Figure 5.1 Louis de Broglie was a member of an aristocratic French family that produced marshals, ambassadors, foreign ministers, and at least one duke, his older brother Maurice de Broglie. Louis de Broglie came rather late to theoretical physics, as he first studied history. Only after serving as a radio operator in World War I did he follow the lead of his older brother and begin his studies of physics. Maurice de Broglie was an outstanding experimental physicist in his own right and conducted experiments in the palatial family mansion in Paris. (*AIP Meggers Gallery of Nobel Laureates*)

5.1 THE PILOT WAVES OF DE BROGLIE

By the early 1920s scientists recognized that the Bohr theory contained many inadequacies:

- It failed to predict the observed intensities of spectral lines.
- It had only limited success in predicting emission and absorption wavelengths for multielectron atoms.
- It failed to provide an equation of motion governing the time development of atomic systems starting from some initial state.
- It overemphasized the particle nature of matter and could not explain the newly discovered wave–particle duality of light.
- It did not supply a general scheme for "quantizing" other systems, especially those without periodic motion.

The first bold step toward a new mechanics of atomic systems was taken by Louis Victor de Broglie in 1923 (Fig. 5.1). In his doctoral dissertation he postulated that *because photons have wave and particle characteristics, perhaps all forms of matter have wave as well as particle properties.* This was a radical idea with no experimental confirmation at that time. According to de Broglie, electrons had a dual particle–wave nature. Accompanying every electron was a wave (not an electromagnetic wave!), which guided, or "piloted," the electron through space. He explained the source of this assertion in his 1929 Nobel prize acceptance speech:

> On the one hand the quantum theory of light cannot be considered satisfactory since it defines the energy of a light corpuscle by the equation $E = hf$ containing the frequency f. Now a purely corpuscular theory contains nothing that enables us to define a frequency; for this reason alone, therefore, we are compelled, in the case of light, to introduce the idea of a corpuscle and that of periodicity simultaneously. On the other hand, determination of the stable motion of electrons in the atom introduces integers, and up to this point the only phenomena involving integers in physics were those of interference and of normal modes of vibration. This fact suggested to me the idea that electrons too could not be considered simply as corpuscles, but that periodicity must be assigned to them also.

Let us look at de Broglie's ideas in more detail. He concluded that the wavelength and frequency of a *matter wave* associated with any moving object were given by

De Broglie wavelength

$$\lambda = \frac{h}{p} \tag{5.1}$$

and

$$f = \frac{E}{h} \tag{5.2}$$

where h is Planck's constant, p is the relativistic momentum, and E is the total relativistic energy of the object. Recall from Chapter 2 that p and E can be written as

$$p = \gamma mv \tag{5.3}$$

and

$$E^2 = p^2c^2 + m^2c^4 = \gamma^2m^2c^4 \tag{5.4}$$

where $\gamma = (1 - v^2/c^2)^{-1/2}$ and v is the object's speed. Equations 5.1 and 5.2 immediately suggest that it should be easy to calculate the speed of a de Broglie wave from the product λf. However, as we will show later, this is not the speed of the particle. Since the correct calculation is a bit complicated, we postpone it to Section 5.3. Before taking up the question of the speed of matter waves, we prefer first to give some introductory examples of the use of $\lambda = h/p$ and a brief description of how de Broglie waves provide a physical picture of the Bohr theory of atoms.

De Broglie's Explanation of Quantization in the Bohr Model

Bohr's model of the atom had many shortcomings and problems. For example, as the electrons revolve around the nucleus, how can one understand the fact that only certain electronic energies are allowed? Why do all atoms of a given element have precisely the same physical properties regardless of the infinite variety of starting velocities and positions of the electrons in each atom?

De Broglie's great insight was to recognize that although these are deep problems for particle theories, wave theories of matter handle these problems neatly by means of interference. For example, a plucked guitar string, although initially subjected to a wide range of wavelengths, supports only standing wave patterns that have nodes at each end. Thus only a discrete set of wavelengths is allowed for standing waves, while other wavelengths not included in this discrete set rapidly vanish by destructive interference. This same reasoning can be applied to electron matter waves bent into a circle around the nucleus. Although initially a continuous distribution of wavelengths may be present, corresponding to a distribution of initial electron velocities, most wavelengths and velocities rapidly die off. The residual standing wave patterns thus account for the identical nature of all atoms of a given element and show that atoms are more like vibrating drum heads with discrete modes of vibration than like miniature solar systems. This point of view is emphasized in Figure 5.2, which shows the standing wave pattern of the electron in the hydrogen atom corresponding to the $n = 3$ state of the Bohr theory.

