

# Quantum Mechanics

## CHAPTER OUTLINE

- 17.1 Blackbody Radiation and Energy Quantization
- 17.2 The Photoelectric Effect and Photons
- 17.3 The Bohr Theory of the Hydrogen Atom
- 17.4 The de Broglie Hypothesis
- 17.5 The Uncertainty Principle
- 17.6 Quantum Mechanics
- 17.7 The Time-Independent Schrödinger Equation
- 17.8 The Particle in a One-Dimensional Box
- 17.9 The Particle in a Three-Dimensional Box
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- 17.12 The One-Dimensional Harmonic Oscillator
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We now begin the study of **quantum chemistry**, which applies quantum mechanics to chemistry. Chapter 17 deals with **quantum mechanics**, the laws governing the behavior of microscopic particles such as electrons and nuclei. Chapters 18 and 19 apply quantum mechanics to atoms and molecules. Chapter 20 applies quantum mechanics to spectroscopy, the study of the absorption and emission of electromagnetic radiation. Quantum mechanics is used in statistical mechanics (Chapter 21) and in theoretical chemical kinetics (Chapter 22).

Unlike thermodynamics, quantum mechanics deals with systems that are not part of everyday macroscopic experience, and the formulation of quantum mechanics is quite mathematical and abstract. This abstractness takes a while to get used to, and it is natural to feel somewhat uneasy when first reading Chapter 17.

In an undergraduate physical chemistry course, it is not possible to give a full presentation of quantum mechanics. Derivations of results that are given without proof may be found in quantum chemistry texts listed in the Bibliography.

Sections 17.1 to 17.4 give the historical background of quantum mechanics. Section 17.5 discusses the uncertainty principle, a key concept that underlies the differences between quantum mechanics and classical (Newtonian) mechanics. Quantum mechanics describes the state of a system using a state function (or wave function)  $\Psi$ . Sections 17.6 and 17.7 describe the meaning of  $\Psi$  and the time-dependent and time-independent Schrödinger equations used to find  $\Psi$ . Sections 17.8, 17.9, 17.10, 17.12, 17.13, and 17.14 consider the Schrödinger equation, the wave functions, and the allowed quantum-mechanical energy levels for several systems. Sections 17.11 and 17.16 discuss operators, which are used extensively in quantum mechanics. Section 17.15 introduces some of the approximation methods used to apply quantum mechanics to chemistry.

Essentially all of chemistry is a consequence of the laws of quantum mechanics. If we want to understand chemistry at the fundamental level of electrons, atoms, and molecules, we must understand quantum mechanics. Quantities such as the heat of combustion of octane, the 25°C entropy of liquid water, the reaction rate of  $\text{N}_2$  and  $\text{H}_2$  gases at specified conditions, the equilibrium constants of chemical reactions, the absorption spectra of coordination compounds, the NMR spectra of organic compounds, the nature of the products formed when organic compounds react, the shape a protein molecule folds into when it is formed in a cell, the structure and function of DNA are all a consequence of quantum mechanics.

In 1929, Dirac, one of the founders of quantum mechanics, wrote that “The general theory of quantum mechanics is now almost complete . . . The underlying physical laws necessary for the mathematical theory of . . . the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” After its discovery, quantum mechanics was used to develop many concepts that helped explain chemical properties. However, because of the very difficult calculations needed to apply quantum mechanics to chemical systems, quantum mechanics was of little practical value in

## 17.6 QUANTUM MECHANICS

The fact that electrons and other microscopic “particles” show wavelike as well as particlelike behavior indicates that electrons do not obey classical mechanics. Classical mechanics was formulated from the observed behavior of macroscopic objects and does not apply to microscopic particles. The form of mechanics obeyed by microscopic systems is called **quantum mechanics**, since a key feature of this mechanics is the quantization of energy. The laws of quantum mechanics were discovered by Heisenberg, Born, and Jordan in 1925 and by Schrödinger in 1926. Before discussing these laws, we consider some aspects of *classical* mechanics.

### Classical Mechanics

The motion of a one-particle, one-dimensional classical-mechanical system is governed by Newton’s second law  $F = ma = m d^2x/dt^2$ . To obtain the particle’s position  $x$  as a function of time, this differential equation must be integrated twice with respect to time. The first integration gives  $dx/dt$ , and the second integration gives  $x$ . Each integration introduces an arbitrary integration constant. Therefore, integration of  $F = ma$  gives an equation for  $x$  that contains two unknown constants  $c_1$  and  $c_2$ ; we have  $x = f(t, c_1, c_2)$ , where  $f$  is some function. To evaluate  $c_1$  and  $c_2$ , we need two pieces of information about the system. If we know that at a certain time  $t_0$ , the particle was at the position  $x_0$  and had speed  $v_0$ , then  $c_1$  and  $c_2$  can be evaluated from the equations  $x_0 = f(t_0, c_1, c_2)$  and  $v_0 = f'(t_0, c_1, c_2)$ , where  $f'$  is the derivative of  $f$  with respect to  $t$ . Thus, provided we know the force  $F$  and the particle’s initial position and velocity (or momentum), we can use Newton’s second law to predict the position of the particle at any future time. A similar conclusion holds for a three-dimensional many-particle classical system.

The **state** of a system in classical mechanics is defined by specifying all the forces acting and all the positions and velocities (or momenta) of the particles. We saw in the preceding paragraph that knowledge of the present state of a classical-mechanical system enables its future state to be predicted with certainty.

The Heisenberg uncertainty principle, Eq. (17.9), shows that simultaneous specification of position and momentum is impossible for a microscopic particle. Hence, the very knowledge needed to specify the classical-mechanical state of a system is unobtainable in quantum theory. The state of a quantum-mechanical system must therefore involve less knowledge about the system than in classical mechanics.

### Quantum Mechanics

In quantum mechanics, the **state** of a system is defined by a mathematical function  $\Psi$  (capital psi) called the **state function** or the **time-dependent wave function**. (As part of the definition of the state, the potential-energy function  $V$  must also be specified.)  $\Psi$  is a function of the coordinates of the particles of the system and (since the state may change with time) is also a function of time. For example, for a two-particle system,  $\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)$ , where  $x_1, y_1, z_1$  and  $x_2, y_2, z_2$  are the coordinates of particles 1 and 2, respectively. The state function is in general a complex quantity; that is,  $\Psi = f + ig$ , where  $f$  and  $g$  are real functions of the coordinates and time and  $i \equiv \sqrt{-1}$ . The state function is an abstract entity, but we shall later see how  $\Psi$  is related to physically measurable quantities.

The state function changes with time. For an  $n$ -particle system, quantum mechanics postulates that the equation governing how  $\Psi$  changes with  $t$  is

$$\begin{aligned}
 -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = & -\frac{\hbar^2}{2m_1} \left( \frac{\partial^2 \Psi}{\partial x_1^2} + \frac{\partial^2 \Psi}{\partial y_1^2} + \frac{\partial^2 \Psi}{\partial z_1^2} \right) - \cdots \\
 & -\frac{\hbar^2}{2m_n} \left( \frac{\partial^2 \Psi}{\partial x_n^2} + \frac{\partial^2 \Psi}{\partial y_n^2} + \frac{\partial^2 \Psi}{\partial z_n^2} \right) + V\Psi
 \end{aligned} \tag{17.10}$$

In this equation,  $\hbar$  (**h-bar**) is Planck's constant divided by  $2\pi$ ,

$$\hbar \equiv h/2\pi \quad (17.11)^*$$

$i$  is  $\sqrt{-1}$ ;  $m_1, \dots, m_n$  are the masses of particles  $1, \dots, n$ ;  $x_1, y_1, z_1$  are the spatial coordinates of particle 1; and  $V$  is the potential energy of the system. Since the potential energy is energy due to the particles' positions,  $V$  is a function of the particles' coordinates. Also,  $V$  can vary with time if an externally applied field varies with time. Hence,  $V$  is in general a function of the particles' coordinates and the time.  $V$  is derived from the forces acting in the system; see Eq. (2.17). The dots in Eq. (17.10) stand for terms involving the spatial derivatives of particles  $2, 3, \dots, n - 1$ .

Equation (17.10) is a complicated partial differential equation. For most of the problems dealt with in this book, it will not be necessary to use (17.10), so don't panic.

The concept of the state function  $\Psi$  and Eq. (17.10) were introduced by the Austrian physicist Erwin Schrödinger (1887–1961) in 1926. Equation (17.10) is the **time-dependent Schrödinger equation**. Schrödinger was inspired by the de Broglie hypothesis to search for a mathematical equation that would resemble the differential equations that govern wave motion and that would have solutions giving the allowed energy levels of a quantum system. Using the de Broglie relation  $\lambda = h/p$  and certain plausibility arguments, Schrödinger proposed Eq. (17.10) and the related time-independent equation (17.24) below. These plausibility arguments have been omitted in this book. It should be emphasized that these arguments can at best make the Schrödinger equation seem plausible. They can in no sense be used to derive or prove the Schrödinger equation. The Schrödinger equation is a fundamental postulate of quantum mechanics and cannot be derived. The reason we believe it to be true is that its predictions give excellent agreement with experimental results. “One could argue that the Schrödinger equation has had more to do with the evolution of twentieth-century science and technology than any other discovery in physics.” (Jeremy Bernstein, *Cranks, Quarks, and the Cosmos*, Basic Books, 1993, p. 54.)

In 1925, several months before Schrödinger's work, Werner Heisenberg (1901–1976), Max Born (1882–1970), and Pascual Jordan (1902–1980) developed a form of quantum mechanics based on mathematical entities called matrices. A matrix is a rectangular array of numbers; matrices are added and multiplied according to certain rules. The *matrix mechanics* of these workers turns out to be fully equivalent to the Schrödinger form of quantum mechanics (which is often called *wave mechanics*). We shall not discuss matrix mechanics.

Schrödinger also contributed to statistical mechanics, relativity, and the theory of color vision and was deeply interested in philosophy. In an epilogue to his 1944 book, *What Is Life?*, Schrödinger wrote: “So let us see whether we cannot draw the correct, non-contradictory conclusion from the following two premises: (i) My body functions as a pure mechanism according to the Laws of Nature. (ii) Yet I know, by incontrovertible direct experience, that I am directing its motions . . . . The only possible inference from these two facts is, I think, that I—I in the widest meaning of the word, that is to say, every conscious mind that has ever said or felt ‘I’—am the person, if any, who controls the ‘motion of the atoms’ according to the Laws of Nature.” Schrödinger's life and loves are chronicled in W. Moore, *Schrödinger, Life and Thought*, Cambridge University Press, 1989.

The time-dependent Schrödinger equation (17.10) contains the first derivative of  $\Psi$  with respect to  $t$ , and a single integration with respect to time gives us  $\Psi$ . Integration of (17.10) therefore introduces only one integration constant, which can be evaluated if  $\Psi$  is known at some initial time  $t_0$ . Therefore, knowing the initial quantum-mechanical state  $\Psi(x_1, \dots, z_n, t_0)$  and the potential energy  $V$ , we can use (17.10) to predict the future quantum-mechanical state. The time-dependent Schrödinger equation

is the quantum-mechanical analog of Newton's second law, which allows the future state of a classical-mechanical system to be predicted from its present state. We shall soon see, however, that knowledge of the state in quantum mechanics usually involves a knowledge of only probabilities, rather than certainties, as in classical mechanics.

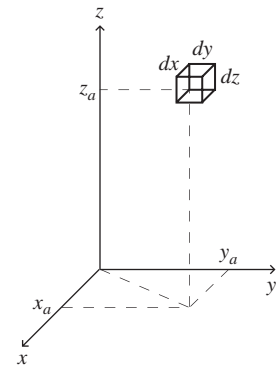
What is the relation between quantum mechanics and classical mechanics? Experiment shows that macroscopic bodies obey classical mechanics (provided their speed is much less than the speed of light). We therefore expect that in the classical-mechanical limit of taking  $\hbar \rightarrow 0$ , the time-dependent Schrödinger equation ought to reduce to Newton's second law. This was shown by Ehrenfest in 1927; for Ehrenfest's proof, see *Park*, sec. 3.3.

