, into the erbium-ion doped fiber.

absorb the incoming 1550 nm photons to reach E_2. To achieve light amplification we must therefore have stimulated emission exceeding absorption. This is only possible if there are more Er^{3+} ions at the E_2 level than at the E_1 level, that is, if we have population inversion. With sufficient optical pumping, population inversion is readily achieved.

In practice the erbium-doped fiber is inserted into the fiber communications line by splicing as shown in the simplified schematic diagram in Figure 3.45 and it is pumped from a laser diode through a coupling fiber arrangement which allows only the pumping wavelength to be coupled.

CD Selected Topics and Solved Problems

Selected Topics

Compton Scattering
Stimulated Emission and Laser Principles
Stimulated Emission and Optical Amplifiers
Time-Dependent Schrödinger Equation

Solved Problems

Modern Physics: Photoelectric Experiment, Ionization Energy
He–Ne Laser Problem

DEFINING TERMS

Angular momentum L about a point O is defined as $\mathbf{L} = \mathbf{p} \times \mathbf{r}$, where $\mathbf{p}$ is the linear momentum and $\mathbf{r}$ is the position vector of the body from O. For a circular orbit around O, the angular momentum is orbital and $L = pr = mvr$.

Bragg diffraction law describes the diffraction of an X-ray beam by a crystal in which the interplanar separation d of a given set of atomic planes causing the X-ray diffraction is related to the diffraction angle 2θ and the wavelength λ of the X-rays through $2d \sin\theta = n\lambda$ where n is an integer, usually unity.

Complementarity principle suggests that the wave model and the particle model are complementary models in that one model alone cannot be used to explain all the observations in nature. For example, the electron diffraction phenomenon is best explained by the wave model, whereas in the Compton experiment, the electron is treated as a particle; that is, it is deflected by an impinging photon that imparts an additional momentum to the electron.

Compton effect is the scattering of a high-energy photon by a "free" electron. The effect is experimentally observed when an X-ray beam is scattered from a target that contains many conduction ("free") electrons, such as a metal or graphite.

De Broglie relationship relates the wave-like properties (*e.g.*, wavelength λ) of matter to its particle-like properties (*e.g.*, momentum p) via $\lambda = h/p$.

Diffraction is the bending of waves as a result of the interaction of the waves with an object of size comparable to the wavelength. If the object has a regular pattern, periodicity, an incident beam of waves can be bent (diffracted) in certain well-defined directions that depend on the periodicity, which is used in the X-ray diffraction study of crystals.

Doppler effect is the change in the measured frequency of a wave due to the motion of the source relative to the observer. In the case of electromagnetic radiation, if v is the relative velocity of the source object toward the observer and ν_o is the source frequency, then the measured electromagnetic wave frequency is $\nu = \nu_o[1 + (v/c)]$ for $(v/c) \ll 1$.

Energy density ρ_E is the amount of energy per unit volume. In a region where the electric field is $\mathcal{E}$, the energy stored per unit volume is $\frac{1}{2}\varepsilon_0\mathcal{E}^2$.

Flux is a term used to describe the rate of flow through a unit area. If ΔN is the number of particles flowing through an area A in time Δt, then particle flux Γ is defined as $\Gamma = \Delta N/(A\Delta t)$. If an amount of energy ΔE flows through an area A in time Δt, energy flux is $\Gamma_E = \Delta E/(A\Delta t)$, which defines the intensity ($\mathcal{I}$) of an electromagnetic wave.

Flux in radiometry is the flow of radiation (electromagnetic wave) energy per unit time in watts. It is simply the radiation power that is flowing. In contrast, the photon or particle flux refers to the number of photons or particles flowing per unit time per unit area. **Radiant flux emitted** by a source refers to the radiation power in watts that is emitted. Flux in radiometry normally has either *radiant* or *luminous* as an adjective, *e.g.*, radiant flux, luminous flux.

Ground state is the state of the electron with the lowest energy.

Heisenberg's uncertainty principle states that the uncertainty Δx in the position of a particle and the uncertainty Δp_x in its momentum in the x direction obey $(\Delta x)(\Delta p_x) \gtrsim \hbar$. This is a consequence of the wave nature of matter and has nothing to do with the precision of measurement. If ΔE is the uncertainty in the energy of a particle during a time Δt, then according to the uncertainty principle, $(\Delta E)(\Delta t) \gtrsim \hbar$. To measure the energy of a particle without any uncertainty means that we would need an infinitely long time $\Delta t \to \infty$.

Hund's rule states that electrons in a given subshell $n\ell$ try to occupy separate orbitals (different m_ℓ) and keep their spins parallel (same m_s). In doing so, they achieve a lower energy than pairing their spins (different m_s) and occupying the same orbital (same m_ℓ).

Intensity ($\mathcal{I}$) is the flow of energy per unit area per unit time. It is equal to an energy flux.

LASER (light amplification by stimulated emission of radiation) is a device within which photon multiplication by stimulated emission produces an output radiation that is nearly monochromatic and coherent (vis-à-vis an incoherent stream of photons from a tungsten light bulb). Furthermore, the output beam has very little divergence.

Luminous flux or power Φ_v is a measure of flow of "visual energy" per unit time that takes into account the wavelength dependence of the efficiency of the human eye, that is, whether the energy that is flowing is perceptible to the human eye. It is a measure of "brightness." One lumen of luminous flux is obtained from a 1.58 mW light source emitting a single wavelength of 555 nm (green).

Magnetic quantum number m_ℓ specifies the component of the orbital angular momentum L_z in the direction of a magnetic field along z so that $L_z = \pm\hbar m_\ell$, where m_ℓ can be a negative or positive integer from $-\ell$ to $+\ell$ including 0, that is, $-\ell, -(\ell-1), \ldots, 0, \ldots, (\ell-1), \ell$. The orbital ψ of the electron depends on m_ℓ, as well as on n and ℓ. The m_ℓ, however, generally determines the angular variation of ψ.

Orbital is a region of space in an atom or molecule where an electron with a given energy may be found. Two electrons with opposite spins can occupy the same orbital. An orbit is a well-defined path for an electron, but it cannot be used to describe the whereabouts of the electron in an atom or molecule, because the electron has a probability distribution. The wavefunction $\psi_{n\ell m_\ell}(r,\theta,\phi)$ is often referred to as an orbital that represents the spatial distribution of the electron, since $|\psi_{n\ell m_\ell}(r,\theta,\phi)|^2$ is the probability of finding the electron per unit volume at (r,θ,ϕ).

Orbital (angular momentum) quantum number specifies the magnitude of the orbital angular momentum of the electron via $L = \hbar\sqrt{[\ell(\ell+1)]}$, where ℓ is the orbital quantum number with values $0, 1, 2, 3, \ldots, n-1$. The ℓ values 0, 1, 2, 3 are labeled the s, p, d, f states.

Orbital wavefunction describes the spatial dependence of the electron, not its spin. It is $\psi(r,\theta,\phi)$, which depends on n, ℓ, and m_ℓ, with the spin dependence m_s excluded. Generally, $\psi(r,\theta,\phi)$ is simply called an orbital.

Pauli exclusion principle requires that no two electrons in a given system may have the same set of quantum numbers, n, ℓ, m_ℓ, m_s. In other words, no two electrons can occupy a given state $\psi(n,\ell,m_\ell,m_s)$. Equivalently, up to two electrons with opposite spins can occupy a given orbital $\psi(n,\ell,m_\ell)$.

Photoelectric effect is the emission of electrons from a metal upon illumination with a frequency of light above a critical value which depends on the material. The kinetic energy of the emitted electron is independent of the light intensity and dependent on the light frequency ν, via $KE = h\nu - \Phi$ where h is Planck's constant and Φ is a material-related constant called the **work function.**

Photon is a quantum of energy $h\nu$ (where h is Planck's constant and ν is the frequency) associated with electromagnetic radiation. A photon has a zero rest mass and a momentum p given by the de Broglie relationship $p = h/\lambda$, where λ the wavelength. A photon does have a "moving mass" of $h\nu/c^2$, so it experiences gravitational attraction from other masses. For example, light from a star gets deflected as it passes by the sun.