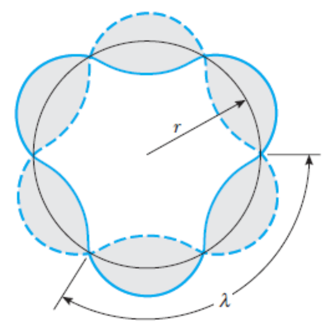

Figure 5.2 Standing waves fit to a circular Bohr orbit. In this particular diagram, three wavelengths are fit to the orbit, corresponding to the $n = 3$ energy state of the Bohr theory.

Another aspect of the Bohr theory that is also easier to visualize physically by using de Broglie's hypothesis is the quantization of angular momentum. One simply assumes that **the allowed Bohr orbits arise because the electron matter waves interfere constructively when an integral number of wavelengths exactly fits into the circumference of a circular orbit.** Thus

$$n\lambda = 2\pi r \tag{5.5}$$

where r is the radius of the orbit. From Equation 5.1, we see that $\lambda = h/m_e v$. Substituting this into Equation 5.5, and solving for $m_e vr$, the angular momentum of the electron, gives

$$\boxed{m_e vr = n\hbar} \tag{5.6}$$

Note that this is precisely the Bohr condition for the quantization of angular momentum.

EXAMPLE 5.1 Why Don't We See the Wave Properties of a Baseball?

An object will appear "wavelike" if it exhibits interference or diffraction, both of which require scattering objects or apertures of about the same size as the wavelength. A baseball of mass 140 g traveling at a speed of 60 mi/h (27 m/s) has a de Broglie wavelength given by

$$\lambda = \frac{h}{p} = \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{(0.14\ \text{kg})(27\ \text{m/s})} = 1.7 \times 10^{-34}\ \text{m}$$

Even a nucleus (whose size is $\approx 10^{-15}$ m) is much too large to diffract this incredibly small wavelength! This explains why all macroscopic objects appear particle-like.

EXAMPLE 5.2 What Size "Particles" Do Exhibit Diffraction?

A particle of charge q and mass m is accelerated from rest through a small potential difference V. (a) Find its de Broglie wavelength, assuming that the particle is non-relativistic.

Solution When a charge is accelerated from rest through a potential difference V, its gain in kinetic energy, $\frac{1}{2}mv^2$, must equal the loss in potential energy qV. That is,

$$\tfrac{1}{2}mv^2 = qV$$

Because $p = mv$, we can express this in the form

$$\frac{p^2}{2m} = qV \qquad \text{or} \qquad p = \sqrt{2mqV}$$

Substituting this expression for p into the de Broglie relation $\lambda = h/p$ gives

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mqV}}$$

(b) Calculate λ if the particle is an electron and $V = 50$ V.

Solution The de Broglie wavelength of an electron accelerated through 50 V is

$$\begin{aligned}\lambda &= \frac{h}{\sqrt{2m_e qV}}\\ &= \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{\sqrt{2(9.11 \times 10^{-31}\ \text{kg})(1.6 \times 10^{-19}\ \text{C})(50\ \text{V})}}\\ &= 1.7 \times 10^{-10}\ \text{m} = 1.7\ \text{Å}\end{aligned}$$

This wavelength is of the order of atomic dimensions and the spacing between atoms in a solid. Such low-energy electrons are routinely used in electron diffraction experiments to determine atomic positions on a surface.

Exercise 1 (a) Show that the de Broglie wavelength for an electron accelerated from rest through a *large* potential difference, V, is

$$\lambda = \frac{12.27}{V^{1/2}}\left(\frac{Ve}{2m_e c^2} + 1\right)^{-1/2} \tag{5.7}$$

where λ is in angstroms (Å) and V is in volts. (b) Calculate the percent error introduced when $\lambda = 12.27/V^{1/2}$ is used instead of the correct relativistic expression for 10 MeV electrons.

Answer (b) 230%.

5.2 THE DAVISSON–GERMER EXPERIMENT

Direct experimental proof that electrons possess a wavelength $\lambda = h/p$ was furnished by the diffraction experiments of American physicists Clinton J. Davisson (1881–1958) and Lester H. Germer (1896–1971) at the Bell Laboratories in New York City in 1927 (Fig. 5.3).[1] In fact, de Broglie had already suggested in 1924 that a stream of electrons traversing a small aperture should exhibit diffraction phenomena. In 1925, Einstein was led to the necessity of postulating matter waves from an analysis of fluctuations of a molecular gas. In addition, he noted that a molecular beam should show small but measurable diffraction effects. In the same year, Walter Elsasser pointed out that the slow

[1] C. J. Davisson and L. H. Germer, *Phys. Rev.* 30:705, 1927.