### Physical Meaning of the State Function $\Psi$

Schrödinger originally conceived of  $\Psi$  as the amplitude of some sort of wave that was associated with the system. It soon became clear that this interpretation was wrong. For example, for a two-particle system,  $\Psi$  is a function of the six spatial coordinates  $x_1, y_1, z_1, x_2, y_2$ , and  $z_2$ , whereas a wave moving through space is a function of only three spatial coordinates. The correct physical interpretation of  $\Psi$  was given by Max Born in 1926. Born postulated that  $|\Psi|^2$  gives the **probability density** for finding the particles at given locations in space. (Probability densities for molecular speeds were discussed in Sec. 14.4.) To be more precise, suppose a one-particle system has the state function  $\Psi(x, y, z, t')$  at time  $t'$ . Consider the probability that a measurement of the particle's position at time  $t'$  will find the particle with its  $x, y$ , and  $z$  coordinates in the infinitesimal ranges  $x_a$  to  $x_a + dx$ ,  $y_a$  to  $y_a + dy$ , and  $z_a$  to  $z_a + dz$ , respectively. This is the probability of finding the particle in a tiny rectangular-box-shaped region located at point  $(x_a, y_a, z_a)$  in space and having edges  $dx, dy$ , and  $dz$  (Fig. 17.5). Born's postulate is that the probability is given by

$$\begin{aligned} \Pr(x_a \leq x \leq x_a + dx, y_a \leq y \leq y_a + dy, z_a \leq z \leq z_a + dz) \\ = |\Psi(x_a, y_a, z_a, t')|^2 dx dy dz \end{aligned} \quad (17.12)^*$$

where the left side of (17.12) denotes the probability the particle is found in the box of Fig. 17.5.



**Figure 17.5**

An infinitesimal box in space.

### EXAMPLE 17.1 Probability for finding a particle

Suppose that at time  $t'$  the state function of a one-particle system is

$$\Psi = (2/\pi c^2)^{3/4} e^{-(x^2+y^2+z^2)/c^2} \quad \text{where } c = 2 \text{ nm}$$

[One nanometer (nm)  $\equiv 10^{-9}$  m.] Find the probability that a measurement of the particle's position at time  $t'$  will find the particle in the tiny cubic region with its center at  $x = 1.2$  nm,  $y = -1.0$  nm, and  $z = 0$  and with edges each of length 0.004 nm.

The distance 0.004 nm is much less than the value of  $c$  and a change of 0.004 nm in one or more of the coordinates will not change the probability density  $|\Psi|^2$  significantly. It is therefore a good approximation to consider the interval 0.004 nm as infinitesimal and to use (17.12) to write the desired probability as

$$\begin{aligned} |\Psi|^2 dx dy dz &= (2/\pi c^2)^{3/2} e^{-2(x^2+y^2+z^2)/c^2} dx dy dz \\ &= [2/(4\pi \text{ nm}^2)]^{3/2} e^{-2[(1.2)^2+(-1)^2+0^2]/4} (0.004 \text{ nm})^3 \\ &= 1.200 \times 10^{-9} \end{aligned}$$

**Exercise**

(a) At what point is the probability density a maximum for the  $\Psi$  of this example? Answer by simply looking at  $|\Psi|^2$ . (b) Redo the calculation with  $x$  changed to its minimum value in the tiny cubic region and then with  $x$  changed to its maximum value in the region. Compare the results with that found when the central value of  $x$  is used. [Answers: (a) At the origin. (b)  $1.203 \times 10^{-9}$ ,  $1.197 \times 10^{-9}$ .]

The state function  $\Psi$  is a complex quantity, and  $|\Psi|$  is the absolute value of  $\Psi$ . Let  $\Psi = f + ig$ , where  $f$  and  $g$  are real functions and  $i \equiv \sqrt{-1}$ . The **absolute value** of  $\Psi$  is defined by  $|\Psi| \equiv (f^2 + g^2)^{1/2}$ . For a real quantity,  $g$  is zero, and the absolute value becomes  $(f^2)^{1/2}$ , which is the usual meaning of absolute value for a real quantity. The **complex conjugate**  $\Psi^*$  of  $\Psi$  is defined by

$$\Psi^* \equiv f - ig, \quad \text{where } \Psi = f + ig \quad (17.13)^*$$

To get  $\Psi^*$ , we replace  $i$  by  $-i$  wherever it occurs in  $\Psi$ . Note that

$$\Psi^* \Psi = (f - ig)(f + ig) = f^2 - i^2 g^2 = f^2 + g^2 = |\Psi|^2 \quad (17.14)$$

since  $i^2 = -1$ . Therefore, instead of  $|\Psi|^2$ , we can write  $\Psi^* \Psi$ . The quantity  $|\Psi|^2 = \Psi^* \Psi = f^2 + g^2$  is real and nonnegative, as a probability density must be.

In a two-particle system,  $|\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t')|^2 dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$  is the probability that, at time  $t'$ , particle 1 is in a tiny rectangular-box-shaped region located at point  $(x_1, y_1, z_1)$  and having dimensions  $dx_1$ ,  $dy_1$ , and  $dz_1$ , and particle 2 is simultaneously in a box-shaped region at  $(x_2, y_2, z_2)$  with dimensions  $dx_2$ ,  $dy_2$ , and  $dz_2$ . Born's interpretation of  $\Psi$  gives results fully consistent with experiment.

For a one-particle, one-dimensional system,  $|\Psi(x, t)|^2 dx$  is the probability that the particle is between  $x$  and  $x + dx$  at time  $t$ . The probability that it is in the region between  $a$  and  $b$  is found by summing the infinitesimal probabilities over the interval from  $a$  to  $b$  to give the definite integral  $\int_a^b |\Psi|^2 dx$ . Thus

$$\text{Pr}(a \leq x \leq b) = \int_a^b |\Psi|^2 dx \quad \text{one-particle, one-dim. syst.} \quad (17.15)^*$$

The probability of finding the particle somewhere on the  $x$  axis must be 1. Hence,  $\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$ . When  $\Psi$  satisfies this equation, it is said to be **normalized**. The normalization condition for a one-particle, three-dimensional system is

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(x, y, z, t)|^2 dx dy dz = 1 \quad (17.16)$$

For an  $n$ -particle, three-dimensional system, the integral of  $|\Psi|^2$  over all  $3n$  coordinates  $x_1, \dots, z_n$ , each integrated from  $-\infty$  to  $\infty$ , equals 1.

The integral in (17.16) is a multiple integral. In a double integral like  $\int_a^b \int_c^d f(x, y) dx dy$ , one first integrates  $f(x, y)$  with respect to  $x$  (while treating  $y$  as a constant) between the limits  $c$  and  $d$ , and then integrates the result with respect to  $y$ . For example,  $\int_0^1 \int_0^4 (2xy + y^2) dx dy = \int_0^1 (x^2 y + xy^2) \Big|_0^4 dy = \int_0^1 (16y + 4y^2) dy = 28/3$ . To evaluate a triple integral like (17.16), we first integrate with respect to  $x$  while treating  $y$  and  $z$  as constants, then integrate with respect to  $y$  while treating  $z$  as constant, and finally integrate with respect to  $z$ .

The normalization requirement is often written

$$\int |\Psi|^2 d\tau = 1 \quad (17.17)^*$$

where  $\int d\tau$  is a shorthand notation that stands for the *definite* integral over the full ranges of all the spatial coordinates of the system. For a one-particle, three-dimensional system,  $\int d\tau$  implies a triple integral over  $x$ ,  $y$ , and  $z$  from  $-\infty$  to  $\infty$  for each coordinate [Eq. (17.16)].

By substitution, it is easy to see that, if  $\Psi$  is a solution of (17.10), then so is  $c\Psi$ , where  $c$  is an arbitrary constant. Thus, there is always an arbitrary multiplicative constant in each solution to (17.10). The value of this constant is chosen so as to satisfy the normalization requirement (17.17).

From the state function  $\Psi$ , we can calculate the probabilities of the various possible outcomes when a measurement of position is made on the system. In fact, Born's work is more general than this. It turns out that  $\Psi$  gives information on the outcome of a measurement of *any* property of the system, not just position. For example, if  $\Psi$  is known, we can calculate the probability of each possible outcome when a measurement of  $p_x$ , the  $x$  component of momentum, is made. The same is true for a measurement of energy, or angular momentum, etc. (The procedure for calculating these probabilities from  $\Psi$  is discussed in *Levine*, sec. 7.6.)

The state function  $\Psi$  is not to be thought of as a physical wave. Instead  $\Psi$  is an abstract mathematical entity that gives information about the state of the system. Everything that can be known about the system in a given state is contained in the state function  $\Psi$ . Instead of saying "the state described by the function  $\Psi$ ," we can just as well say "the state  $\Psi$ ." The information given by  $\Psi$  is the probabilities for the possible outcomes of measurements of the system's physical properties.

The state function  $\Psi$  describes a physical system. In Chapters 17 to 20, the system will usually be a particle, atom, or molecule. One can also consider the state function of a system that contains a large number of molecules, for example, a mole of some compound; this will be done in Chapter 21 on statistical mechanics.

Classical mechanics is a deterministic theory in that it allows us to predict the exact paths taken by the particles of the system and tells us where they will be at any future time. In contrast, quantum mechanics gives only the probabilities of finding the particles at various locations in space. The concept of a path for a particle becomes rather fuzzy in a time-dependent quantum-mechanical system and disappears in a time-independent quantum-mechanical system.

Some philosophers have used the Heisenberg uncertainty principle and the nondeterministic nature of quantum mechanics as arguments in favor of human free will.

The probabilistic nature of quantum mechanics disturbed many physicists, including Einstein, Schrödinger, and de Broglie. (Einstein wrote in 1926: "Quantum mechanics . . . says a lot, but does not really bring us any closer to the secret of the Old One. I, at any rate, am convinced that He does not throw dice." When someone pointed out to Einstein that Einstein himself had introduced probability into quantum theory when he interpreted a light wave's intensity in each small region of space as being proportional to the probability of finding a photon in that region, Einstein replied, "A good joke should not be repeated too often.") These scientists believed that quantum mechanics does not furnish a complete description of physical reality. However, attempts to replace quantum mechanics by an underlying deterministic theory have failed. There appears to be a fundamental randomness in nature at the microscopic level.

## Summary

The state of a quantum-mechanical system is described by its state function  $\Psi$ , which is a function of time and the spatial coordinates of the particles of the system. The state function provides information on the probabilities of the outcomes of measurements on the system. For example, when a position measurement is made on a one-particle system at time  $t'$ , the probability that the particle's coordinates are found to be in the

ranges  $x$  to  $x + dx$ ,  $y$  to  $y + dy$ ,  $z$  to  $z + dz$  is given by  $|\Psi(x, y, z, t')|^2 dx dy dz$ . The function  $|\Psi|^2$  is the probability density for position. Because the total probability of finding the particles somewhere is 1, the state function is normalized, meaning that the definite integral of  $|\Psi|^2$  over the full range of all the spatial coordinates is equal to 1. The state function  $\Psi$  changes with time according to the time-dependent Schrödinger equation (17.10), which allows the future state (function) to be calculated from the present state (function).

## 17.7 THE TIME-INDEPENDENT SCHRÖDINGER EQUATION

For an isolated atom or molecule, the forces acting depend only on the coordinates of the charged particles of the system and are independent of time. Therefore, the potential energy  $V$  is independent of  $t$  for an isolated system. For systems where  $V$  is independent of time, the time-dependent Schrödinger equation (17.10) has solutions of the form  $\Psi(x_1, \dots, z_n, t) = f(t)\psi(x_1, \dots, z_n)$ , where  $\psi$  (lowercase psi) is a function of the  $3n$  coordinates of the  $n$  particles and  $f$  is a certain function of time. We shall demonstrate this for a one-particle, one-dimensional system.