Population inversion is the phenomenon of having more atoms occupy an excited energy level E_2, higher than a lower energy level, E_1, which means that the normal equilibrium distribution is reversed; that is, $N(E_2) > N(E_1)$. Population inversion occurs temporarily as a result of the excitation of a medium (pumping). If left on its own, the medium will eventually return to its equilibrium population distribution, with more atoms at E_1 than at E_2. For gas atoms, this means $N(E_2)/N(E_1) \approx \exp[-(E_2 - E_1)/kT]$.

Principal quantum number n is an integer quantum number with values $1, 2, 3, \ldots$ that characterizes the total energy of an electron in an atom. The energy increases with n. With the other quantum numbers ℓ and m_ℓ, n determines the orbital of the electron in an atom, or $\psi_{n\ell m_\ell}(r,\theta,\phi)$. The values $n = 1, 2, 3, 4, \ldots$ are labeled the $K, L, M, N, \ldots$ shells, within each of which there may be subshells based on $\ell = 0, 1, 2, \ldots (n-1)$ and corresponding to the $s, p, d, \ldots$ states.

Pumping means exciting atoms from their ground states to higher energy states.

Radiant is a common adjective used to imply the involvement of radiation, that is, electromagnetic waves, in the noun that it qualifies; *e.g.*, *radiant energy* is the energy transmitted by radiation.

Radiant power is radiation energy flowing, or emitted from a source, per unit time, which is also known as **optical power** even if the wavelength is not within the visible spectrum. **Radiant flux** signifies radiant power flow in radiometry, measured in watts.

Radiation normally signifies a traveling electromagnetic wave that is carrying energy. Due to the particle-like behavior of waves, radiation can also mean a *stream of photons*.

Schrödinger equation is a fundamental equation in nature, the solution of which describes the wave-like behavior of a particle. The equation cannot be derived from a more fundamental law. Its validity is based on its ability to predict any known physical phenomena. The solution requires as input the potential energy function $V(x, y, z, t)$ of the particle and the boundary and initial conditions. The *PE* function $V(x, y, z, t)$ describes the interaction of the particle with its environment. The time-independent Schrödinger equation describes the wave behavior of a particle under steady-state conditions, that is, when the *PE* is time-independent $V(x, y, z)$. If E is the total energy and $\nabla^2 = (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$, then

$$\nabla^2\psi + \left(\frac{2m}{\hbar^2}\right)[E - V(x, y, z)]\psi = 0$$

The solution of the time-independent Schrödinger equation gives the wavefunction $\psi(x, y, z)$ of the electron and its energy E. The interpretation of the wavefunction $\psi(x, y, z)$ is that $|\psi(x, y, z)|^2$ is the probability of finding the electron per unit volume at point x, y, z.

Selection rules determine what values of ℓ and m_ℓ are allowed for an electron transition involving the emission and absorption of electromagnetic radiation, that is, a photon. In summary, $\Delta\ell = \pm 1$ and $\Delta m_\ell = 0, \pm 1$. The spin number m_s of the electron remains unchanged. Within an atom, the transition of the electron from one state $\psi(n, \ell, m_\ell, m_s)$ to another $\psi(n', \ell', m'_\ell, m'_s)$, due to collisions with other atoms or electrons, does not necessarily obey the selection rules.

Spin of an electron S is its intrinsic angular momentum (analogous to the spin of Earth around its own axis), which is space quantized to have two possibilities. The magnitude of the electron's spin is a constant, $\hbar\sqrt{3}/2$, but its component along a magnetic field in the z direction is $m_s\hbar$, where m_s is the **spin magnetic quantum number,** which is $+\frac{1}{2}$ or $-\frac{1}{2}$.

Spontaneous emission is the phenomenon in which a photon is emitted when an electron in a high energy state $\psi(n, \ell, m_\ell, m_s)$ with energy E_2 spontaneously falls down to a lower, unoccupied energy state $\psi(n', \ell', m'_\ell, m'_s)$ with energy E_1. The photon energy is $h\nu = (E_2 - E_1)$. Since the emitted photon has an angular momentum, the orbital quantum number ℓ of the electron must change, that is $\Delta\ell = \ell' - \ell = \pm 1$.

State is a possible wavefunction for the electron that defines its spatial (orbital) and spin properties. For example, $\psi(n, \ell, m_\ell, m_s)$ is a state of the electron. From the Schrödinger equation, each state corresponds to a certain electron energy E. We use the terms state of energy E, or *energy state*. There is generally more than one state ψ with the same energy E.

Stimulated emission is the phenomenon in which an incoming photon of energy $h\nu = E_2 - E_1$ interacts with an electron in a high-energy state $\psi(n, \ell, m_\ell, m_s)$ at E_2, and induces that electron to oscillate down to a lower, unoccupied energy state, $\psi(n', \ell', m'_\ell, m'_s)$ at E_1. The photon emitted by stimulation has the same energy and phase as the incoming photon, and it moves in the same direction. Consequently, stimulated emission results in two coherent photons, with the same energy, traveling in the same direction. The stimulated emission process must obey the selection rule $\Delta\ell = \ell' - \ell = \pm 1$, just as spontaneous emission must.

Tunneling is the penetration of an electron through a potential energy barrier by virtue of the electron's wave-like behavior. In classical mechanics, if the energy E of the electron is less than the *PE* barrier V_o, the electron cannot cross the barrier. In quantum mechanics, there is a distinct probability that the electron will "tunnel" through the barrier to appear on the other side. The probability of tunneling depends very strongly on the height and width of the *PE* barrier.

Wave is a periodically occurring disturbance, such as the displacement of atoms from their equilibrium positions in a solid carrying sound waves, or a periodic variation in a measurable quantity, such as the electric field $\mathcal{E}(x, t)$ in a medium or space. In a traveling wave, energy is transferred from one location to another by the oscillations. For example, $\mathcal{E}_y(x, t) = \mathcal{E}_o \sin(kx - \omega t)$ is a traveling wave in the x direction, where $k = 2\pi/\lambda$ and $\omega = 2\pi\nu$. The electric field in the y direction varies periodically along x, with a period λ called the wavelength. The field also varies with time, with a period $1/\nu$, where ν is the frequency. The wave propagates along the x direction with a velocity of propagation c. Electromagnetic waves are transverse waves in which the electric and magnetic fields $\mathcal{E}_y(x, t)$ and $B_z(x, t)$ are at right angles to each other, as well as to the direction of propagation x. A traveling wave in the electric field must be accompanied by a similar traveling wave in the associated magnetic field $B_z(x, t) = B_{zo} \sin(kx - \omega t)$. Typical wave-like properties are interference and diffraction.

Wave equation is a general partial differential equation in classical physics, of the form

$$v^2 \frac{\partial^2 u}{\partial x^2} - \frac{\partial^2 u}{\partial t^2} = 0$$

the solution of which describes the space and time dependence of the displacement $u(x, t)$ from equilibrium or zero, given the boundary conditions. The parameter v in the wave equation is the propagation velocity of the wave. In the case of electromagnetic waves in a vacuum, the wave equation describes the variation of the electric (or magnetic) field $\mathcal{E}(x, t)$ with space and time, $(c^2\partial^2\mathcal{E}/\partial x^2) - (\partial^2\mathcal{E}/\partial t^2) = 0$, where c is the speed of light.

Wavefunction $\Psi(x, y, z, t)$ is a probability-based function used to describe the wave-like properties of a particle. It is obtained by solving the Schrödinger equation, which in turn requires a knowledge of the *PE* of the particle and the boundary and initial conditions. The term $|\Psi(x, y, z, t)|^2$ is the probability per unit volume of finding the electron at (x, y, z) at time t. In other words, $|\Psi(x, y, z, t)|^2\,dx\,dy\,dz$ is the probability of finding the electron in the small volume $dx\,dy\,dz$ at (x, y, z) at time t. Under steady-state conditions, the wavefunction can be separated into a space-dependent component and a time-dependent component, *i.e.*, $\Psi(x, y, z, t) = \psi(x, y, z)\exp(-jEt/\hbar)$, where E is the energy of the particle and $\hbar = h/2\pi$. The spatial component $\psi(x, y, z)$ satisfies the time-independent Schrödinger equation.