Figure 5.3 Clinton J. Davisson (left) and Lester H. Germer (center) at Bell Laboratories in New York City. (*Bell Laboratories, courtesy AIP Emilio Segrè Visual Archives*)

electron scattering experiments of C. J. Davisson and C. H. Kunsman at the Bell Labs could be explained by electron diffraction.

Clear-cut proof of the wave nature of electrons was obtained in 1927 by the work of Davisson and Germer in the United States and George P. Thomson (British physicist, 1892–1975, the son of J. J. Thomson) in England. Both cases are intriguing not only for their physics but also for their human interest. The first case was an accidental discovery, and the second involved the discovery of the particle properties of the electron by the father and the wave properties by the son.

The crucial experiment of Davisson and Germer was an offshoot of an attempt to understand the arrangement of atoms on the surface of a nickel sample by elastically scattering a beam of low-speed electrons from a polycrystalline nickel target. A schematic drawing of their apparatus is shown in Figure 5.4. Their device allowed for the variation of three experimental parameters—electron energy; nickel target orientation, α; and scattering angle, ϕ. Before a fortunate accident occurred, the results seemed quite pedestrian. For constant electron energies of about 100 eV, the scattered intensity rapidly decreased as ϕ increased. But then someone dropped a flask of liquid air on the glass vacuum system, rupturing the vacuum and oxidizing the nickel target, which had been at high temperature. To remove the oxide, the sample was reduced by heating it cautiously[2] in a flowing stream of hydrogen. When the apparatus was reassembled, quite different results were found: Strong variations in the intensity of scattered electrons with angle were observed, as shown in Figure 5.5. The prolonged heating had evidently annealed the nickel target, causing large single-crystal regions to develop in the polycrystalline sample. These crystalline regions furnished the extended regular lattice needed to observe electron diffraction. Once Davisson and Germer realized that it was the elastic scattering from *single crystals* that produced such unusual results (1925), they initiated a thorough investigation of elastic scattering from large single crystals

[2]At present this can be done without the slightest fear of "stinks or bangs," because 5% hydrogen–95% argon safety mixtures are commercially available.

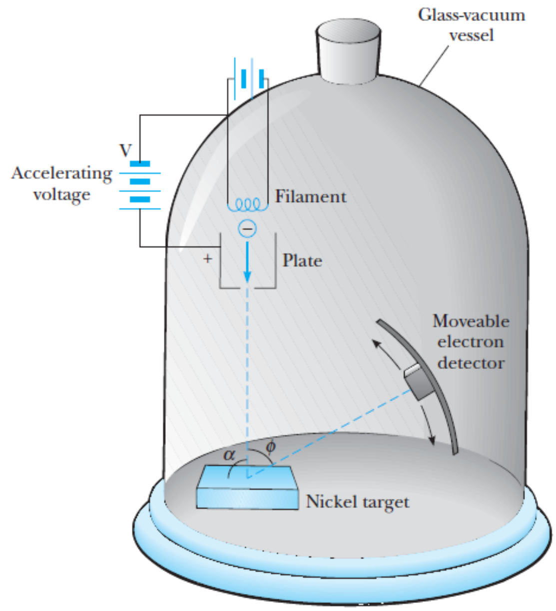

Figure 5.4 A schematic diagram of the Davisson–Germer apparatus.

with predetermined crystallographic orientation. Even these experiments were not conducted at first as a test of de Broglie's wave theory, however. Following discussions with Richardson, Born, and Franck, the experiments and their analysis finally culminated in 1927 in the proof that electrons experience diffraction with an electron wavelength that is given by $\lambda = h/p$.

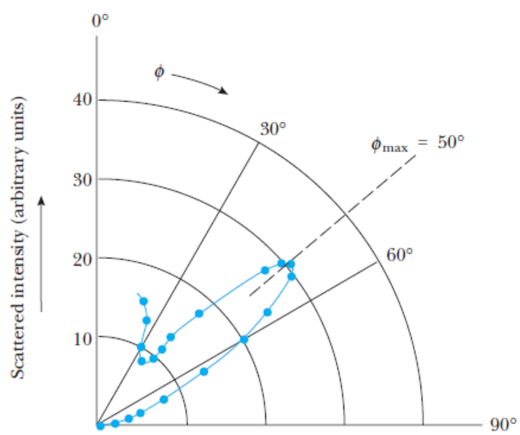

Figure 5.5 A polar plot of scattered intensity versus scattering angle for 54-eV electrons, based on the original work of Davisson and Germer. The scattered intensity is proportional to the distance of the point from the origin in this plot.