For a one-particle, one-dimensional system with  $V$  independent of  $t$ , Eq. (17.10) becomes

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi = -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} \quad (17.18)$$

Let us look for those solutions of (17.18) that have the form

$$\Psi(x, t) = f(t)\psi(x) \quad (17.19)$$

We have  $\partial^2 \Psi / \partial x^2 = f(t) d^2 \psi / dx^2$  and  $\partial \Psi / \partial t = \psi(x) df/dt$ . Substitution into (17.18) followed by division by  $f\psi = \Psi$  gives

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi}{dx^2} + V(x) = -\frac{\hbar}{i} \frac{1}{f(t)} \frac{df(t)}{dt} \equiv E \quad (17.20)$$

where the parameter  $E$  was defined as  $E \equiv -(\hbar/i)f'(t)/f(t)$ .

From the definition of  $E$ , it is equal to a function of  $t$  only and hence is independent of  $x$ . However, (17.20) shows that  $E = -(\hbar^2/2m)\psi''(x)/\psi(x) + V(x)$ , which is a function of  $x$  only and is independent of  $t$ . Hence,  $E$  is independent of  $t$  as well as independent of  $x$  and must therefore be a constant. Since the constant  $E$  has the same dimensions as  $V$ , it has the dimensions of energy. Quantum mechanics postulates that  $E$  is in fact the energy of the system.

Equation (17.20) gives  $df/f = -(iE/\hbar) dt$ , which integrates to  $\ln f = -iEt/\hbar + C$ . Therefore  $f = e^C e^{-iEt/\hbar} = A e^{-iEt/\hbar}$ , where  $A \equiv e^C$  is an arbitrary constant. The constant  $A$  can be included as part of the  $\psi(x)$  factor in (17.19), so we omit it from  $f$ . Thus

$$f(t) = e^{-iEt/\hbar} \quad (17.21)$$

Equation (17.20) also gives

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (17.22)$$

which is the **(time-independent) Schrödinger equation** for a one-particle, one-dimensional system. Equation (17.22) can be solved for  $\psi$  when the potential-energy function  $V(x)$  has been specified.

For an  $n$ -particle, three-dimensional system, the same procedure that led to Eqs. (17.19), (17.21), and (17.22) gives

$$\Psi = e^{-iEt/\hbar} \psi(x_1, y_1, z_1, \dots, x_n, y_n, z_n) \quad (17.23)$$

where the function  $\psi$  is found by solving

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial y_1^2} + \frac{\partial^2\psi}{\partial z_1^2}\right) - \cdots - \frac{\hbar^2}{2m_n}\left(\frac{\partial^2\psi}{\partial x_n^2} + \frac{\partial^2\psi}{\partial y_n^2} + \frac{\partial^2\psi}{\partial z_n^2}\right) + V\psi = E\psi \quad (17.24)^*$$

The solutions  $\psi$  to the time-independent Schrödinger equation (17.24) are the **(time-independent) wave functions**. States for which  $\Psi$  is given by (17.23) are called **stationary states**. We shall see that for a given system there are many different solutions to (17.24), different solutions corresponding to different values of the energy  $E$ . In general, quantum mechanics gives only probabilities and not certainties for the outcome of a measurement. However, when a system is in a stationary state, a measurement of its energy is certain to give the particular energy value that corresponds to the wave function  $\psi$  of the system. Different systems have different forms for the potential-energy function  $V(x_1, \dots, z_n)$ , and this leads to different sets of allowed wave functions and energies when (17.24) is solved for different systems. All this will be made clearer by the examples in the next few sections.

For a stationary state, the probability density  $|\Psi|^2$  becomes

$$|\Psi|^2 = |f\psi|^2 = (f\psi)^*f\psi = f^*\psi^*f\psi = e^{iEt/\hbar}\psi^*e^{-iEt/\hbar}\psi = e^0\psi^*\psi = |\psi|^2 \quad (17.25)$$

where we used (17.19), (17.21) and the identity

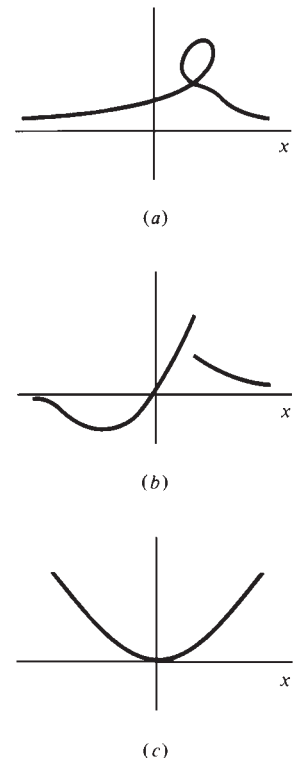
$$(f\psi)^* = f^*\psi^*$$

(Prob. 17.19). Hence, for a stationary state,  $|\Psi|^2 = |\psi|^2$ , which is independent of time. For a stationary state, the probability density and the energy are constant with time. There is no implication, however, that the particles of the system are at rest in a stationary state.

It turns out that the probabilities for the outcomes of measurements of any physical property involve  $|\Psi|$ , and since  $|\Psi| = |\psi|$ , these probabilities are independent of time for a stationary state. Thus, the  $e^{-iEt/\hbar}$  factor in (17.23) is of little consequence, and *the essential part of the state function for a stationary state is the time-independent wave function  $\psi(x_1, \dots, z_n)$* . For a stationary state, the normalization condition (17.17) becomes  $\int |\psi|^2 d\tau = 1$ , where  $\int d\tau$  denotes the definite integral over all space.

The wave function  $\psi$  of a stationary state of energy  $E$  must satisfy the time-independent Schrödinger equation (17.24). However, quantum mechanics postulates that not all functions that satisfy (17.24) are allowed as wave functions for the system. In addition to being a solution of (17.24), a wave function must meet the following three conditions: (a) The wave function must be **single-valued**. (b) The wave function must be **continuous**. (c) The wave function must be **quadratically integrable**. Condition (a) means that  $\psi$  has one and only one value at each point in space. The function of Fig. 17.6a, which is multiple-valued at some points, is not a possible wave function for a one-particle, one-dimensional system. Condition (b) means that  $\psi$  makes no sudden jumps in value. A function like that in Fig. 17.6b is ruled out. Condition (c) means that the integral over all space  $\int |\psi|^2 d\tau$  is a finite number. The function  $x^2$  (Fig. 17.6c) is not quadratically integrable, since  $\int_{-\infty}^{\infty} x^4 dx = (x^5/5)|_{-\infty}^{\infty} = \infty - (-\infty) = \infty$ . Condition (c) allows the wave function to be multiplied by a constant that normalizes it, that is, that makes  $\int |\psi|^2 d\tau = 1$ . [If  $\psi$  is a solution of the Schrödinger equation (17.24), then so is  $k\psi$ , where  $k$  is any constant; see Prob. 17.20.] A function obeying conditions (a), (b), and (c) is said to be **well-behaved**.

Since  $E$  occurs as an undetermined parameter in the Schrödinger equation (17.24), the solutions  $\psi$  that are found by solving (17.24) will depend on  $E$  as a parameter:  $\psi = \psi(x_1, \dots, z_n; E)$ . It turns out that  *$\psi$  is well-behaved only for certain particular values of  $E$ , and it is these values that are the allowed energy levels*. An example is given in the next section.



**Figure 17.6**

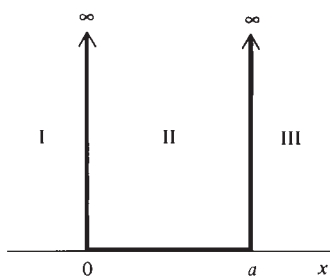
(a) A multivalued function. (b) A discontinuous function. (c) A function that is not quadratically integrable.



We shall mainly be interested in the stationary states of atoms and molecules, since these give the allowed energy levels. For a collision between two molecules or for a molecule exposed to the time-varying electric and magnetic fields of electromagnetic radiation, the potential energy  $V$  depends on time, and one must deal with the time-dependent Schrödinger equation and with nonstationary states.

### Summary

In an isolated atom or molecule, the potential energy  $V$  is independent of time and the system can exist in a stationary state, which is a state of constant energy and time-independent probability density. For a stationary state, the probability density for the particles' locations is given by  $|\psi|^2$ , where the time-independent wave function  $\psi$  is a function of the coordinates of the particles of the system. The possible stationary-state wave functions and energies for a system are found by solving the time-independent Schrödinger equation (17.24) and picking out only those solutions that are single-valued, continuous, and quadratically integrable.



**Figure 17.7**

Potential-energy function for a particle in a one-dimensional box.

## 17.8 THE PARTICLE IN A ONE-DIMENSIONAL BOX

The introduction to quantum mechanics in the last two sections is quite abstract. To help make the ideas of quantum mechanics more understandable, this section examines the stationary states of a simple system, **a particle in a one-dimensional box**. By this is meant a single microscopic particle of mass  $m$  moving in one dimension  $x$  and subject to the potential-energy function of Fig. 17.7. The potential energy is zero for  $x$  between 0 and  $a$  (region II) and is infinite elsewhere (regions I and III):

$$V = \begin{cases} 0 & \text{for } 0 \leq x \leq a \\ \infty & \text{for } x < 0 \text{ and for } x > a \end{cases}$$

This potential energy confines the particle to move in the region between 0 and  $a$  on the  $x$  axis. No real system has a  $V$  as simple as Fig. 17.7, but the particle in a box can be used as a crude model for dealing with  $\pi$  electrons in conjugated molecules (Sec. 19.11).

We restrict ourselves to considering the states of constant energy, the stationary states. For these states, the (time-independent) wave functions  $\psi$  are found by solving the Schrödinger equation (17.24), which for a one-particle, one-dimensional system is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad (17.26)$$

Since a particle cannot have infinite energy, there must be zero probability of finding the particle in regions I and III, where  $V$  is infinite. Therefore, the probability density  $|\psi|^2$  and hence  $\psi$  must be zero in these regions:  $\psi_I = 0$  and  $\psi_{III} = 0$ , or

$$\psi = 0 \quad \text{for } x < 0 \text{ and for } x > a \quad (17.27)$$

Inside the box (region II),  $V$  is zero and (17.26) becomes

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi \quad \text{for } 0 \leq x \leq a \quad (17.28)$$

To solve this equation, we need a function whose second derivative gives us the same function back again, but multiplied by a constant. Two functions that behave this way are the sine function and the cosine function, so let us try as a solution

$$\psi = A \sin rx + B \cos sx$$

where  $A$ ,  $B$ ,  $r$ , and  $s$  are constants. Differentiation of  $\psi$  gives  $d^2\psi/dx^2 = -Ar^2 \sin rx - Bs^2 \cos sx$ . Substitution of the trial solution in (17.28) gives

$$-Ar^2 \sin rx - Bs^2 \cos sx = -2mE\hbar^{-2}A \sin rx - 2mE\hbar^{-2}B \cos sx \quad (17.29)$$

If we take  $r = s = (2mE)^{1/2}\hbar^{-1}$ , Eq. (17.29) is satisfied. The solution of (17.28) is therefore

$$\psi = A \sin[(2mE)^{1/2}\hbar^{-1}x] + B \cos[(2mE)^{1/2}\hbar^{-1}x] \quad \text{for } 0 \leq x \leq a \quad (17.30)$$

A more formal derivation than we have given shows that (17.30) is indeed the general solution of the differential equation (17.28).