Wavenumber (or wavevector) k is the number of waves per 2π of length, that is, $k = 2\pi/\lambda$.

Work function is the minimum energy required to remove an electron from inside a metal to vacuum.

X-rays are electromagnetic waves of wavelength typically in the range 10 pm–1 nm, which is shorter than ultraviolet light wavelengths. X-rays can be diffracted by crystals due to their wave-like properties.

QUESTIONS AND PROBLEMS

3.1 Photons and photon flux

a. Consider a 1 kW AM radio transmitter at 700 kHz. Calculate the number of photons emitted from the antenna per second.

b. The average intensity of sunlight on Earth's surface is about 1 kW m^{-2}. The maximum intensity is at a wavelength around 800 nm. Assuming that all the photons have an 800 nm wavelength, calculate the number of photons arriving on Earth's surface per unit time per unit area. What is the magnitude of the electric field in the sunlight?

c. Suppose that a solar cell device can convert each sunlight photon into an electron, which can then give rise to an external current. What is the maximum current that can be supplied per unit area (m^2) of this solar cell device?

3.2 Yellow, cyan, magenta, and white *Three primary colors*, red, green, and blue (RGB), can be added together in various proportions to generate any color on various displays and light emitting devices in what is known as the *additive theory of color*. For example, yellow can be generated from adding red and green, cyan from blue and green, and magenta from red and blue.

a. A device engineer wants to use three light emitting diodes (LEDs) to generate various colors in an LED-based color display that is still in the research stage. His three LEDs have wavelengths of 660 nm for red, 563 nm for green, and 450 nm for blue. He simply wishes to generate the yellow and cyan by mixing equal optical powers from these LEDs; *optical power*, or *radiant power*, is defined as the radiation energy emitted per unit time. What are the numbers of red and blue photons needed (to the nearest integer) to generate yellow and cyan, respectively, for every 100 green photons?

b. An equi-energy white light is generated by mixing red, green, and blue light in equal optical powers. Suppose that the wavelengths are 700 nm for red, 546 nm for green, and 436 nm for blue (which is one set of possible standard primary colors). Suppose that the optical power in each primary color is 0.1 W. Calculate the *total photon flux* (photons per second) needed from each primary color.

c. There are bright white LEDs on the market that generate the white light by mixing yellow (a combination of red and green) with blue emissions. The inexpensive types use a single blue LED to generate a strong blue radiation, some of which is absorbed by a phosphor in front of the LED which then emits yellow light. The yellow and the blue passing through the phosphor mix and make up the white light. In one type of white LED, the blue and yellow wavelengths are 450 nm and 564 nm, respectively. White light can be generated by setting the optical (radiative) power ratio of yellow to blue light emerging from the LED to be about 1.74. What is the ratio of the number of blue to yellow photons needed? (Sometimes the mix is not perfect and the white LED light tends to have a noticeable slight blue tint.) If the total optical power output from the white LED is 100 mW, calculate the blue and yellow total photon fluxes (photons per second).

3.3 **Brightness of laser pointers** The brightness of a light source depends not only on the radiation (optical) power emitted by the source but also on its wavelength because the human eye perceives each wavelength with a different efficiency. The visual "brightness" of a source as observed by an average daylight-adapted eye is proportional to the radiation power emitted, called the *radiant flux* Φ_e, and the efficiency of the eye to detect the spectrum of the emitted radiation. While the eye can see a red color source, it cannot see an infrared source and the brightness of the infrared source would be zero. The **luminous flux** Φ_v is a measure of *brightness*, in lumens (lm), and is defined by

$$\Phi_v = \Phi_e \times (633 \text{ lm W}^{-1}) \times \eta_{\text{eye}} \qquad \textbf{[3.57]}$$

Luminous flux, brightness

where Φ_e is the radiant flux or the radiation power emitted (in watts) and $\eta_{\text{eye}} = \eta_{\text{eye}}(\lambda)$ is the *relative luminous efficiency* (or the relative sensitivity) of an average light-adapted eye which depends on the wavelength; η_{eye} is a Gaussian looking function with a peak of unity at 555 nm. (See Figure 3.46 for η_{eye} vs. λ.) One lumen of luminous flux, or brightness, is obtained from a 1.58 mW light source emitting at a single wavelength of 555 nm (green). A typical 60 W incandescent lamp provides roughly 900 lm. When we buy a light bulb, we are buying lumens. Consider one 5 mW red 650 nm laser pointer, and another weaker 2 mW green 532 nm laser: $\eta_{\text{eye}}(650 \text{ nm}) = 0.11$ and $\eta_{\text{eye}}(532 \text{ nm}) = 0.86$. Find the luminous flux (brightness) of each laser pointer. Which is brighter? Calculate the number of photons emitted per unit time, the total *photon flux*, by each laser.

3.4 **Human eye** Photons passing through the pupil are focused by the lens onto the retina of the eye and are detected by two types of photosensitive cells, called *rods* and *cones*, as visualized in Figure 3.46. Rods are highly sensitive photoreceptors with a peak response at a wavelength of about 507 nm (green-cyan). They do not register color and are responsible for our vision under dimmed light conditions, termed **scotopic vision.** Cones are responsible for our color perception and daytime vision, called **photopic vision.** These three types of cone photoreceptors are sensitive to blue, green, and red at wavelengths, respectively, of 430 nm, 535 nm, and 575 nm. All three cones have an overall peak response at 555 nm (green), which represents the peak response of an average daylight-adapted eye or in our photopic vision.

a. Calculate the photon energy (in eV) for the peak responsivity for each of the photoreceptors in the eye (one rod and three cones).

b. Various experiments (the most well known being by Hecht et al., *J. Opt. Soc. America*, **38**, 196, 1942) have tested the threshold sensitivity of the dark-adapted eye and have estimated that visual

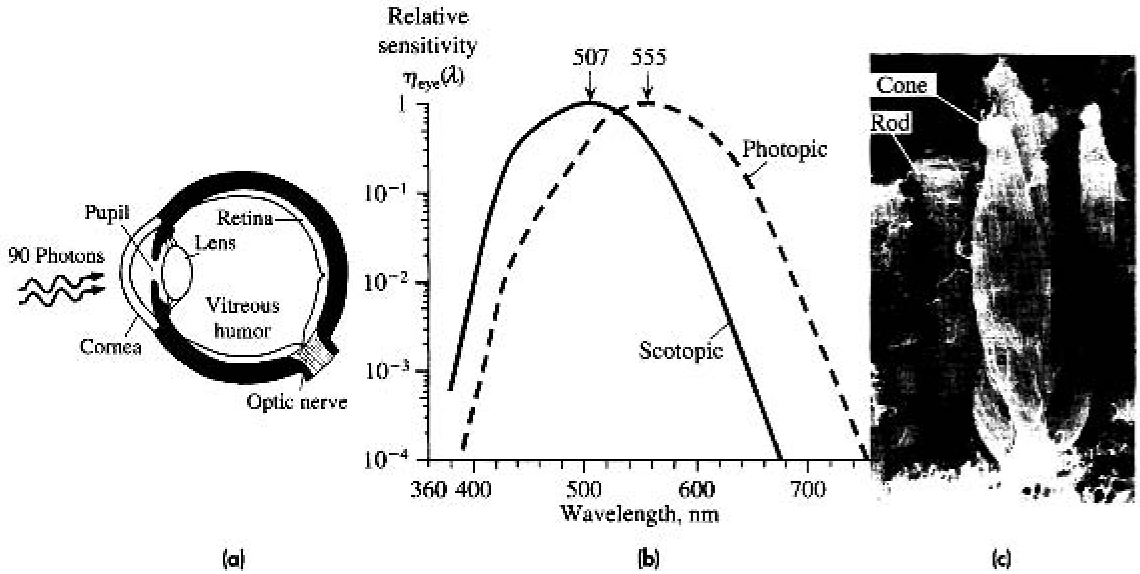

Figure 3.46

(a) The retina in the eye has photoreceptors that can sense the incident photons on them and hence provide necessary visual perception signals. It has been estimated that for minimum visual perception there must be roughly 90 photons falling on the cornea of the eye.