The idea that electrons behave like waves when interacting with the atoms of a crystal is so striking that Davisson and Germer's proof deserves closer scrutiny. In effect, they calculated the wavelength of electrons from a simple diffraction formula and compared this result with de Broglie's formula $\lambda = h/p$. Although they tested this result over a wide range of target orientations and electron energies, we consider in detail only the simple case shown in Figures 5.4 and 5.5 with $\alpha = 90.0°$, $V = 54.0$ V, and $\phi = 50.0°$, corresponding to the $n = 1$ diffraction maximum. In order to calculate the de Broglie wavelength for this case, we first obtain the velocity of a nonrelativistic electron accelerated through a potential difference V from the energy relation

$$\frac{1}{2} m_e v^2 = eV$$

Substituting $v = \sqrt{2Ve/m_e}$ into the de Broglie relation gives

$$\lambda = \frac{h}{m_e v} = \frac{h}{\sqrt{2Vem_e}} \tag{5.8}$$

Thus the wavelength of 54.0-V electrons is

$$\begin{aligned}\lambda &= \frac{6.63 \times 10^{-34}\,\mathrm{J \cdot s}}{\sqrt{2(54.0\ \mathrm{V})(1.60 \times 10^{-19}\ \mathrm{C})(9.11 \times 10^{-31}\ \mathrm{kg})}} \\ &= 1.67 \times 10^{-10}\ \mathrm{m} = 1.67\ \text{Å}\end{aligned}$$

The experimental wavelength may be obtained by considering the nickel atoms to be a reflection diffraction grating, as shown in Figure 5.6. Only the surface layer of atoms is considered because low-energy electrons, unlike x-rays, do not penetrate deeply into the crystal. Constructive interference occurs when the path length difference between two adjacent rays is an integral number of wavelengths or

$$d \sin \phi = n\lambda \tag{5.9}$$

As d was known to be 2.15 Å from x-ray diffraction measurements, Davisson and Germer calculated λ to be

$$\lambda = (2.15\ \text{Å})(\sin 50.0°) = 1.65\ \text{Å}$$

in excellent agreement with the de Broglie formula.

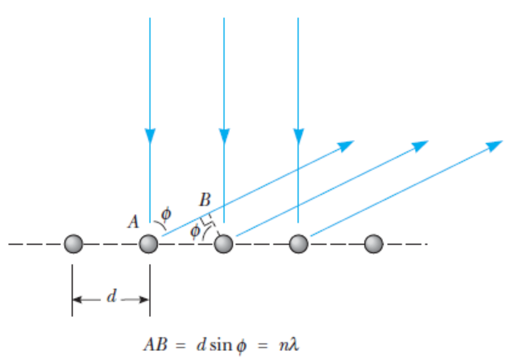

Figure 5.6 Constructive interference of electron matter waves scattered from a single layer of atoms at an angle ϕ.

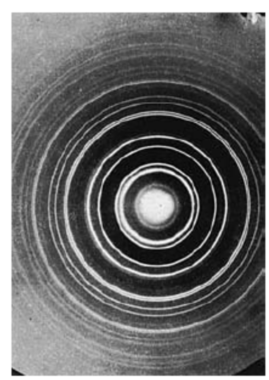

Figure 5.7 Diffraction of 50-kV electrons from a film of Cu_3Au. The alloy film was 400 Å thick. (*Courtesy of the late Dr. L. H. Germer*)

It is interesting to note that while the diffraction lines from low-energy reflected electrons are quite broad (see Fig. 5.5), the lines from high-energy electrons transmitted through metal foils are quite sharp (see Fig. 5.7). This effect occurs because hundreds of atomic planes are penetrated by high-energy electrons, and consequently Equation 5.9, which treats diffraction from a surface layer, no longer holds. Instead, the Bragg law, $2d \sin \theta = n\lambda$, applies to high-energy electron diffraction. The maxima are extremely sharp in this case because if $2d \sin \theta$ is not exactly equal to $n\lambda$, there will be no diffracted wave. This occurs because there are scattering contributions from so many atomic planes that eventually the path length difference between the wave from the first plane and some deeply buried plane will be *an odd multiple of* $\lambda/2$, resulting in complete cancellation of these waves (see Problem 13).