As noted in Sec. 17.7, not all solutions of the Schrödinger equation are acceptable wave functions. Only well-behaved functions are allowed. The solution of the particle-in-a-box Schrödinger equation is the function defined by (17.27) and (17.30), where  $A$  and  $B$  are arbitrary constants of integration. For this function to be continuous, the wave function inside the box must go to zero at the two ends of the box, since  $\psi$  equals zero outside the box. We must require that  $\psi$  in (17.30) go to zero as  $x \rightarrow 0$  and as  $x \rightarrow a$ . Setting  $x = 0$  and  $\psi = 0$  in (17.30), we get  $0 = A \sin 0 + B \cos 0 = A \cdot 0 + B \cdot 1$ , so  $B = 0$ . Therefore

$$\psi = A \sin[(2mE)^{1/2}\hbar^{-1}x] \quad \text{for } 0 \leq x \leq a \quad (17.31)$$

Setting  $x = a$  and  $\psi = 0$  in (17.31), we get  $0 = \sin[(2mE)^{1/2}\hbar^{-1}a]$ . The function  $\sin w$  equals zero when  $w$  is  $0, \pm\pi, \pm2\pi, \dots, \pm n\pi$ , so we must have

$$(2mE)^{1/2}\hbar^{-1}a = \pm n\pi \quad (17.32)$$

Substitution of (17.32) in (17.31) gives  $\psi = A \sin(\pm n\pi x/a) = \pm A \sin(n\pi x/a)$ , since  $\sin(-z) = -\sin z$ . The use of  $-n$  instead of  $n$  multiplies  $\psi$  by  $-1$ . Since  $A$  is arbitrary, this doesn't give a solution different from the  $+n$  solution, so there is no need to consider the  $-n$  values. Also, the value  $n = 0$  must be ruled out, since it would make  $\psi = 0$  everywhere (Prob. 17.26), meaning there is no probability of finding the particle in the box. The allowed wave functions are therefore

$$\psi = A \sin(n\pi x/a) \quad \text{for } 0 \leq x \leq a, \quad \text{where } n = 1, 2, 3, \dots \quad (17.33)$$

The allowed energies are found by solving (17.32) for  $E$  to get

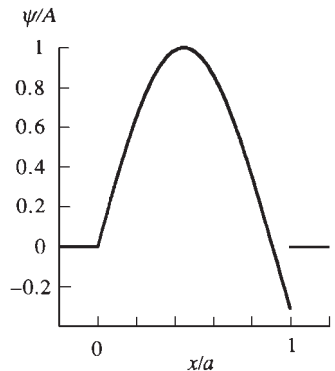
$$E = \frac{n^2\hbar^2}{8ma^2}, \quad n = 1, 2, 3, \dots \quad (17.34)^*$$

where  $\hbar \equiv h/2\pi$  was used. Only these values of  $E$  make  $\psi$  a well-behaved (continuous) function. For example, Fig. 17.8 plots  $\psi$  of (17.27) and (17.31) for  $E = (1.1)^2\hbar^2/8ma^2$ . Because of the discontinuity at  $x = a$ , this is not an acceptable wave function.

Confining the particle to be between 0 and  $a$  requires that  $\psi$  be zero at  $x = 0$  and  $x = a$ , and this quantizes the energy. An analogy is the quantization of the vibrational modes of a string that occurs when the string is held fixed at both ends. The energy levels (17.34) are proportional to  $n^2$ , and the separation between adjacent levels increases as  $n$  increases (Fig. 17.9).

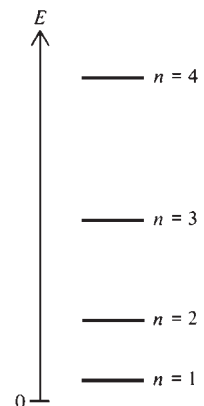
The magnitude of the constant  $A$  in  $\psi$  in (17.33) is found from the normalization condition (17.17) and (17.25):  $\int |\psi|^2 d\tau = 1$ . Since  $\psi = 0$  outside the box, we need only integrate from 0 to  $a$ , and

$$1 = \int_{-\infty}^{\infty} |\psi|^2 dx = \int_0^a |\psi|^2 dx = |A|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$



**Figure 17.8**

Plot of the solution to the particle-in-a-box Schrödinger equation for  $E = (1.1)^2\hbar^2/8ma^2$ . This solution is discontinuous at  $x = a$ .



**Figure 17.9**

Lowest four energy levels of a particle in a one-dimensional box.

A table of integrals gives  $\int \sin^2 cx \, dx = x/2 - (1/4c) \sin 2cx$ , and we find  $|A| = (2/a)^{1/2}$ . The **normalization constant**  $A$  can be taken as any number having absolute value  $(2/a)^{1/2}$ . We could take  $A = (2/a)^{1/2}$ , or  $A = -(2/a)^{1/2}$ , or  $A = i(2/a)^{1/2}$  (where  $i = \sqrt{-1}$ ), etc. Choosing  $A = (2/a)^{1/2}$ , we get

$$\psi = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a} \quad \text{for } 0 \leq x \leq a, \quad \text{where } n = 1, 2, 3, \dots \quad (17.35)$$

For a one-particle, one-dimensional system,  $|\psi(x)|^2 dx$  is a probability. Since probabilities have no units,  $\psi(x)$  must have dimensions of  $\text{length}^{-1/2}$ , as is true for  $\psi$  in (17.35).

The state functions for the stationary states of the particle in a box are given by (17.19), (17.21), and (17.35) as  $\Psi = e^{-iEt/\hbar} (2/a)^{1/2} \sin(n\pi x/a)$ , for  $0 \leq x \leq a$ , where  $E = n^2\hbar^2/8ma^2$  and  $n = 1, 2, 3, \dots$ .

## EXAMPLE 17.2 Calculation of a transition wavelength

Find the wavelength of the light emitted when a  $1 \times 10^{-27} \text{ g}$  particle in a  $3\text{-}\text{\AA}$  one-dimensional box goes from the  $n = 2$  to the  $n = 1$  level.

The wavelength  $\lambda$  can be found from the frequency  $\nu$ . The quantity  $h\nu$  is the energy of the emitted photon and equals the energy *difference* between the two levels involved in the transition [Eq. (17.7)]:

$$h\nu = E_{\text{upper}} - E_{\text{lower}} = 2^2\hbar^2/8ma^2 - 1^2\hbar^2/8ma^2 \quad \text{and} \quad \nu = 3h/8ma^2$$

where (17.34) was used. Use of  $\lambda = c/\nu$  and  $1 \text{ \AA} \equiv 10^{-10} \text{ m}$  [Eq. (2.87)] gives

$$\lambda = \frac{8ma^2c}{3h} = \frac{8(1 \times 10^{-30} \text{ kg})(3 \times 10^{-10} \text{ m})^2(3 \times 10^8 \text{ m/s})}{3(6.6 \times 10^{-34} \text{ J s})} = 1 \times 10^{-7} \text{ m}$$

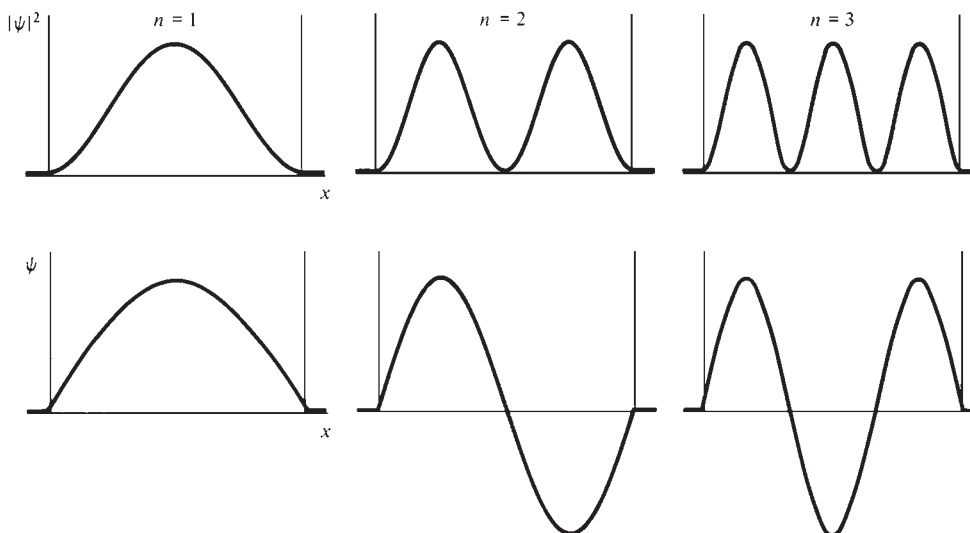
(The mass  $m$  is that of an electron, and the wavelength lies in the ultraviolet.)

### Exercise

(a) For a particle of mass  $9.1 \times 10^{-31} \text{ kg}$  in a certain one-dimensional box, the  $n = 3$  to  $n = 2$  transition occurs at  $\nu = 4.0 \times 10^{14} \text{ s}^{-1}$ . Find the length of the box. (Answer:  $1.07 \text{ nm}$ .) (b) Show that the frequency of the  $n = 3$  to  $2$  particle-in-a-one-dimensional-box transition is  $5/3$  times the frequency of the  $2$  to  $1$  transition.

Let us contrast the quantum-mechanical and classical pictures. Classically, the particle can rattle around in the box with any nonnegative energy;  $E_{\text{classical}}$  can be any number from zero on up. (The potential energy is zero in the box, so the particle's energy is entirely kinetic. Its speed  $v$  can have any nonnegative value, so  $\frac{1}{2}mv^2$  can have any nonnegative value.) Quantum-mechanically, the energy can take on only the values (17.34). The energy is quantized in quantum mechanics, whereas it is continuous in classical mechanics.

Classically, the minimum energy is zero. Quantum-mechanically, the particle in a box has a minimum energy that is greater than zero. This energy,  $\hbar^2/8ma^2$ , is the **zero-point energy**. Its existence is a consequence of the uncertainty principle. Suppose the particle could have zero energy. Since its energy is entirely kinetic, its speed  $v_x$  and momentum  $mv_x = p_x$  would then be zero. With  $p_x$  known to be zero, the uncertainty  $\Delta p_x$  is zero, and the uncertainty principle  $\Delta x \Delta p_x \geq \hbar$  gives  $\Delta x = \infty$ . However, we know the particle to be somewhere between  $x = 0$  and  $x = a$ , so  $\Delta x$  cannot exceed  $a$ . Hence, a zero energy is impossible for a particle in a box.

**Figure 17.10**

Wave functions and probability densities for the lowest three particle-in-a-box stationary states.

The stationary states of a particle in a box are specified by giving the value of the integer  $n$  in (17.35).  $n$  is called a **quantum number**. The lowest-energy state ( $n = 1$ ) is the **ground state**. States higher in energy than the ground state are **excited states**.

Figure 17.10 plots the wave functions  $\psi$  and the probability densities  $|\psi|^2$  for the first three particle-in-a-box stationary states. For  $n = 1$ ,  $n\pi x/a$  in the wave function (17.35) goes from 0 to  $\pi$  as  $x$  goes from 0 to  $a$ , so  $\psi$  is half of one cycle of a sine function.

Classically, all locations for the particle in the box are equally likely. Quantum-mechanically, the probability density is not uniform along the length of the box, but shows oscillations. In the limit of a very high quantum number  $n$ , the oscillations in  $|\psi|^2$  come closer and closer together and ultimately become undetectable; this corresponds to the classical result of uniform probability density. The relation  $8ma^2E/h^2 = n^2$  shows that for a macroscopic system ( $E$ ,  $m$ , and  $a$  having macroscopic magnitudes),  $n$  is very large, so the limit of large  $n$  is the classical limit.

A point at which  $\psi = 0$  is called a **node**. The number of nodes increases by 1 for each increase in  $n$ . The existence of nodes is surprising from a classical viewpoint. For example, for the  $n = 2$  state, it is hard to understand how the particle can be found in the left half of the box or in the right half but never at the center. The behavior of microscopic particles (which have a wave aspect) cannot be rationalized in terms of a visualizable model.

The wave functions  $\psi$  and probability densities  $|\psi|^2$  are spread out over the length of the box, much like a wave (compare Figs. 17.10 and 17.2). However, quantum mechanics does not assert that the particle itself is spread out like a wave; a measurement of position will give a definite location for the particle. It is the wave function  $\psi$  (which gives the probability density  $|\psi|^2$ ) that is spread out in space and obeys a wave equation.

### EXAMPLE 17.3 Probability calculations

- (a) For the ground state of a particle in a one-dimensional box of length  $a$ , find the probability that the particle is within  $\pm 0.001a$  of the point  $x = a/2$ . (b) For the particle-in-a-box stationary state with quantum number  $n$ , write down (but do not evaluate) an expression for the probability that the particle will be found

between  $a/4$  and  $a/2$ . (c) For a particle-in-a-box stationary state, what is the probability that the particle will be found in the left half of the box?