(b) The wavelength dependence of the relative efficiency $\eta_{\text{eye}}(\lambda)$ of the eye is different for daylight vision, or *photopic* vision (involves mainly cones), and for vision under dimmed light, or *scotopic* vision, which represents the dark-adapted eye, and involves rods.

(c) SEM photo of rods and cones in the retina.

SOURCE: Dr. Frank Werblin, University of California, Berkeley.

perception requires a minimum of roughly 90 photons to be incident onto the cornea in front of the eye's pupil and within 1/10 second. Taking 90 incident photons every 100 ms as the threshold sensitivity, calculate the total photon flux (photons per second), total energy in eV (within 100 ms), and the optical power that is needed for threshold visual perception.

c. Not all photons incident on the eye make it to the actual photoreceptors in the retina. It has been estimated that only 1 in 10 photons arriving at the eye's cornea actually make it to rod photoreceptors, due to various reflections and absorptions in the eye and other loss mechanisms. Thus, only nine photons make it to photoreceptors on the retina.[14] It is estimated that the nine test photons fall randomly onto a circular area of about 0.0025 mm^2. What is the estimated threshold intensity for visual perception? If there are 150,000 rods mm^{-2} in this area of the eye, estimate the number of rods in this test spot. If there are a large number of rods, more than 100 in this spot, then it is likely that no single rod receives more than one photon since the nine photons arrive randomly. Thus, a rod must be able to *sense* a single photon, but it takes nine excited rods, somehow summed up by the visual system, to generate the visual sensation. Do you agree with the latter conclusion?

d. It is estimated that at least 200,000 photons per second must be incident on the eye to generate a color sensation by exciting the cones. Assuming that this occurs at the peak sensitivity at 555 nm,

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[14] Sometimes one comes across a statement that the eye can detect a single photon. While a rod photoreceptor can indeed sense a single photon (or, put differently, a photon can activate a single rod), the overall human visual perception needs roughly nine photons at around 507 nm to consciously register a visual sensation.

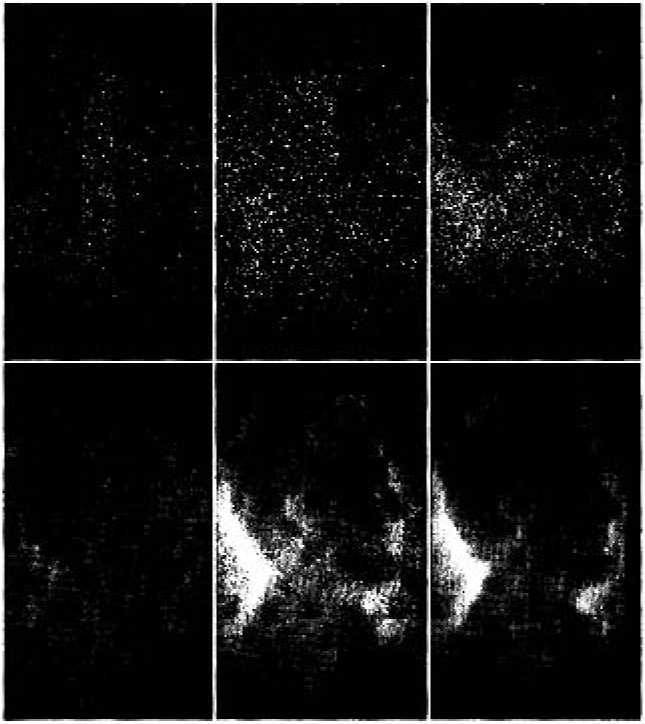
and that as in part (b) only about 10 percent of the photons make it to the retina, estimate the threshold optical power stimulating the cones in the retina.

3.5 **X-ray photons** In *chest radiology*, a patient's chest is exposed to X-rays, and the X-rays passing through the patient are recorded on a photographic film to generate an X-ray image of the chest for medical diagnosis. The average wavelength of X-rays in chest radiology is about 0.2 Å (0.02 nm). Numerous measurements indicate that the patient, on average, is exposed to a total radiation energy per unit area of roughly 0.1 μJ cm^{-2} for one chest X-ray image. Find the photon energy used in chest radiology, and the average number of photons incident on the patient per unit area (per cm^2).

*3.6 **X-rays, exposure, and roentgens** X-rays are widely used in many applications such as medical imaging, security scans, X-ray diffraction studies of crystals, and for examining defects such as cracks in objects and structures. X-rays are highly energetic photons that can easily penetrate and pass though various objects. Different materials attenuate X-rays differently, so when X-rays are passed through an object, the emerging X-rays can be recorded on a photographic film, or be captured by a modern flat panel X-ray image detector, to generate an X-ray image of the interior of the object; this is called **radiography.** X-rays also cause ionization in a medium and hence are known as *ionization radiation*. The amount of exposure (denoted by X) to X-rays, ionizing radiation, is measured in terms of the ionizing effects of the X-ray photons. One **roentgen** (1 R) is defined as an X-ray exposure that ionizes 1 cm^3 of air to generate 0.33 nC of charge in this volume at standard temperature and pressure (STP). When a body is exposed to X-rays, it will receive a certain amount of radiation energy per unit area, called **energy fluence** Ψ_E, that is, so many joules per cm^2, that depends on the exposure X. If X in roentgens is the exposure, then the energy fluence is given by

$$\Psi_E = \left[\frac{8.73 \times 10^{-6}}{\mu_{\text{en,air}}/\rho_{\text{air}}}\right] X \quad \text{J cm}^{-2} \qquad [3.58]$$

Fluence and roentgens



X-ray image of an American one-cent coin captured using an X-ray a-Se HARP camera. The first image at the top left is obtained under extremely low exposure, and the subsequent images are obtained with increasing exposure of approximately one order of magnitude between each image. The slight attenuation of the X-ray photons by Lincoln provides the image. The image sequence clearly shows the discrete nature of X-rays, and hence their description in terms of photons.

SOURCE: Courtesy of Dylan Hunt and John Rowlands, Sunnybrook Hospital, University of Toronto.

where Ψ_E is in J cm^{-2}, and $\mu_{\text{en,air}}/\rho_{\text{air}}$ is the *mass energy absorption coefficient* of air in g cm^{-2} at the photon energy E_{ph} of interest; the $\mu_{\text{en,air}}/\rho_{\text{air}}$ values are listed in radiological tables. For example, for 1 R of exposure, $X = 1$, $E_{\text{ph}} = 20$ keV, and $\mu_{\text{en,air}}/\rho_{\text{air}} = 0.539$ cm^2 g^{-1}. Equation 3.54 gives $\Psi_E = 1.62 \times 10^{-5}$ J cm^{-2} incident on the object.

a. In mammography (X-ray imaging of the breasts for breast cancer), the average photon energy is about 20 keV, and the X-ray mean exposure is 12 mR. At $E_{\text{ph}} = 20$ keV, $\mu_{\text{en,air}}/\rho_{\text{air}} = 0.539$ cm^2 g^{-1}. Find the mean energy incident per unit area in μJ cm^{-2}, and the mean number of X-ray photons incident per unit area (photons cm^{-2}), called **photon fluence** Φ.

b. In chest radiography, the average photon energy is about 60 keV, and the X-ray mean exposure is 300 μR. At $E_{\text{ph}} = 60$ keV, $\mu_{\text{en,air}}/\rho_{\text{air}} = 0.0304$ cm^2 g^{-1}. Find the mean energy incident per unit area in μJ cm^{-2}, and the mean number of X-ray photons incident per unit area.

c. A modern flat panel *X-ray image detector* is a large area image sensor that has numerous arrays of tiny pixels (millions) all tiled together to make one large continuous image sensor. Each pixel is an independent X-ray detector and converts the X-rays it receives to an electrical signal. Each tiny detector is responsible for capturing a small pixel of the whole image. (Typically, the image resolution is determined by the detector pixel size.) Each pixel in a particular experimental chest radiology X-ray sensor is 150 μm × 150 μm. If the mean exposure is 300 μR, what is the number of photons received by each pixel detector? If each pixel is required to have at least 10 photons for an acceptable signal-to-noise ratio, what is the minimum exposure required in μR?