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If de Broglie's postulate is true for all matter, then any object of mass m has wavelike properties and a wavelength $\lambda = h/p$. In the years following Davisson and Germer's discovery, experimentalists tested the universal character of de Broglie's postulate by searching for diffraction of other "particle" beams. In subsequent experiments, diffraction was observed for helium atoms (Estermann and Stern in Germany) and hydrogen atoms (Johnson in the United States). Following the discovery of the neutron in 1932, it was shown that neutron beams of the appropriate energy also exhibit diffraction when incident on a crystalline target (Fig. 5.8).

EXAMPLE 5.3 Thermal Neutrons

What kinetic energy (in electron volts) should neutrons have if they are to be diffracted from crystals?

Solution Appreciable diffraction will occur if the de Broglie wavelength of the neutron is of the same order of magnitude as the interatomic distance. Taking $\lambda = 1.00$ Å, we find

$$p = \frac{h}{\lambda} = \frac{6.63 \times 10^{-34}\,\mathrm{J\cdot s}}{1.00 \times 10^{-10}\,\mathrm{m}} = 6.63 \times 10^{-24}\,\mathrm{kg\cdot m/s}$$

The kinetic energy is given by

$$K = \frac{p^2}{2m_\mathrm{n}} = \frac{(6.63 \times 10^{-24}\,\mathrm{J\cdot s})^2}{2(1.66 \times 10^{-27}\,\mathrm{kg})}$$
$$= 1.32 \times 10^{-20}\,\mathrm{J} = 0.0825\,\mathrm{eV}$$

Note that these neutrons are nonrelativistic because K is much less than the neutron rest energy of 940 MeV, and so our use of the classical expression $K = p^2/2m_\mathrm{n}$ is justified. Because the average thermal energy of a particle in thermal equilibrium is $\frac{1}{2}k_\mathrm{B}T$ for each independent direction of motion, neutrons at room temperature (300 K) possess a kinetic energy of

$$K = \tfrac{3}{2}k_\mathrm{B}T = (1.50)(8.62 \times 10^{-5}\,\mathrm{eV/K})(300\,\mathrm{K})$$
$$= 0.0388\,\mathrm{eV}$$

Thus "thermal neutrons," or neutrons in thermal equilibrium with matter at room temperature, possess energies of the right order of magnitude to diffract appreciably from single crystals. Neutrons produced in a nuclear reactor are far too energetic to produce diffraction from crystals and must be slowed down in a graphite column as they leave the reactor. In the graphite moderator, repeated collisions with carbon atoms ultimately reduce the average neutron energies to the average thermal energy of the carbon atoms. When this occurs, these so-called thermalized neutrons possess a distribution of velocities and a corresponding distribution of de Broglie wavelengths with average wavelengths comparable to crystal spacings.

Exercise 2 *Monochromatic Neutrons.* A beam of neutrons with a single wavelength may be produced by means of a mechanical velocity selector of the type shown in Figure 5.9. (a) Calculate the speed of neutrons with a wavelength of 1.00 Å. (b) What rotational speed (in rpm) should the shaft have in order to pass neutrons with wavelength of 1.00 Å?

Answers (a) 3.99×10^3 m/s. (b) 13,300 rev/min.

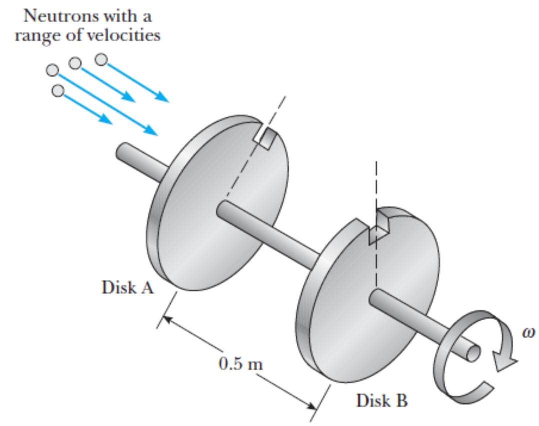
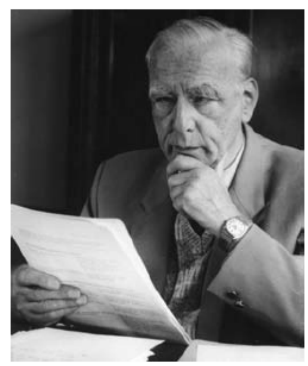


Figure 5.9 A neutron velocity selector. The slot in disk B lags the slot in disk A by 10°.