(a) The probability density (the probability per unit length) equals  $|\psi|^2$ . Figure 17.10 shows that  $|\psi|^2$  for  $n = 1$  is essentially constant over the very small interval  $0.002a$ , so we can consider this interval to be infinitesimal and take  $|\psi|^2 dx$  as the desired probability. For  $n = 1$ , Eq. (17.35) gives  $|\psi|^2 = (2/a) \sin^2(\pi x/a)$ . With  $x = a/2$  and  $dx = 0.002a$ , the probability is  $|\psi|^2 dx = (2/a) \sin^2(\pi/2) \times 0.002a = 0.004$ .

(b) From Eq. (17.15), the probability that the particle is between points  $c$  and  $d$  is  $\int_c^d |\Psi|^2 dx$ . But  $|\Psi|^2 = |\psi|^2$  for a stationary state [Eq. (17.25)], so the probability is  $\int_c^d |\psi|^2 dx$ . The desired probability is  $\int_{a/4}^{a/2} (2/a) \sin^2(n\pi x/a) dx$ , where (17.35) was used for  $\psi$ .

(c) For each particle-in-a-box stationary state, the graph of  $|\psi|^2$  is symmetric about the midpoint of the box, so the probabilities of being in the left and right halves are equal and are each equal to 0.5.

### Exercise

For the  $n = 2$  state of a particle in a box of length  $a$ , (a) find the probability the particle is within  $\pm 0.0015a$  of  $x = a/8$ ; (b) find the probability the particle is between  $x = 0$  and  $x = a/8$ . (Answers: (a) 0.0030; (b)  $1/8 - 1/4\pi = 0.0454$ .)

If  $\psi_i$  and  $\psi_j$  are particle-in-a-box wave functions with quantum numbers  $n_i$  and  $n_j$ , one finds (Prob. 17.29) that

$$\int_0^a \psi_i^* \psi_j d\tau = 0 \quad \text{for } n_i \neq n_j \quad (17.36)$$

where  $\psi_i = (2/a)^{1/2} \sin(n_i \pi x/a)$  and  $\psi_j = (2/a)^{1/2} \sin(n_j \pi x/a)$ . The functions  $f$  and  $g$  are said to be **orthogonal** when  $\int f^* g d\tau = 0$ , where the integral is a definite integral over the full range of the spatial coordinates. One can show that two wave functions that correspond to different energy levels of a quantum-mechanical system are orthogonal (Sec. 17.16).

## 17.9

### THE PARTICLE IN A THREE-DIMENSIONAL BOX

The particle in a three-dimensional box is a single particle of mass  $m$  confined to remain within the volume of a box by an infinite potential energy outside the box. The simplest box shape to deal with is a rectangular parallelepiped. The potential energy is therefore  $V = 0$  for points such that  $0 \leq x \leq a$ ,  $0 \leq y \leq b$ , and  $0 \leq z \leq c$  and  $V = \infty$  elsewhere. The dimensions of the box are  $a$ ,  $b$ , and  $c$ . In Secs. 20.3 and 21.6, this system will be used to give the energy levels for translational motion of ideal-gas molecules in a container.

Let us solve the time-independent Schrödinger equation for the stationary-state wave functions and energies. Since  $V = \infty$  outside the box,  $\psi$  is zero outside the box, just as for the corresponding one-dimensional problem. Inside the box,  $V = 0$ , and the Schrödinger equation (17.24) becomes

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi \quad (17.37)$$

Let us assume that solutions of (17.37) exist that have the form  $X(x)Y(y)Z(z)$ , where  $X(x)$  is a function of  $x$  only and  $Y$  and  $Z$  are functions of  $y$  and  $z$ . For an arbitrary partial differential equation, it is not in general possible to find solutions in which the variables are present in separate factors. However, it can be proved mathematically

that, if we succeed in finding well-behaved solutions to (17.37) that have the form  $X(x)Y(y)Z(z)$ , then there are no other well-behaved solutions, so we shall have found the general solution of (17.37). Our assumption is then

$$\psi = X(x)Y(y)Z(z) \quad (17.38)$$

Partial differentiation of (17.38) gives

$$\partial^2\psi/\partial x^2 = X''(x)Y(y)Z(z), \quad \partial^2\psi/\partial y^2 = X(x)Y''(y)Z(z), \quad \partial^2\psi/\partial z^2 = X(x)Y(y)Z''(z)$$

Substitution in (17.37) followed by division by  $X(x)Y(y)Z(z) = \psi$  gives

$$-\frac{\hbar^2}{2m} \frac{X''(x)}{X(x)} - \frac{\hbar^2}{2m} \frac{Y''(y)}{Y(y)} - \frac{\hbar^2}{2m} \frac{Z''(z)}{Z(z)} = E \quad (17.39)$$

Let  $E_x \equiv -(\hbar^2/2m)X''(x)/X(x)$ . Then (17.39) gives

$$E_x \equiv -\frac{\hbar^2}{2m} \frac{X''(x)}{X(x)} = E + \frac{\hbar^2}{2m} \frac{Y''(y)}{Y(y)} + \frac{\hbar^2}{2m} \frac{Z''(z)}{Z(z)} \quad (17.40)$$

From its definition,  $E_x$  is a function of  $x$  only. However, the relation  $E_x = E + \hbar^2 Y''/2mY + \hbar^2 Z''/2mZ$  in (17.40) shows  $E_x$  to be independent of  $x$ . Therefore  $E_x$  is a constant, and we have from (17.40)

$$-(\hbar^2/2m)X''(x) = E_x X(x) \quad \text{for } 0 \leq x \leq a \quad (17.41)$$

Equation (17.41) is the same as the Schrödinger equation (17.28) for a particle in a one-dimensional box if  $X$  and  $E_x$  in (17.41) are identified with  $\psi$  and  $E$ , respectively, in (17.28). Moreover, the condition that  $X(x)$  be continuous requires that  $X(x) = 0$  at  $x = 0$  and at  $x = a$ , since the three-dimensional wave function is zero outside the box. These are the same requirements that  $\psi$  in (17.28) must satisfy. Therefore, the well-behaved solutions of (17.41) and (17.28) are the same. Replacing  $\psi$  and  $E$  in (17.34) and (17.35) by  $X$  and  $E_x$ , we get

$$X(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n_x \pi x}{a}, \quad E_x = \frac{n_x^2 \hbar^2}{8ma^2}, \quad n_x = 1, 2, 3, \dots \quad (17.42)$$

where the quantum number is called  $n_x$ .

Equation (17.39) is symmetric with respect to  $x$ ,  $y$ , and  $z$ , so the same reasoning that gave (17.42) gives

$$Y(y) = \left(\frac{2}{b}\right)^{1/2} \sin \frac{n_y \pi y}{b}, \quad E_y = \frac{n_y^2 \hbar^2}{8mb^2}, \quad n_y = 1, 2, 3, \dots \quad (17.43)$$

$$Z(z) = \left(\frac{2}{c}\right)^{1/2} \sin \frac{n_z \pi z}{c}, \quad E_z = \frac{n_z^2 \hbar^2}{8mc^2}, \quad n_z = 1, 2, 3, \dots \quad (17.44)$$

where, by analogy to (17.40),

$$E_y \equiv -\frac{\hbar^2}{2m} \frac{Y''(y)}{Y(y)}, \quad E_z \equiv -\frac{\hbar^2}{2m} \frac{Z''(z)}{Z(z)} \quad (17.45)$$

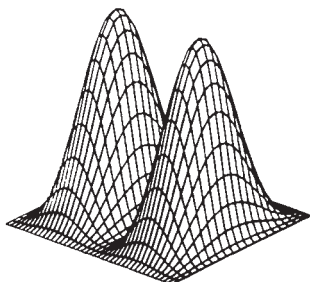
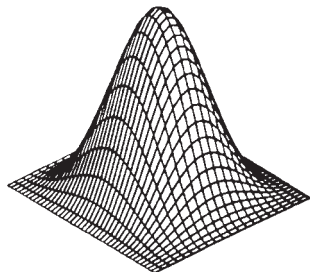
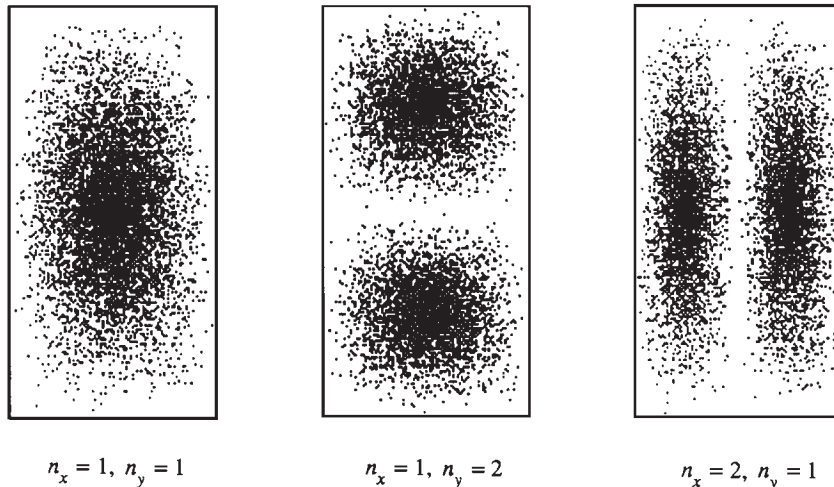
We assumed in Eq. (17.38) that the wave function  $\psi$  is the product of separate factors  $X(x)$ ,  $Y(y)$ , and  $Z(z)$  for each coordinate. Having found  $X$ ,  $Y$ , and  $Z$  [Eqs. (17.42), (17.43), and (17.44)], we have as the stationary-state wave functions for a particle in a three-dimensional rectangular box

$$\psi = \left(\frac{8}{abc}\right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad \text{inside the box} \quad (17.46)$$

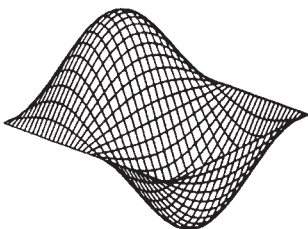
Outside the box,  $\psi = 0$ .

**Figure 17.11**

Probability densities for three states of a particle in a two-dimensional box whose dimensions have a 2:1 ratio. The states are the  $\psi_{11}$ ,  $\psi_{12}$ , and  $\psi_{21}$  states, where the subscripts give the  $n_x$  and  $n_y$  values.

**Figure 17.12**

Three-dimensional plot of  $|\psi|^2$  for the  $\psi_{11}$  and  $\psi_{12}$  states of a two-dimensional box with  $b = 2a$ .

**Figure 17.13**

Three-dimensional plot of  $\psi_{12}$  for a particle in a two-dimensional box with  $b = 2a$ .

Equations (17.39), (17.40), and (17.45) give  $E = E_x + E_y + E_z$ , and use of (17.42) to (17.44) for  $E_x$ ,  $E_y$ , and  $E_z$  gives the allowed energy levels as

$$E = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad (17.47)$$

The quantities  $E_x$ ,  $E_y$ , and  $E_z$  are the kinetic energies associated with motion in the  $x$ ,  $y$ , and  $z$  directions.

The procedure used to solve (17.37) is called **separation of variables**. The conditions under which it works are discussed in Sec. 17.11.

The wave function has three quantum numbers because this is a three-dimensional problem. The quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$  vary independently of one another. The state of the particle in the box is specified by giving the values of  $n_x$ ,  $n_y$ , and  $n_z$ . The ground state is  $n_x = 1$ ,  $n_y = 1$ , and  $n_z = 1$ .