3.7 **Photoelectric effect** A photoelectric experiment indicates that violet light of wavelength 420 nm is the longest wavelength radiation that can cause the photoemission of electrons from a particular multi-alkali photocathode surface.

a. What is the work function of the photocathode surface, in eV?

b. If a UV radiation of wavelength 300 nm is incident upon the photocathode surface, what will be the maximum kinetic energy of the photoemitted electrons, in eV?

c. Given that the UV light of wavelength 300 nm has an intensity of 20 mW cm^{-2}, if the emitted electrons are collected by applying a positive bias to the opposite electrode, what will be the photoelectric current density in mA cm^{-2}?

3.8 **Photoelectric effect and quantum efficiency** Cesium metal is to be used as the photocathode material in a photoemissive electron tube because electrons are relatively easily removed from a cesium surface. The work function of a clean cesium surface is 1.9 eV.

a. What is the longest wavelength of radiation which can result in photoemission?

b. If blue radiation of wavelength 450 nm is incident onto the Cs photocathode, what will be the kinetic energy of the photoemitted electrons in eV? What should be the voltage required on the opposite electrode to extinguish the external photocurrent?

c. **Quantum efficiency** (*QE*) of a photocathode is defined by,

Quantum efficiency definition

$$\text{Quantum efficiency} = \frac{\text{Number of photoemitted electrons}}{\text{Number of incident photons}} \qquad [3.59]$$

QE is 100 percent if each incident photon ejects one electron. Suppose that blue light of wavelength 450 nm with an intensity of 30 mW cm^{-2} is incident on a Cs photocathode that is a circular disk of diameter 6 mm. If the emitted electrons are collected by applying a positive bias voltage to the anode, and the photocathode has a *QE* of 25 percent, what will be the photoelectric current?

3.9 **Photoelectric effect** A multi-alkali metal alloy is to be used as the photocathode material in a photoemissive electron tube. The work function of the metal is 1.6 eV, and the photocathode area is 0.5 cm^2. Suppose that blue light of wavelength 420 nm with an intensity of 50 mW cm^{-2} is incident on the photocathode.

a. If the photoemitted electrons are collected by applying a positive bias to the anode, what will be the photoelectric current density assuming that the quantum efficiency η is 15 percent? *Quantum efficiency* as a percentage is the number of photoemitted electrons per 100 absorbed photons and is defined in Equation 3.60. What is the kinetic energy of a photoemitted electron at 420 nm?

b. What should be the voltage and its polarity to extinguish the current?

c. What should be the intensity of an incident red light beam of wavelength 600 nm that would give the same photocurrent if the quantum efficiency is 5 percent at this wavelength? (Normally the quantum efficiency depends on the wavelength.)

***3.10 Planck's law and photon energy distribution of radiation** Planck's law, stated in Equation 3.9, provides the spectral distribution of the black body radiation intensity in terms of wavelength through I_λ, intensity per unit wavelength. Suppose that we wish to find the distribution in terms of frequency ν or photon energy $h\nu$. Frequency $\nu = c/\lambda$ and the wavelength range λ to $\lambda + d\lambda$ corresponds to a frequency range ν to $\nu + d\nu$. ($d\lambda$ and $d\nu$ have opposite signs since ν increases as λ decreases.) The intensity $I_\lambda\, d\lambda$ in λ to $\lambda + d\lambda$ must be the same as the intensity in ν to $\nu + d\nu$, which we can write as $I_\nu\, d\nu$ where I_ν is the radiation intensity per unit frequency. Thus,

$$I_\nu = I_\lambda \left|\frac{d\lambda}{d\nu}\right|$$

The magnitude sign is needed because $\lambda = c/\nu$ results in a negative $d\lambda/d\nu$, and I_ν must be positive by definition. We can simply substitute $\lambda = c/\nu$ for λ in I_λ and obtain I_λ as a function of ν, and then find $|d\lambda/d\nu|$ to find I_ν from the preceding expression.

a. Show that

$$I_\nu = \frac{2\pi(h\nu)^3}{c^2h^3[\exp(-h\nu/kT) - 1]} \qquad [3.60]$$

Black body photon energy distribution

Equation 3.60 is written to highlight that it is a function of the *photon energy* $h\nu$, which is in joules in Equation 3.60 but can be converted to eV by dividing by 1.6×10^{-19} J eV^{-1}.

b. If we integrate I_ν over all photon energies (numerically on a calculator or a computer from 0 to say 6 eV), we would obtain the total intensity at a temperature T. Find the total intensity I_T emitted at $T = 2600$ K (a typical incandescent light bulb filament temperature) and at 6000 K (roughly representing the sun's spectrum). Plot $y = I_\nu/I_T$ versus the photon energy in eV. What are the photon energies for the peaks in the distributions? Calculate the corresponding wavelength for each using $\lambda = c/\nu$ and then compare these wavelengths with those predicted by Wien's law, $\lambda_{\max}T \approx 2.89 \times 10^{-3}$ m K.

3.11 Wien's law The maximum in the intensity distribution of black body radiation depends on the temperature. Substitute $x = hc/(\lambda kT)$ in Planck's law and plot I_λ versus x and find $\lambda_{\max}$ which corresponds to the peak of the distribution, and hence derive Wien's law. Find the peak intensity wavelength $\lambda_{\max}$ for a 40 W light bulb given that its filament operates at roughly 2400 °C.

3.12 Diffraction by X-rays and an electron beam Diffraction studies on a polycrystalline Al sample using X-rays gives the smallest diffraction angle (2θ) of 29.5° corresponding to diffraction from the (111) planes. The lattice parameter a of Al (FCC), is 0.405 nm. If we wish to obtain the same diffraction pattern (same angle) using an electron beam, what should be the voltage needed to accelerate the electron beam? Note that the interplanar separation d for planes (h, k, ℓ) and the lattice parameter a for cubic crystals are related by $d = a/(h^2 + k^2 + \ell^2)^{1/2}$.

3.13 Heisenberg's uncertainty principle Show that if the uncertainty in the position of a particle is on the order of its de Broglie wavelength, then the uncertainty in its momentum is about the same as the momentum value itself.

3.14 Heisenberg's uncertainty principle An excited electron in an Na atom emits radiation at a wavelength 589 nm and returns to the ground state. If the mean time for the transition is about 20 ns, calculate the inherent width in the emission line. What is the length of the photon emitted?

3.15 **Tunneling**

a. Consider the phenomenon of tunneling through a potential energy barrier of height V_o and width a, as shown in Figure 3.16. What is the probability that the electron will be reflected? Given the transmission coefficient T, can you find the reflection coefficient R? What happens to R as a or V_o or both become very large?

b. For a wide barrier ($\alpha a \gg 1$), show that T_o can at most be 4 and that $T_o = 4$ when $E = \frac{1}{2}V_o$.

3.16 **Electron impact excitation**

a. A projectile electron of kinetic energy 12.2 eV collides with a hydrogen atom in a gas discharge tube. Find the nth energy level to which the electron in the hydrogen atom gets excited.

b. Calculate the possible wavelengths of radiation (in nm) that will be emitted from the excited H atom in part (a) as the electron returns to its ground state. Which one of these wavelengths will be in the visible spectrum?

c. In neon street lighting tubes, gaseous discharge in the Ne tube involves electrons accelerated by the electric field impacting Ne atoms and exciting some of them to the $2p^5 3p^1$ states, as shown in Figure 3.42. What is the wavelength of emission? Can the Ne atom fall from the $2p^5 3p^1$ state to the ground state by spontaneous emission?