The Electron Microscope

The idea that electrons have a controllable wavelength that can be made much shorter than visible light wavelengths and, accordingly, possess a much better ability to resolve fine details was only one of the factors that led to the development of the electron microscope. In fact, ideas of such a device were tossed about in the cafés and bars of Paris and Berlin as early as 1928. What really made the difference was the coming together of several lines of development—electron tubes and circuits, vacuum technology, and electron beam control—all pioneered in the development of the cathode ray tube (CRT). These factors led to the construction of the first transmission electron microscope (TEM) with magnetic lenses by electrical engineers Max Knoll and Ernst Ruska in Berlin in 1931. The testament to the fortitude and brilliance of Knoll and Ruska in overcoming the "cussedness of objects" and building and getting such a complicated experimental device to work for the first time is shown in Figure 5.10. It is remarkable that although the overall performance of the TEM has been improved thousands of times since its invention, it is basically the same in principle as that first designed by Knoll and Ruska: a device that focuses electron beams with magnetic lenses and creates a flat-looking two-dimensional shadow pattern on its screen, the result of varying degrees of electron transmission through the object. Figure 5.11a is a diagram showing this basic design and Figure 5.11b shows, for comparison, an optical projection microscope. The best optical microscopes using ultraviolet light have a magnification of about 2000 and can resolve two objects separated by 100 nm, but a TEM using electrons accelerated through 100 kV has a magnification of as much as 1,000,000 and a maximum resolution of 0.2 nm. In practice, magnifications of 10,000 to 100,000 are easier to use. Figure 5.12 shows typical TEM micrographs of microbes, Figure 5.12b showing a microbe and its DNA strands magnified 40,000 times. Although it would seem that increasing electron energy should lead to shorter electron wavelength and increased resolution, imperfections or aberrations in the magnetic lenses actually set the limit of resolution at about 0.2 nm. Increasing electron energy above 100 keV does not



Ernst Ruska played a major role in the invention of the TEM. He was awarded the Nobel prize in physics for this work in 1986. (*AIP Emilio Segre Visual Archives, W. F. Meggers Gallery of Nobel Laureates*)

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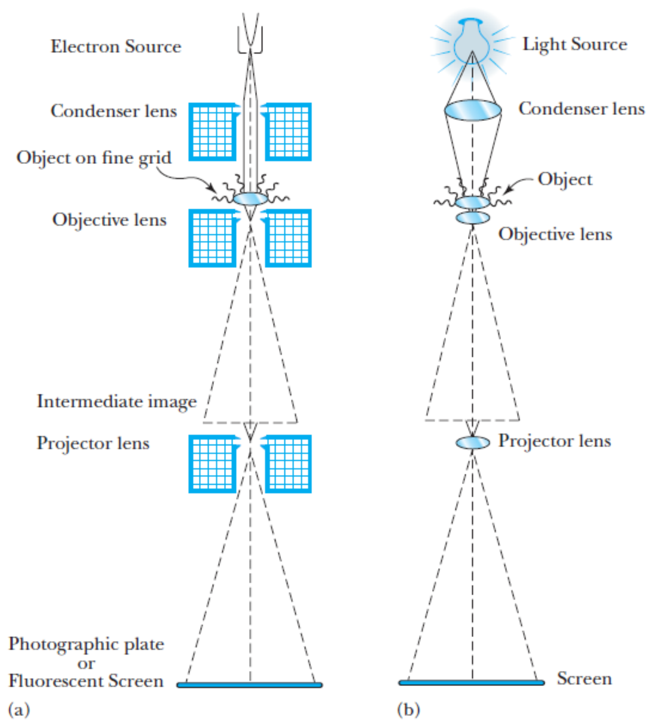
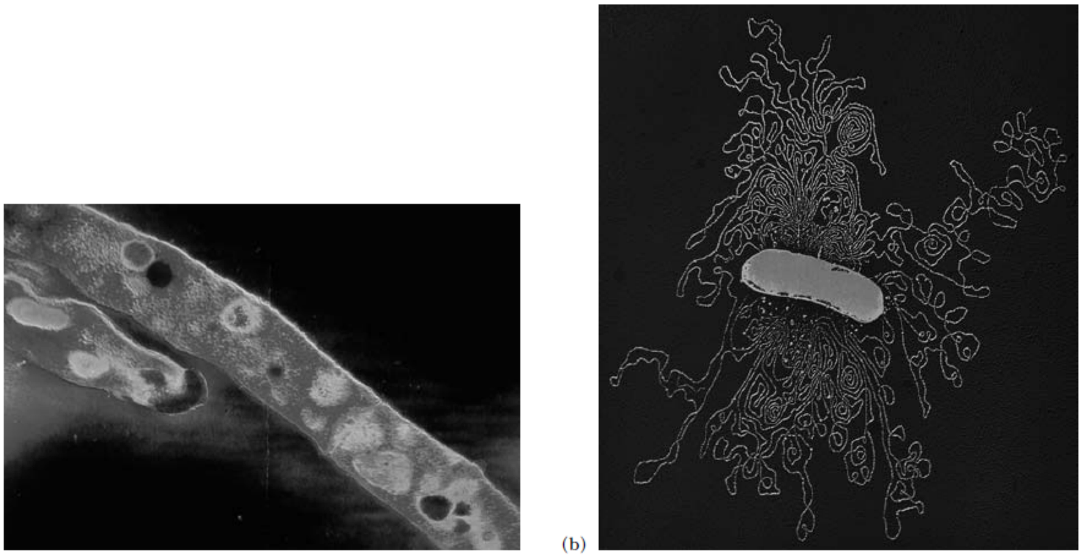