### The Particle in a Two-Dimensional Box

For a particle in a two-dimensional rectangular box with sides  $a$  and  $b$ , the same procedure that gave (17.46) and (17.47) gives

$$\psi = (4/ab)^{1/2} \sin(n_x \pi x/a) \sin(n_y \pi y/b) \quad \text{for } 0 \leq x \leq a, 0 \leq y \leq b \quad (17.48)$$

and  $E = (h^2/8m) (n_x^2/a^2 + n_y^2/b^2)$ . For a two-dimensional box with  $b = 2a$ , Fig. 17.11 shows the variation of the probability density  $|\psi|^2$  in the box for three states. The greater the density of dots in a region, the greater the value of  $|\psi|^2$ . Figure 17.12 shows three-dimensional graphs of  $|\psi|^2$  for the lowest two states. The height of the surface above the  $xy$  plane gives the value of  $|\psi|^2$  at point  $(x, y)$ . Figure 17.13 is a three-dimensional graph of  $\psi$  for the  $n_x = 1$ ,  $n_y = 2$  state;  $\psi$  is positive in half the box, negative in the other half, and zero on the line that separates these two halves. Figure 17.14 shows contour plots of constant  $|\psi|$  for the  $n_x = 1$ ,  $n_y = 2$  state; the contours shown are those for which  $|\psi|/|\psi|_{\max} = 0.9$  (the two innermost loops), 0.7, 0.5, 0.3, and 0.1, where  $|\psi|_{\max}$  is the maximum value of  $|\psi|$ . These contours correspond to  $|\psi|^2/|\psi|_{\max}^2 = 0.81$ , 0.49, 0.25, 0.09, and 0.01.

## 17.10 DEGENERACY

Suppose the sides of the three-dimensional box of the last section have equal lengths:  $a = b = c$ . Then (17.46) and (17.47) become

$$\psi = (2/a)^{3/2} \sin(n_x \pi x/a) \sin(n_y \pi y/a) \sin(n_z \pi z/a) \quad (17.49)$$

$$E = (n_x^2 + n_y^2 + n_z^2)h^2/8ma^2 \quad (17.50)$$

Let us use numerical subscripts on  $\psi$  to specify the  $n_x$ ,  $n_y$ , and  $n_z$  values. The lowest-energy state is  $\psi_{111}$  with  $E = 3h^2/8ma^2$ . The states  $\psi_{211}$ ,  $\psi_{121}$ , and  $\psi_{112}$  each have energy  $6h^2/8ma^2$ . Even though they have the same energy, these are different states. With  $n_x = 2$ ,  $n_y = 1$ , and  $n_z = 1$  in (17.49), we get a different wave function than with  $n_x = 1$ ,  $n_y = 2$ , and  $n_z = 1$ . The  $\psi_{211}$  state has zero probability density of finding the particle at  $x = a/2$  (see Fig. 17.10), but the  $\psi_{121}$  state has a maximum probability density at  $x = a/2$ .

The terms “state” and “energy level” have different meanings in quantum mechanics. A **stationary state** is specified by giving the wave function  $\psi$ . Each different  $\psi$  is a different state. An **energy level** is specified by giving the value of the energy. Each different value of  $E$  is a different energy level. The three different particle-in-a-box states  $\psi_{211}$ ,  $\psi_{121}$ , and  $\psi_{112}$  belong to the same energy level,  $6h^2/8ma^2$ . Figure 17.15 shows the lowest few stationary states and energy levels of a particle in a cubic box.

An energy level that corresponds to more than one state is said to be **degenerate**. The number of different states belonging to the level is the **degree of degeneracy** of the level. The particle-in-a-cubic-box level  $6h^2/8ma^2$  is threefold degenerate. The particle-in-a-box degeneracy arises when the dimensions of the box are made equal. Degeneracy usually arises from the symmetry of the system.

## 17.11 OPERATORS

### Operators

Quantum mechanics is most conveniently formulated in terms of operators. An **operator** is a rule for transforming a given function into another function. For example, the operator  $d/dx$  transforms a function into its first derivative:  $(d/dx)f(x) = f'(x)$ . Let  $\hat{A}$  symbolize an arbitrary operator. (We shall use a circumflex to denote an operator.) If  $\hat{A}$  transforms the function  $f(x)$  into the function  $g(x)$ , we write  $\hat{A}f(x) = g(x)$ . If  $\hat{A}$  is the operator  $d/dx$ , then  $g(x) = f'(x)$ . If  $\hat{A}$  is the operator “multiplication by  $3x^2$ ,” then  $g(x) = 3x^2f(x)$ . If  $\hat{A} = \log$ , then  $g(x) = \log f(x)$ .

The **sum** of two operators  $\hat{A}$  and  $\hat{B}$  is defined by

$$(\hat{A} + \hat{B})f(x) \equiv \hat{A}f(x) + \hat{B}f(x) \quad (17.51)^*$$

For example,  $(\ln + d/dx)f(x) = \ln f(x) + (d/dx)f(x) = \ln f(x) + f'(x)$ . Similarly,  $(\hat{A} - \hat{B})f(x) \equiv \hat{A}f(x) - \hat{B}f(x)$ .

The **square** of an operator is defined by  $\hat{A}^2f(x) \equiv \hat{A}[\hat{A}f(x)]$ . For example,

$$(d/dx)^2 f(x) = (d/dx) [(d/dx) f(x)] = (d/dx) [f'(x)] = f''(x) = (d^2/dx^2) f(x)$$

Therefore,  $(d/dx)^2 = d^2/dx^2$ .

The **product** of two operators is defined by

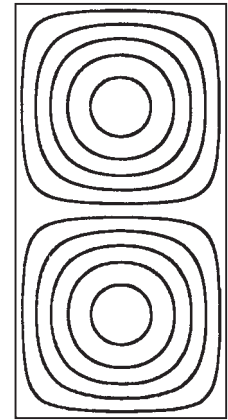
$$(\hat{A}\hat{B})f(x) \equiv \hat{A}[\hat{B}f(x)] \quad (17.52)^*$$

The notation  $\hat{A}[\hat{B}f(x)]$  means that we first apply the operator  $\hat{B}$  to the function  $f(x)$  to get a new function, and then we apply the operator  $\hat{A}$  to this new function.

Two operators are **equal** if they produce the same result when operating on an arbitrary function:  $\hat{B} = \hat{C}$  if and only if  $\hat{B}f = \hat{C}f$  for every function  $f$ .

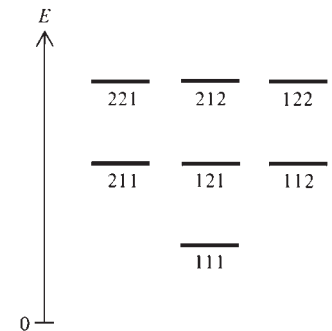
### EXAMPLE 17.4 Operator algebra

Let the operators  $\hat{A}$  and  $\hat{B}$  be defined as  $\hat{A} \equiv x \cdot$  and  $\hat{B} \equiv d/dx$ . (a) Find  $(\hat{A} + \hat{B})(x^3 + \cos x)$ . (b) Find  $\hat{A}\hat{B}f(x)$  and  $\hat{B}\hat{A}f(x)$ . Are the operators  $\hat{A}\hat{B}$  and  $\hat{B}\hat{A}$  equal? (c) Find  $\hat{A}\hat{B} - \hat{B}\hat{A}$ .



**Figure 17.14**

Contour plot of constant  $|\psi|$  for the state of Fig. 17.13.



**Figure 17.15**

Lowest seven stationary states (and lowest three energy levels) for a particle in a cubic box. The numbers are the values of the quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$ .



(a) Using the definition (17.51) of the sum of operators, we have

$$\begin{aligned}(\hat{A} + \hat{B})(x^3 + \cos x) &= (x + d/dx)(x^3 + \cos x) \\&= x(x^3 + \cos x) + (d/dx)(x^3 + \cos x) \\&= x^4 + x \cos x + 3x^2 - \sin x\end{aligned}$$

(b) The definition (17.52) of the operator product gives

$$\begin{aligned}\hat{A}\hat{B}f(x) &\equiv \hat{A}[\hat{B}f(x)] = x[(d/dx)f(x)] = x[f'(x)] = xf'(x) \\ \hat{B}\hat{A}f(x) &\equiv \hat{B}[\hat{A}f(x)] = (d/dx)[xf(x)] = xf'(x) + f(x)\end{aligned}$$

In this example,  $\hat{A}\hat{B}$  and  $\hat{B}\hat{A}$  produce different results when they operate on  $f(x)$ , so  $\hat{A}\hat{B}$  and  $\hat{B}\hat{A}$  are not equal in this case. In multiplication of numbers, the order doesn't matter. In multiplication of operators, the order may matter.

(c) To find the operator  $\hat{A}\hat{B} - \hat{B}\hat{A}$ , we examine the result of applying it to an arbitrary function  $f(x)$ . We have  $(\hat{A}\hat{B} - \hat{B}\hat{A})f(x) = \hat{A}\hat{B}f - \hat{B}\hat{A}f = xf' - (xf' + f) = -f$ , where the definition of the difference of operators and the results of (b) were used. Since  $(\hat{A}\hat{B} - \hat{B}\hat{A})f(x) = -1 \cdot f(x)$  for all functions  $f(x)$ , the definition of equality of operators gives

$$\hat{A}\hat{B} - \hat{B}\hat{A} = -1$$

where the multiplication sign after the  $-1$  is omitted, as is customary.

The operator  $\hat{A}\hat{B} - \hat{B}\hat{A}$  is called the **commutator** of  $\hat{A}$  and  $\hat{B}$  and is symbolized by  $[\hat{A}, \hat{B}]$ :

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

### Exercise

Let  $\hat{R} \equiv x^2$  and  $\hat{S} \equiv d^2/dx^2$ . (a) Find  $(\hat{R} + \hat{S})(x^4 + 1/x)$ . (b) Find  $\hat{R}\hat{S}f(x)$  and  $\hat{S}\hat{R}f(x)$ . (c) Find  $[\hat{R}, \hat{S}]$ . [Answers: (a)  $x^6 + 12x^2 + x + 2/x^3$ ; (b)  $x^2f''(x)$ ,  $2f(x) + 4xf'(x) + x^2f''(x)$ ; (c)  $-2 - 4x(d/dx)$ .]

## Operators in Quantum Mechanics

In quantum mechanics, each physical property of a system has a corresponding operator. The operator that corresponds to  $p_x$ , the  $x$  component of momentum of a particle, is postulated to be  $(\hbar/i)(\partial/\partial x)$ , with similar operators for  $p_y$  and  $p_z$ :

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad \hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y}, \quad \hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z} \quad (17.53)^*$$

where  $\hat{p}_x$  is the quantum-mechanical operator for the property  $p_x$  and  $i \equiv \sqrt{-1}$ . The operator that corresponds to the  $x$  coordinate of a particle is multiplication by  $x$ , and the operator that corresponds to  $f(x, y, z)$ , where  $f$  is any function, is multiplication by that function. Thus,

$$\hat{x} = x \times, \quad \hat{y} = y \times, \quad \hat{z} = z \times, \quad \hat{f}(x, y, z) = f(x, y, z) \times \quad (17.54)^*$$

To find the operator that corresponds to any other physical property, we write down the classical-mechanical expression for that property as a function of cartesian coordinates and corresponding momenta and then replace the coordinates and momenta by their corresponding operators (17.53) and (17.54). For example, the energy of a one-particle system is the sum of its kinetic and potential energies:

$$E = K + V = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + V(x, y, z, t)$$

To express  $E$  as a function of the momenta and coordinates, we note that  $p_x = mv_x$ ,  $p_y = mv_y$ ,  $p_z = mv_z$ . Therefore,

$$E = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z, t) \equiv H \quad (17.55)*$$

The expression for the energy as a function of coordinates and momenta is called the system's **Hamiltonian**  $H$  [after W. R. Hamilton (1805–1865), who reformulated Newton's second law in terms of  $H$ ]. The use of Eq. (17.53) and  $i^2 = -1$  gives

$$\hat{p}_x^2 f(x, y, z) = (\hbar/i)(\partial/\partial x)[(\hbar/i)(\partial/\partial x)f] = (\hbar^2/i^2) \partial^2 f/\partial x^2 = -\hbar^2 \partial^2 f/\partial x^2$$

so  $\hat{p}_x^2 = -\hbar^2 \partial^2/\partial x^2$  and  $\hat{p}_x^2/2m = -(\hbar^2/2m) \partial^2/\partial x^2$ . From (17.54), the potential-energy operator is simply multiplication by  $V(x, y, z, t)$ . (Time is a parameter in quantum mechanics, and there is no time operator.) Replacing  $p_x^2$ ,  $p_y^2$ ,  $p_z^2$ , and  $V$  in (17.55) by their operators, we get as the energy operator, or **Hamiltonian operator**, for a one-particle system

$$\hat{E} = \hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z, t) \times \quad (17.56)$$

To save time in writing, we define the **Laplacian operator**  $\nabla^2$  (read as “del squared”) by  $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$  and write the one-particle Hamiltonian operator as

$$\hat{H} = -(\hbar^2/2m) \nabla^2 + V \quad (17.57)$$

where the multiplication sign after  $V$  is understood.