3.17 **Line spectra of hydrogenic atoms** Spectra of hydrogen-like atoms are classified in terms of electron transitions to a common lower energy level.

a. All transitions from energy levels $n = 2, 3, \ldots$ to $n = 1$ (the K shell) are labeled K lines and constitute the **Lyman series.** The spectral line corresponding to the smallest energy difference ($n = 2$ to $n = 1$) is labeled the K_α line, next is labeled K_β, and so on. The transition from $n = \infty$ to $n = 1$ has the largest energy difference and defines the greatest photon energy (shortest wavelength) in the K series; hence it is called the absorption edge K_{ae}. What is the range of wavelengths for the K lines? What is K_{ae}? Where are these lines with respect to the visible spectrum?

b. All transitions from energy levels $n = 3, 4, \ldots$ to $n = 2$ (L shell) are labeled L lines and constitute the **Balmer series.** What is the range of wavelengths for the L lines (*i.e.*, L_α and L_{ae})? Are these in the visible range?

c. All transitions from energy levels $n = 4, 5, \ldots$ to $n = 3$ (M shell) are labeled M lines and constitute the **Paschen series.** What is the range of wavelengths for the M lines? Are these in the visible range?

d. How would you expect the spectral lines to depend on the atomic number Z?

3.18 **Ionization energy and effective Z**

a. Consider the singly ionized Li ion, Li^+, which has lost its $2s$ electron. If the energy required to ionize one of the $1s$ electrons in Li^+ is 18.9 eV, calculate the effective nuclear charge seen by a $1s$ electron, that is, $Z_{\text{effective}}$ in the hydrogenic atom ionization energy expression in Equation 3.45; $E_{I,n} = (Z_{\text{effective}}/n)^2(13.6\text{ eV})$.

b. The B atom has a total of five electrons, two in the $1s$ orbital, two in the $2s$, and one in the $2p$. The experimental ionization energy of B is 8.30 eV. Calculate $Z_{\text{effective}}$.

c. The experimental ionization energy of Na is 3.49 eV. Calculate the effective nuclear charge seen by the $3s$ valence electron.

d. The chemical tables typically list the first, second, and third ionization energies E_1, E_2, E_3, respectively, and so on. Consider Al. E_1 represents the energy required to remove the first electron from neutral Al; E_2, the second electron from Al^+; E_3, the third electron from Al^{2+} to generate Al^{3+}. For Al, experimentally, $E_1 = 6.0$ eV, $E_2 = 18.8$ eV, and $E_3 = 28.4$ eV. For each case find the $Z_{\text{effective}}$ seen by the electron that is removed.

3.19 **Atomic and ionic radii** The maximum in the radial probability distribution of an electron in a hydrogen-like atom is given by Equation 3.38, that is, $r_{\max} = (n^2 a_o)/Z$, for $\ell = n - 1$. The average distance $\bar{r}$ of an electron from the nucleus can be calculated by using the definition of an average and the probability distribution function $P_{n,\ell}(r)$, that is,

$$\bar{r} = \int_0^\infty r P_{n,\ell}(r)\,dr = \frac{a_o n^2}{Z}\left[\frac{3}{2} - \frac{\ell(\ell+1)}{2n^2}\right]$$

Average distance of electron from nucleus

in which the right-hand side represents the result of the integration (which has been done by physicists). Calculate $r_{\max}$ and $\bar{r}$ for the $2p$ valence electron in the B atom. Which value is closer to the radius of the B atom, 0.085 nm, given in the Period Table? Consider only the outermost electrons, and calculate r_{average} for Li, Li$^+$, Be^{2+}, and B, and compare with the experimental values of the atomic or ionic sizes: 0.15 nm for Li, 0.070 nm for Li$^+$, 0.035 nm for Be^{2+}, and 0.085 nm for B.

*3.20 **X-rays and the Moseley relation** X-rays are photons with wavelengths in the range 0.01–10 nm, with typical energies in the range 100 eV to 100 keV. When an electron transition occurs in an atom from the L to the K shell, the emitted radiation is generally in the X-ray spectrum. For all atoms with atomic number $Z > 2$, the K shell is full. Suppose that one of the electrons in the K shell has been knocked out by an energetic projectile electron impacting the atom (the projectile electron would have been accelerated by a large voltage difference). The resulting vacancy in the K shell can then be filled by an electron in the L shell transiting down and emitting a photon. The emission resulting from the L to K shell transition is labeled the K_α line. The table shows the K_α line data obtained for various materials.

	Material								
	Mg	**Al**	**S**	**Ca**	**Cr**	**Fe**	**Cu**	**Rb**	**W**
Z	12	13	16	20	24	26	29	37	74
K_α line (nm)	0.987	0.834	0.537	0.335	0.229	0.194	0.154	0.093	0.021

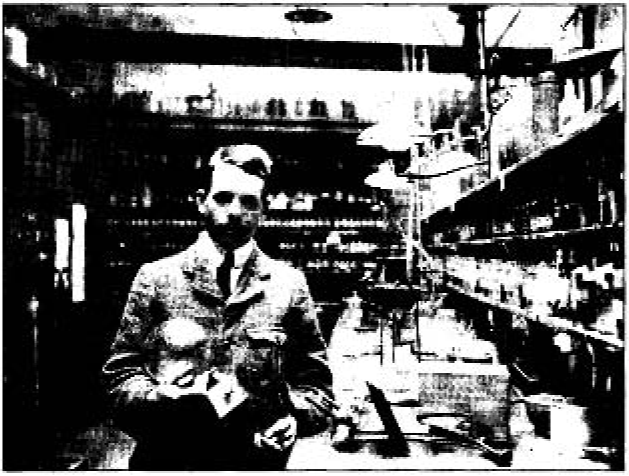
a. If ν is the frequency of emission, plot $\nu^{1/2}$ against the atomic number Z of the element.

b. H. G. Moseley, while still a graduate student of E. Rutherford in 1913, found the empirical relationship

$$\nu^{1/2} = B(Z - C)$$

Moseley relation

where B and C are constants. What are B and C from the plot? Can you give a simple explanation as to why K_α absorption should follow this relationship?



Henry G. J. Moseley (1887–1915), around 1910, carrying out experiments at Balliol-Trinity Laboratory at Oxford.

SOURCE: University of Oxford Museum of Science, courtesy AIP Emilio Segre Visual Archives.

3.21 **The He atom** Suppose that for the He atom, zero energy is taken to be the two electrons stationary at infinity (and infinitely apart) from the nucleus (He^{++}). Estimate the energy (in eV) of the electrons in the He atom by neglecting the electron–electron repulsion, that is, neglecting the potential energy due to the mutual Coulombic repulsion between the electrons. How does this compare with the experimental value of -79 eV? How strong is the electron–electron repulsion energy?

3.22 **Excitation energy of He** In the HeNe laser, an energetic electron is accelerated by the applied field impacts and excites the He from its ground state, $1s^2$, to an excited state He*, $1s^1 2s^1$, which has one of the electrons in the $2s$ orbital. The ground energy of the He atom is -79 eV with respect to both electrons isolated at infinity, which defines the zero energy. Consider the $1s^1 2s^1$ state. If we neglect the electron–electron interactions, we can calculate the energy of the $1s$ and $2s$ electrons using the energy for a hydrogenic atom, $E_n = -(Z^2/n^2)(13.6 \text{ eV})$. We can then add the electron–electron interaction energy by assuming that the $1s$ and $2s$ electrons are effectively separated by $3a_o$, which is the difference, $4a_o - 1a_o$, between the $1s$ and $2s$ Bohr radii. Calculate the overall energy of He^* and hence the excitation energy from He to He^*. The experimental value is about 20.6 eV.