Figure 5.11 (a) Schematic drawing of a transmission electron microscope with magnetic lenses. (b) Schematic of a light-projection microscope.



(a) (b)

Figure 5.12 (a) A false-color TEM micrograph of tuberculosis bacteria. (b) A TEM micrograph of a microbe leaking DNA (×40,000). (*CNRI/Photo Researchers, Inc., Dr. Gopal Murti/Photo Researchers, Inc.*)

improve resolution—it only permits electrons to sample regions deeper inside an object. Figures 5.13a and 5.13b show, respectively, a diagram of a modern TEM and a photo of the same instrument.

A second type of electron microscope with less resolution and magnification than the TEM, but capable of producing striking three-dimensional images, is the scanning electron microscope (SEM). Figure 5.14 shows dramatic three-dimensional SEM micrographs made possible by the large range of focus (depth of field) of the SEM, which is several hundred times better than that of a light microscope. The SEM was the brainchild of the same Max Knoll who helped invent the TEM. Knoll had recently moved to the television department at Telefunken when he conceived of the idea in 1935. The SEM produces a sort of giant television image by collecting electrons scattered from an object, rather than light. The first operating scanning microscope was built by M. von Ardenne in 1937, and it was extensively developed and perfected by Vladimir Zworykin and collaborators at RCA Camden in the early 1940s.

Figure 5.15 shows how a typical SEM works. Such a device might be operated with 20-keV electrons and have a resolution of about 10 nm and a magnification ranging from 10 to 100,000. As shown in Figure 5.15, an electron beam is sharply focused on a specimen by magnetic lenses and then scanned (rastered) across a tiny region on the surface of the specimen. The high-energy primary beam scatters lower-energy secondary electrons out of the object depending on specimen composition and surface topography. These secondary electrons are detected by a plastic scintillator coupled to a photomultiplier, amplified, and used to modulate the brightness of a simultaneously

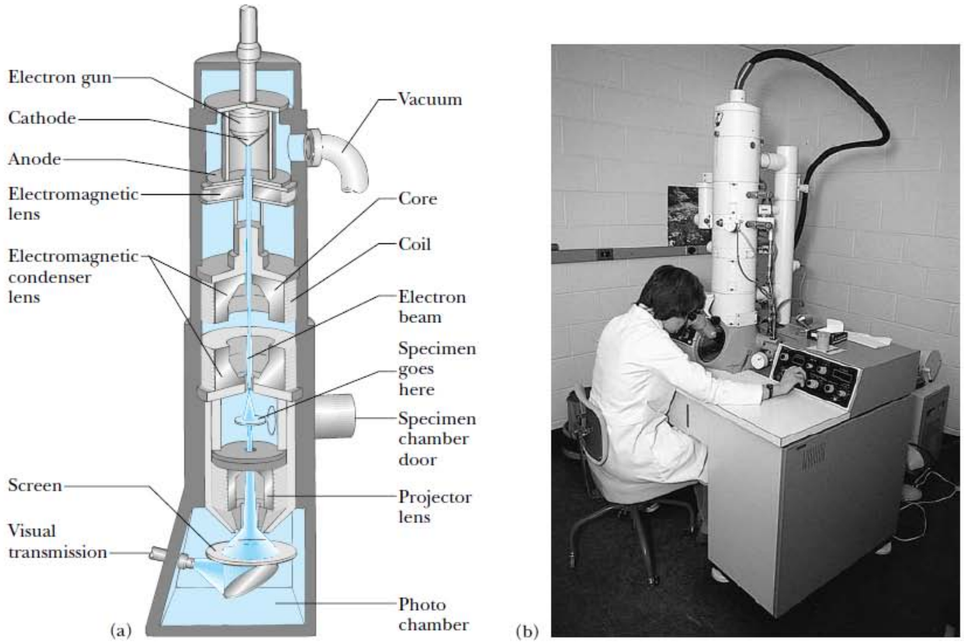


Figure 5.13 (a) Diagram of a transmission electron microscope. (b) A photo of the same TEM. (*W. Ormerod/Visuals Unlimited*)