For a many-particle system, we have  $\hat{p}_{x,1} = (\hbar/i) \partial/\partial x_1$  for particle 1, and the Hamiltonian operator is readily found to be

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 - \dots - \frac{\hbar^2}{2m_n} \nabla_n^2 + V(x_1, \dots, z_n, t) \quad (17.58)*$$

$$\nabla_1^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \quad (17.59)*$$

with similar definitions for  $\nabla_2^2, \dots, \nabla_n^2$ . The terms in (17.58) are the operators for the kinetic energies of particles 1, 2,  $\dots$ ,  $n$  and the potential energy of the system.

From (17.58), we see that the time-dependent Schrödinger equation (17.10) can be written as

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (17.60)$$

and the time-independent Schrödinger equation (17.24) can be written as

$$\hat{H} \psi = E \psi \quad (17.61)*$$

where  $V$  in (17.61) is independent of time. Since there is a whole set of allowed stationary-state wave functions and energies, (17.61) is often written as  $\hat{H} \psi_j = E_j \psi_j$ , where the subscript  $j$  labels the various wave functions (states) and their energies.

When an operator  $\hat{B}$  applied to the function  $f$  gives the function back again but multiplied by the constant  $c$ , that is, when

$$\hat{B}f = cf$$

one says that  $f$  is an **eigenfunction** of  $\hat{B}$  with **eigenvalue**  $c$ . (However, the function  $f = 0$  everywhere is not allowed as an eigenfunction.) The wave functions  $\psi$  in (17.61) are eigenfunctions of the Hamiltonian operator  $\hat{H}$ , the eigenvalues being the allowed energies  $E$ .

Operator algebra differs from ordinary algebra. From  $\hat{H}\psi = E\psi$  [Eq. (17.61)], one cannot conclude that  $\hat{H} = E$ .  $\hat{H}$  is an operator and  $E$  is a number, and the two are not equal. Note, for example, that  $(d/dx)e^{2x} = 2e^{2x}$ , but  $d/dx \neq 2$ . In Example 17.4, we found that  $(\hat{A}\hat{B} - \hat{B}\hat{A})f(x) = -1 \cdot f(x)$  (for  $\hat{A} = x \cdot$  and  $\hat{B} = d/dx$ ) and concluded that  $\hat{A}\hat{B} - \hat{B}\hat{A} = -1 \cdot$ . Because this equation applies to all functions  $f(x)$ , it is valid to delete the  $f(x)$  here. However, the relation  $(d/dx)e^{2x} = 2e^{2x}$  applies only to the function  $e^{2x}$ , and this function cannot be deleted.

## EXAMPLE 17.5 Eigenfunctions

Verify directly that  $\hat{H}\psi = E\psi$  for the particle in a one-dimensional box.

Inside the box (Fig. 17.7),  $V = 0$  and Eq. (17.56) gives  $\hat{H} = -(\hbar^2/2m) d^2/dx^2$  for this one-dimensional problem. The wave functions are given by (17.35) as  $\psi = (2/a)^{1/2} \sin(n\pi x/a)$ . We have, using (1.27) and (17.11):

$$\begin{aligned}\hat{H}\psi &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left[ \left( \frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] = -\frac{\hbar^2}{4\pi^2(2m)} \left( \frac{2}{a} \right)^{1/2} \left( -\frac{n^2\pi^2}{a^2} \right) \sin \frac{n\pi x}{a} \\ &= \frac{n^2\hbar^2}{8ma^2} \left( \frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} = E\psi\end{aligned}$$

since  $E = n^2\hbar^2/8ma^2$  [Eq. (17.34)].

### Exercise

Verify that the function  $Ae^{ikx}$ , where  $A$  and  $k$  are constants, is an eigenfunction of the operator  $\hat{p}_x$ . What is the eigenvalue? (Answer:  $k\hbar$ .)

The operators that correspond to physical quantities in quantum mechanics are linear. A **linear operator**  $\hat{L}$  is one that satisfies the following two equations for all functions  $f$  and  $g$  and all constants  $c$ :

$$\hat{L}(f + g) = \hat{L}f + \hat{L}g \quad \text{and} \quad \hat{L}(cf) = c\hat{L}f$$

The operator  $\partial/\partial x$  is linear, since  $(\partial/\partial x)(f + g) = \partial f/\partial x + \partial g/\partial x$  and  $(\partial/\partial x)(cf) = c \partial f/\partial x$ . The operator  $\sqrt{\phantom{x}}$  is nonlinear, since  $\sqrt{f + g} \neq \sqrt{f} + \sqrt{g}$ .

If the function  $\psi$  satisfies the time-independent Schrödinger equation  $\hat{H}\psi = E\psi$ , then so does the function  $c\psi$ , where  $c$  is any constant. Proof of this follows from the fact that the Hamiltonian operator  $\hat{H}$  is a linear operator. We have  $\hat{H}(c\psi) = c\hat{H}\psi = cE\psi = E(c\psi)$ . The freedom to multiply  $\psi$  by a constant enables us to normalize  $\psi$ .

### Measurement

Multiplication of  $\hat{H}\psi = E\psi$  [Eq. (17.61)] by  $e^{-iEt/\hbar}$  gives  $e^{-iEt/\hbar}\hat{H}\psi = Ee^{-iEt/\hbar}\psi$ . For a stationary state,  $\hat{H}$  does not involve time and  $e^{-iEt/\hbar}\hat{H}\psi = \hat{H}(e^{-iEt/\hbar}\psi)$ . Using  $\Psi = e^{-iEt/\hbar}\psi$  [Eq. (17.23)], we have

$$\hat{H}\Psi = E\Psi$$

so  $\Psi$  is an eigenfunction of  $\hat{H}$  with eigenvalue  $E$  for a stationary state. A stationary state has a definite energy, and measurement of the system's energy will always give a single predictable value when the system is in a stationary state. For example, for the  $n = 2$  particle-in-a-box stationary state, measurement of the energy will always give the result  $2^2\hbar^2/8ma^2$  [Eq. (17.34)].

What about properties other than the energy? Let the operator  $\hat{M}$  correspond to the property  $M$ . Quantum mechanics postulates that *if the system's state function  $\Psi$  happens to be an eigenfunction of  $\hat{M}$  with eigenvalue  $c$  (that is, if  $\hat{M}\Psi = c\Psi$ ), then a*

measurement of  $M$  is certain to give the value  $c$  as the result. (Examples will be given when we consider angular momentum in Sec. 18.4). If  $\Psi$  is not an eigenfunction of  $\hat{M}$ , then the result of measuring  $M$  cannot be predicted. (However, the probabilities of the various possible outcomes of a measurement of  $M$  can be calculated from  $\Psi$ , but discussion of how this is done is omitted.) For stationary states, the essential part of  $\Psi$  is the time-independent wave function  $\psi$ , and  $\psi$  replaces  $\Psi$  in the italicized statement in this paragraph.

### Average Values

From (14.38), the average value of  $x$  for a one-particle, one-dimensional quantum-mechanical system equals  $\int_{-\infty}^{\infty} xg(x) dx$ , where  $g(x)$  is the probability density for finding the particle between  $x$  and  $x + dx$ . But the Born postulate (Sec. 17.6) gives  $g(x) = |\Psi(x)|^2$ . Hence,  $\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi(x)|^2 dx$ . Since  $|\Psi|^2 = \Psi^*\Psi$ , we have  $\langle x \rangle = \int_{-\infty}^{\infty} \Psi^* x \Psi dx = \int_{-\infty}^{\infty} \Psi^* \hat{x} \Psi dx$ , where (17.54) was used.

What about the average value of an arbitrary physical property  $M$  for a general quantum-mechanical system? Quantum mechanics *postulates* that the average value of any physical property  $M$  in a system whose state function is  $\Psi$  is given by

$$\langle M \rangle = \int \Psi^* \hat{M} \Psi d\tau \quad (17.62)$$

where  $\hat{M}$  is the operator for the property  $M$  and the integral is a definite integral over all space. In (17.62),  $\hat{M}$  operates on  $\Psi$  to produce the result  $\hat{M}\Psi$ , which is a function. The function  $\hat{M}\Psi$  is then multiplied by  $\Psi^*$ , and the resulting function  $\Psi^* \hat{M} \Psi$  is integrated over the full range of the spatial coordinates of the system. For example, Eq. (17.53) gives the  $p_x$  operator as  $\hat{p}_x = (\hbar/i) \partial/\partial x$ , and the average value of  $p_x$  for a one-particle, three-dimensional system whose state function is  $\Psi$  is  $\langle p_x \rangle = (\hbar/i) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^* (\partial\Psi/\partial x) dx dy dz$ .

The average value of  $M$  is the average of the results of a very large number of measurements of  $M$  made on identical systems, each of which is in the same state  $\Psi$  just before the measurement.

If  $\Psi$  happens to be an eigenfunction of  $\hat{M}$  with eigenvalue  $c$ , then  $\hat{M}\Psi = c\Psi$  and (17.62) becomes  $\langle M \rangle = \int \Psi^* \hat{M} \Psi d\tau = \int \Psi^* c\Psi d\tau = c \int \Psi^* \Psi d\tau = c$ , since  $\Psi$  is normalized. This result makes sense since, as noted in the last subsection,  $c$  is the only possible result of a measurement of  $M$  if  $\hat{M}\Psi = c\Psi$ .

For a stationary state,  $\Psi$  equals  $e^{-iEt/\hbar}\psi$  [Eq. (17.23)]. Since  $\hat{M}$  doesn't affect the  $e^{-iEt/\hbar}$  factor, we have

$$\Psi^* \hat{M} \Psi = e^{iEt/\hbar} \psi^* \hat{M} e^{-iEt/\hbar} \psi = e^{iEt/\hbar} e^{-iEt/\hbar} \psi^* \hat{M} \psi = \psi^* \hat{M} \psi$$

Therefore, for a stationary state,

$$\langle M \rangle = \int \psi^* \hat{M} \psi d\tau \quad (17.63)^*$$

### EXAMPLE 17.6 Average value

For a particle in a one-dimensional-box stationary state, give the expression for  $\langle x^2 \rangle$ .

For a one-particle, one-dimensional problem,  $d\tau = dx$ . Since  $\hat{x}^2 = x^2$ , we have

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi^* x^2 \psi dx = \int_{-\infty}^0 x^2 |\psi|^2 dx + \int_0^a x^2 |\psi|^2 dx + \int_a^{\infty} x^2 |\psi|^2 dx$$

since  $\psi^*\psi = |\psi|^2$  [Eq. (17.14)]. For  $x < 0$  and  $x > a$ , we have  $\psi = 0$  [Eq. (17.27)] and inside the box  $\psi = (2/a)^{1/2} \sin(n\pi x/a)$  [Eq. (17.35)]. Therefore

$$\langle x^2 \rangle = \frac{2}{a} \int_0^a x^2 \sin^2 \frac{n\pi x}{a} dx$$

Evaluation of the integral is left as a homework problem (Prob. 17.42).

### Exercise

Evaluate  $\langle p_x \rangle$  for a particle in a one-dimensional-box stationary state. [Answer:  $(2n\pi\hbar/ia^2) \int_0^a \sin(n\pi x/a) \cos(n\pi x/a) dx = 0$ .]