3.23 **Electron affinity** The fluorine atom has the electronic configuration $[\text{He}]2s^2p^5$. The F atom can actually capture an electron to become a F^- ion, and release energy, which is listed as its *electron affinity*, 328 kJ mol^{-1}. We will assume that the two $1s$ electrons in the closed K shell (very close to the nucleus) and the two electrons in the $2s$ orbitals will shield four positive charges and thereby expose $+9e - 4e = +5e$ for the $2p$ orbital. Suppose that we try to calculate the energy of the F^- ion by simply assuming that the additional electron is attracted by an effective positive charge, $+e(5 - Z_{2p})$ or $+eZ_{\text{effective}}$, where Z_{2p} is the overall shielding effect of the five electrons in the $2p$ orbital, so that the tenth electron we have added sees an effective charge of $+eZ_{\text{effective}}$. Calculate Z_{2p} and $Z_{\text{effective}}$. The F atom does not enjoy losing an electron. The ionization energy of the F atom is 1681 kJ mol^{-1}. What is the $Z_{\text{effective}}$ that is experienced by a $2p$ electron? (Note: 1 kJ mol^{-1} = 0.01036 eV/atom.)

*3.24 **Electron spin resonance (ESR)** It is customary to write the spin magnetic moment of an electron as

Spin magnetic moment

$$\mu_{\text{spin}} = -\frac{ge}{2m_e}S$$

where S is the spin angular momentum, and g is a numerical factor, called the **g factor**, which is 2 for a free electron. Consider the interaction of an electron's spin with an external magnetic field. Show that the additional potential energy E_{BS} is given by

Electron spin in a magnetic field

$$E_{BS} = -\beta g m_s B$$

where $\beta = e\hbar/2m_e$ is called the **Bohr magneton.** Frequently **electron spin resonance** is used to examine various defects and impurities in semiconductors. A defect such as a dangling bond, for example, will have a single unpaired electron in an orbital and thus will possess a spin magnetic moment. A strong magnetic field is applied to the specimen to split the energy level E_1 of the unpaired spin to two levels $E_1 - E_{BS}$ and $E_1 + E_{BS}$, separated by ΔE_{BS}. The electron occupies the lower level $E_1 - E_{BS}$. Electromagnetic waves (usually in the microwave range) of known frequency ν, and hence of known photon energy $h\nu$, are passed through the specimen. The magnetic field B is varied until the EM waves are absorbed by the specimen, which corresponds to the excitation of the electron at each defect from $E_1 - E_{BS}$ to $E_1 + E_{BS}$, that is, $h\nu = \Delta E_{BS}$ at a certain field B. This maximum absorption condition is called **electron spin resonance,** as the electron's spin is made to resonate with the EM wave. If $B = 2$ T, calculate the frequency of the EM waves needed for ESR, taking $g = 2$. Note: For many molecules, and impurities and defects in crystals, g is not exactly 2, because the electron is in a different environment in each case. The experimentally measured value of g can be used to characterize molecules, impurities, and defects.

3.25 **Spin–orbit coupling** An electron in an atom will experience an internal magnetic field B_{int} because, from the electron's reference frame, it is the positive nucleus that is orbiting the electron. The electron will "see" the nucleus, take as charge $+e$, circling around it, which is equivalent to a current $I = +ef$ where f is the electron's frequency of rotation around the nucleus. The current I generates the internal magnetic field B_{int} at the electron. From electromagnetism texts, B_{int} is given by

$$B_{\text{int}} = \frac{\mu_o I}{2r}$$

where r is the radius of the electron's orbit and μ_o is the absolute permeability. Show that

Internal magnetic field at an electron in an atom

$$B_{\text{int}} = \frac{\mu_o e}{2\pi m_e r^3} L$$

Consider the hydrogen atom with $Z = 1$, $2p$ orbital, $n = 2$, $\ell = 1$, and take $r \approx n^2 a_o$. Calculate B_{int}.

The electron's spin magnetic moment $\boldsymbol{\mu}_{\text{spin}}$ will couple with this internal field, which means that the electron will now possess a magnetic potential energy E_{SL} that is due to the coupling of the *spin* with the *orbital motion*, called **spin-orbit coupling.** E_{SL} will be either negative or positive, with only two values, depending on whether the electron's spin magnetic moment is along or opposite $\mathbf{B}_{\text{int}}$. Take z along B_{int} so that $E_{SL} = -B_{\text{int}}\mu_{\text{spin},z}$, where $\mu_{\text{spin},z}$ is μ_{spin} along z, and then show that the energy E_2 of the $2p$ orbital splits into two closely separated levels whose separation is

Spin–orbit coupling potential energy

$$\Delta E_{SL} = \left(\frac{e\hbar}{m_e}\right) B_{\text{int}}$$

Calculate ΔE_{SL} in eV and compare it with $E_2(n = 2)$ and the separation $\Delta E = E_2 - E_1$. (The exact calculation of E_{SL} is much more complicated, but the calculated value here is sufficiently close to be useful.) What is the effect of E_{SL} on the observed emission spectrum from the H-atom transition from $2p$ to $1s$? What is the separation of the two wavelengths? The observation is called **fine structure splitting.**

3.26 **Hund's rule** For each of the following atoms and ions, sketch the electronic structure, using a box for an orbital wavefunction, and an arrow (up or down for the spin) for an electron.

a. Aluminum, [Ne]$3s^2p^1$
b. Silicon, [Ne]$3s^2p^2$
c. Phosphorus, [Ne]$3s^2p^3$
d. Sulfur, [Ne]$3s^2p^4$
e. Chlorine, [Ne]$3s^2p^5$
f. Titanium, [Ar]$3d^2 4s^2$
g. Vanadium, [Ar]$3d^3 4s^2$
h. Manganese, [Ar]$3d^5 4s^2$
i. Cobalt, [Ar]$3d^7 4s^2$
j. Cu^{2+}, [Ar]$3d^9 4s^0$

3.27 **Hund's rule** The carbon atom has the electronic structure $2s^2 2p^2$ in its ground state. The ground state and various possible excited states of C are shown in Figure 3.47. The following energies are known for the states a to e in Figure 3.47, not in any particular order: 0, 7.3 eV, 4.1 eV, 7.9 eV, and 1.2 eV. Using reasonable arguments match these energies to the states a to e. Use Hund's rule to establish the ground state with 0 eV. If you have to flip a spin to go from the ground to another configuration, that would cost energy. If you have to move an electron from a lower s to p or from p to a higher s, that would cost a lot of energy. Two electrons in the same orbital (obviously with paired electrons) would have substantial Coulombic repulsion energy.

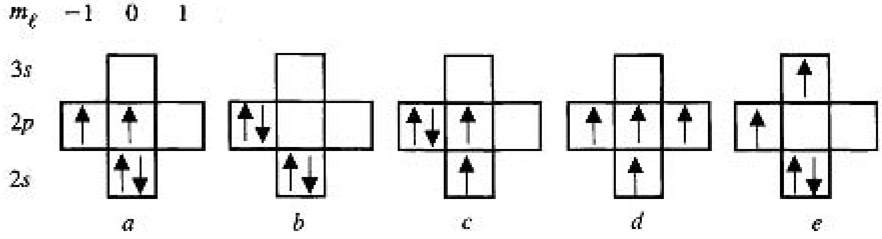


Figure 3.47
Some possible states of the carbon atom, not in any particular order.

3.28 **The HeNe laser** A particular HeNe laser operating at 632.8 nm has a tube that is 40 cm long. The operating gas temperature is about 130 °C.

a. Calculate the Doppler-broadened linewidth $\Delta\lambda$ in the output spectrum.

b. What are the n values that satisfy the resonant cavity condition? How many modes are therefore allowed?

c. Calculate the frequency separation and the wavelength separation of the laser modes. How do these change as the tube warms up during operation? Taking the linear expansion coefficient to be 10^{-6} K^{-1}, estimate the change in the mode frequency separation.