rastered display CRT. The ratio of the display raster size to the microscope electron beam raster size determines the magnification. Modern SEM's can also collect x-rays and high-energy electrons from the specimen to detect chemical elements at certain locations on the specimen's surface, thus answering the bonus question, "Is the bitty bump on the bilayer boron or bismuth?"

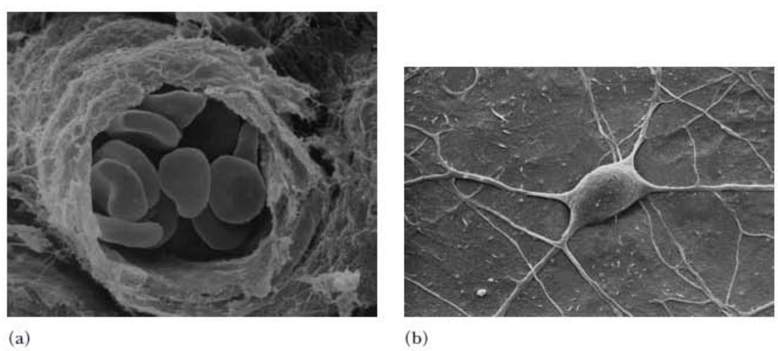


Figure 5.14 (a) A SEM micrograph showing blood cells in a tiny artery. (b) A SEM micrograph of a single neuron (×4000). (*P. Motta & S. Correr/Photo Researchers, Inc., David McCarthy/Photo Researchers, Inc.*)

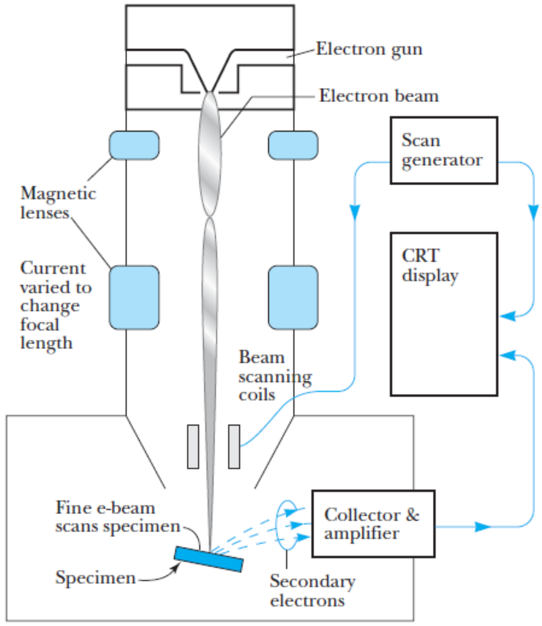


Figure 5.15 The working parts of a scanning electron microscope.

The newer, higher-resolution scanning tunneling microscope (STM) and atomic force microscope (AFM), which can image individual atoms and molecules, are discussed in Chapter 7. These instruments are exciting not only for their superb pictures of surface topography and individual atoms (see Figure 5.16 for an AFM picture) but also for their potential as microscopic machines capable of detecting and moving a few atoms at a time in proposed microchip terabit memories and mass spectrometers.

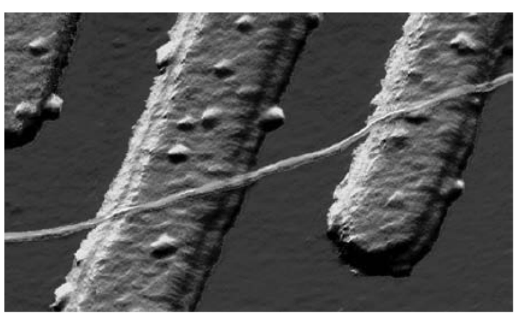


Figure 5.16 World's smallest electrical wire. An AFM image of a carbon nanotube wire on platinum electrodes. The wire is 1.5 nm wide, a mere 10 atoms. The magnification is 120,000. (*Delft University of Technology/Photo Researchers, Inc.*)