3.29 **Er^{3+}-doped fiber amplifier** When the Er^{3+} ion in the Er^{3+}-doped fiber amplifer (EDFA) is pumped with 980 nm of radiation, the Er^{3+} ions absorb energy from the pump signal and become excited to E_3 (Figure 3.44). Later the Er^{3+} ions at E_2 are stimulated to add energy (coherent photons) to the signal at 1550 nm. What is the wasted energy (in eV) from the pump to the signal at each photon amplification step? (This energy is lost as heat in the glass medium.) An Er-doped fiber amplifier is 10 m long, and the cross section of the core is 5 μm. The Er concentration in the core is 10^{18} cm^{-3}. The nominal power gain of the amplifier is 100 (or 20 dB). The pump wavelength is 980 nm, and the signal wavelength is 1550 nm. If the output power from the amplifier is 100 mW and assuming the signal and pump are confined to the core, what is the minimum intensity of the pump signal? How much power is wasted in this EDFA? (The pump must provide enough photons to pump the Er^{3+} ions needed to generate the additional output photons over that of input photons. The concentration of Er^{3+} ions in the fiber is given for information only.)

Wolfgan Pauli (1900–1958) won the Nobel prize in 1945 for his contributions to quantum mechanics. His exclusion principle was announced in 1925. "I don't mind your thinking slowly; I mind your publishing faster than you think." (Translation from German. Attributed to Pauli by H. Coblaus. From A. L. Mackay, *A Dictionary of Scientific Quotations*, Bristol: IOP Publishing, 1991, p. 191.)

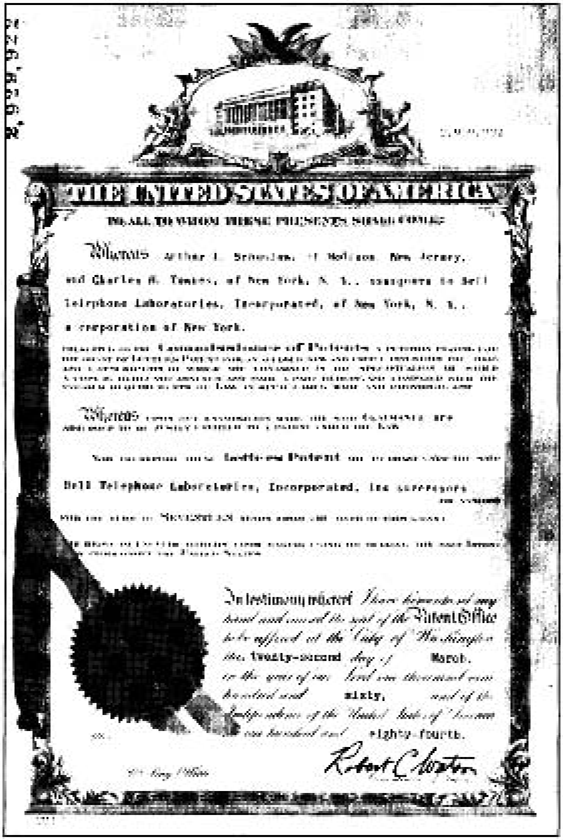
SOURCE: AIP Emilio Segrè Visual Archives, Goudsmit Collection.

Arthur Holly Compton (1892–1962) won the Nobel prize in physics in 1927 for his discovery of the Compton effect with C. T. R. Wilson in 1923.

SOURCE: King Features Syndicate, Inc., New York and Argonne National Laboratory, courtesy AIP Emilio Segrè Visual Archives.

Theodore Harold Maiman was born in 1927 in Los Angeles, son of an electrical engineer. He studied engineering physics at Colorado University, while repairing electrical appliances to pay for college, and then obtained a Ph.D. from Stanford. Theodore Maiman constructed this first laser in 1960 while working at Hughes Research Laboratories. There is a vertical chromium ion–doped ruby rod in the center of a helical xenon flash tube. The ruby rod has mirrored ends. The xenon flash provides optical pumping of the chromium ions in the ruby rod. The output is a pulse of red laser light.

SOURCE: Courtesy of HRL Laboratories, LLC, Malibu, California.



2,929,922

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

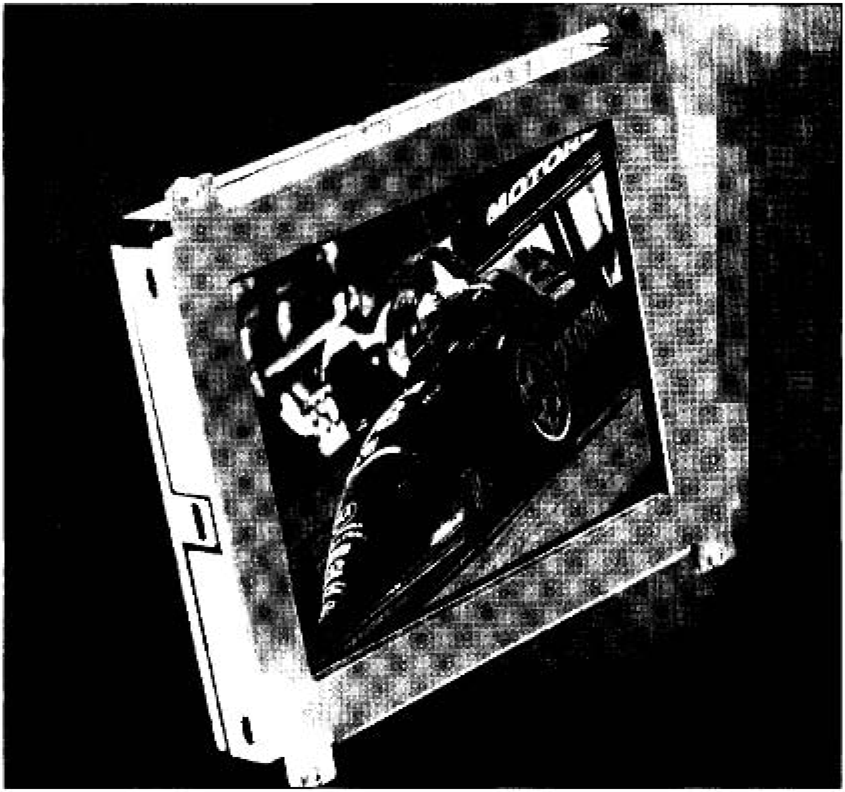
Whereas Arthur L. Schawlow, of Madison, New Jersey, and Charles H. Townes, of New York, N. Y., assignors to Bell Telephone Laboratories, Incorporated, of New York, N. Y., a corporation of New York,

Bell Telephone Laboratories, Incorporated, its successors

In testimony whereof I have hereunto set my hand and caused the seal of the Patent Office to be affixed at the City of Washington this twenty-second day of March, in the year of our Lord one thousand nine hundred and sixty, and of the Independence of the United States of America the one hundred and eighty-fourth.

Robert C. Watson

The patent for the invention of the laser by Charles H. Townes and Arthur L. Schawlow in 1960 (Courtesy of Bell Laboratories). The laser patent was later bitterly disputed for almost three decades in "the patent wars" by Gordon Gould, an American physicist, and his designated agents. Gordon Gould eventually received the U.S. patent for optical pumping of the laser in 1977 since the original laser patent did not detail such a pumping procedure. In 1987 he also received a patent for the gas discharge laser, thereby winning his 30 year patent war. His original notebook even contained the word *laser*.



Motorola's prototype flat panel display based on the Fowler–Nordheim field emission principle. The display is 14 cm in diagonal and 3.5 mm thick with a viewing angle 160°. Each pixel (325 μm thick) uses field emission of electrons from microscopic sharp point sources (icebergs). Emitted electrons impinge on colored phosphors on a screen and cause light emission by cathodoluminescence. There are millions of these microscopic field emitters to constitute the image.

SOURCE: Courtesy of Dr. Babu Chalamala, Flat Panel Display Division, Motorola.

Left: A scanning electron microscope image of an array of electron field emitters (icebergs). Center: One iceberg. Right: A cross section of a field emitter. Each iceberg is a source of electron emission arising from Fowler–Nordheim field emission; for further information see B. Chalamala, et al., *IEEE Spectrum*, April 1998, pp. 42–51.

SOURCE: Courtesy of Dr. Babu Chalamala, Flat Panel Display Division, Motorola.