### Separation of Variables

Let  $q_1, q_2, \dots, q_r$  be the coordinates of a system. For example, for a two-particle system,  $q_1 = x_1, q_2 = y_1, \dots, q_6 = z_2$ . Suppose the Hamiltonian operator has the form

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \dots + \hat{H}_r \quad (17.64)$$

where the operator  $\hat{H}_1$  involves only  $q_1$ , the operator  $\hat{H}_2$  involves only  $q_2$ , etc. An example is the particle in a three-dimensional box, where one has  $\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$ , with  $\hat{H}_x \equiv -(\hbar^2/2m) \partial^2/\partial x^2$ , etc. We saw in Sec. 17.9 that, for this case,  $\psi = X(x)Y(y)Z(z)$  and  $E = E_x + E_y + E_z$ , where  $\hat{H}_x X(x) = E_x X(x)$ ,  $\hat{H}_y Y(y) = E_y Y(y)$ ,  $\hat{H}_z Z(z) = E_z Z(z)$  [Eqs. (17.41) and (17.45)].

The same type of argument used in Sec. 17.9 shows (Prob. 17.43) that when  $\hat{H}$  is the sum of separate terms for each coordinate, as in (17.64), then each stationary-state wave function is the product of separate factors for each coordinate and each stationary-state energy is the sum of energies for each coordinate:

$$\psi = f_1(q_1)f_2(q_2) \cdots f_r(q_r) \quad (17.65)^*$$

$$E = E_1 + E_2 + \dots + E_r \quad (17.66)^*$$

where  $E_1, E_2, \dots$  and the functions  $f_1, f_2, \dots$  are found by solving

$$\hat{H}_1 f_1 = E_1 f_1, \quad \hat{H}_2 f_2 = E_2 f_2, \quad \dots, \quad \hat{H}_r f_r = E_r f_r \quad (17.67)$$

The equations in (17.67) are, in effect, separate Schrödinger equations, one for each coordinate.

### Noninteracting Particles

An important case where separation of variables applies is a system of  $n$  noninteracting particles, meaning that the particles exert no forces on one another. For such a system, the classical-mechanical energy is the sum of the energies of the individual particles, so the classical Hamiltonian  $H$  and the quantum-mechanical Hamiltonian operator  $\hat{H}$  have the forms  $H = H_1 + H_2 + \dots + H_n$  and  $\hat{H} = \hat{H}_1 + \hat{H}_2 + \dots + \hat{H}_n$ , where  $\hat{H}_1$  involves only the coordinates of particle 1,  $\hat{H}_2$  involves only particle 2, etc. Here, by analogy to (17.65) to (17.67), we have

$$\psi = f_1(x_1, y_1, z_1)f_2(x_2, y_2, z_2) \cdots f_n(x_n, y_n, z_n) \quad (17.68)^*$$

$$E = E_1 + E_2 + \dots + E_n \quad (17.69)^*$$

$$\hat{H}_1 f_1 = E_1 f_1, \quad \hat{H}_2 f_2 = E_2 f_2, \quad \dots, \quad \hat{H}_n f_n = E_n f_n \quad (17.70)^*$$

*For a system of noninteracting particles, there is a separate Schrödinger equation for each particle, the wave function is the product of wave functions of the individual*

particles, and the energy is the sum of the energies of the individual particles. (For noninteracting particles, the probability density  $|\psi|^2$  is the product of probability densities for each particle:  $|\psi|^2 = |f_1|^2 |f_2|^2 \cdots |f_n|^2$ . This is in accord with the theorem that the probability that several independent events will all occur is the product of the probabilities of the separate events.)

## 17.12 THE ONE-DIMENSIONAL HARMONIC OSCILLATOR

The one-dimensional **harmonic oscillator** is a useful model for treating the vibration of a diatomic molecule (Sec. 20.3) and is also relevant to vibrations of polyatomic molecules (Sec. 20.8) and crystals (Sec. 23.12).

### Classical Treatment

Before examining the quantum mechanics of a harmonic oscillator, we review the classical treatment. Consider a particle of mass  $m$  that moves in one dimension and is attracted to the coordinate origin by a force proportional to its displacement from the origin:  $F = -kx$ , where  $k$  is called the **force constant**. When  $x$  is positive, the force is in the  $-x$  direction, and when  $x$  is negative,  $F$  is in the  $+x$  direction. A physical example is a mass attached to a frictionless spring,  $x$  being the displacement from the equilibrium position. From (2.17),  $F = -dV/dx$ , where  $V$  is the potential energy. Hence  $-dV/dx = -kx$ , and  $V = \frac{1}{2}kx^2 + c$ . The choice of zero of potential energy is arbitrary. Choosing the integration constant  $c$  as zero, we have (Fig. 17.16)

$$V = \frac{1}{2}kx^2 \quad (17.71)$$

Newton's second law  $F = ma$  gives  $m d^2x/dt^2 = -kx$ . The solution to this differential equation is

$$x = A \sin [(k/m)^{1/2}t + b] \quad (17.72)$$

as can be verified by substitution in the differential equation (Prob. 17.52). In (17.72),  $A$  and  $b$  are integration constants. The maximum and minimum values of the sine function are  $+1$  and  $-1$ , so the particle's  $x$  coordinate oscillates back and forth between  $+A$  and  $-A$ .  $A$  is the *amplitude* of the motion.

The *period*  $\tau$  (tau) of the oscillator is the time required for one complete cycle of oscillation. For one cycle of oscillation, the argument of the sine function in (17.72) must increase by  $2\pi$ , since  $2\pi$  is the period of a sine function. Hence the period satisfies  $(k/m)^{1/2}\tau = 2\pi$ , and  $\tau = 2\pi(m/k)^{1/2}$ . The **frequency**  $\nu$  is the reciprocal of the period and equals the number of vibrations per second ( $\nu = 1/\tau$ ); thus

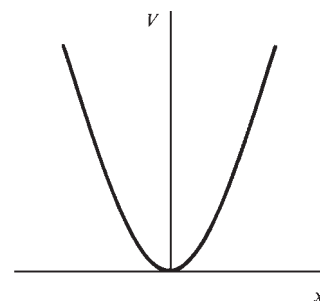
$$\nu = \frac{1}{2\pi} \left( \frac{k}{m} \right)^{1/2} \quad (17.73)^*$$

The energy of the harmonic oscillator is  $E = K + V = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2$ . The use of (17.72) for  $x$  and of  $v_x = dx/dt = (k/m)^{1/2}A \cos [(k/m)^{1/2}t + b]$  leads to (Prob. 17.52)

$$E = \frac{1}{2}kA^2 \quad (17.74)$$

Equation (17.74) shows that the classical energy can have any nonnegative value. As the particle oscillates, its kinetic energy and potential energy continually change, but the total energy remains constant at  $\frac{1}{2}kA^2$ .

Classically, the particle is limited to the region  $-A \leq x \leq A$ . When the particle reaches  $x = A$  or  $x = -A$ , its speed is zero (since it reverses its direction of motion at  $+A$  and  $-A$ ) and its potential energy is a maximum, being equal to  $\frac{1}{2}kA^2$ . If the particle were to move beyond  $x = \pm A$ , its potential energy would increase above  $\frac{1}{2}kA^2$ . This is impossible for a classical particle. The total energy is  $\frac{1}{2}kA^2$  and the



**Figure 17.16**

The potential-energy function for a one-dimensional harmonic oscillator.

kinetic energy is nonnegative, so the potential energy ( $V = E - K$ ) cannot exceed the total energy.

### Quantum-Mechanical Treatment

Now for the quantum-mechanical treatment. Substitution of  $V = \frac{1}{2}kx^2$  in (17.26) gives the time-independent Schrödinger equation as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \quad (17.75)$$

Solution of the harmonic-oscillator Schrödinger equation (17.75) is complicated and is omitted in this book (see any quantum chemistry text). Here, we examine the results. One finds that quadratically integrable (Sec. 17.7) solutions to (17.75) exist only for the following values of  $E$ :

$$E = (v + \frac{1}{2})h\nu \quad \text{where } v = 0, 1, 2, \dots \quad (17.76)^*$$

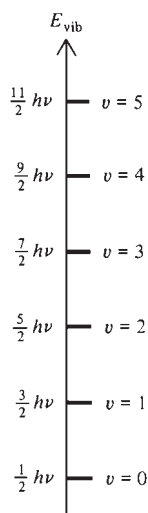
where the vibrational frequency  $\nu$  is given by (17.73) and the quantum number  $v$  takes on nonnegative integral values. [Don't confuse the typographically similar symbols  $\nu$  (nu) and  $v$  (vee).] The energy is quantized. The allowed energy levels (Fig. 17.17) are equally spaced (unlike the particle in a box). The zero-point energy is  $\frac{1}{2}h\nu$ . (For a collection of harmonic oscillators in thermal equilibrium, all the oscillators will fall to the ground state as the temperature goes to absolute zero; hence the name *zero-point energy*.) For all values of  $E$  other than (17.76), one finds that the solutions to (17.75) go to infinity as  $x$  goes to  $\pm\infty$ , so these solutions are not quadratically integrable and are not allowed as wave functions.

The well-behaved solutions to (17.75) turn out to have the form

$$\psi_v = \begin{cases} e^{-\alpha x^2/2} (c_0 + c_2 x^2 + \dots + c_v x^v) & \text{for } v \text{ even} \\ e^{-\alpha x^2/2} (c_1 x + c_3 x^3 + \dots + c_v x^v) & \text{for } v \text{ odd} \end{cases}$$

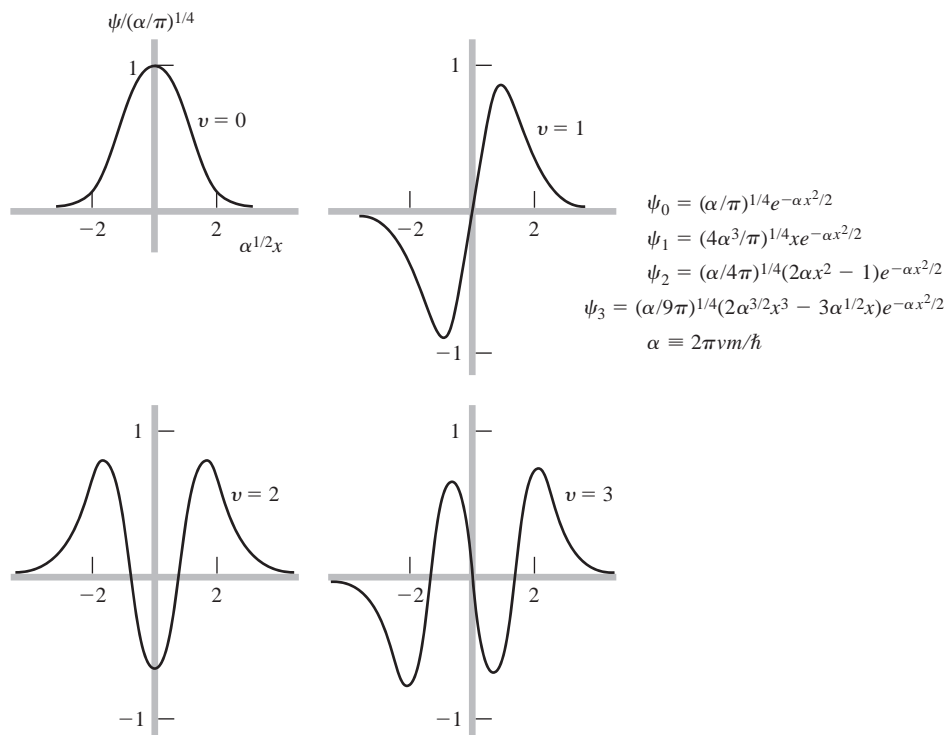
where  $\alpha \equiv 2\pi\nu m/\hbar$ . The polynomial that multiplies  $e^{-\alpha x^2/2}$  contains only even powers of  $x$  or only odd powers, depending on whether the quantum number  $v$  is even or odd. The explicit forms of the lowest few wave functions  $\psi_0$ ,  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  (where the subscript on  $\psi$  gives the value of the quantum number  $v$ ) are given in Fig. 17.18, which plots these  $\psi$ 's. As with the particle in a one-dimensional box, the number of nodes increases by one for each increase in the quantum number. Note the qualitative resemblance of the wave functions in Figs. 17.18 and 17.10.

The harmonic-oscillator wave functions fall off exponentially to zero as  $x \rightarrow \pm\infty$ . Note, however, that even for very large values of  $x$ , the wave function  $\psi$  and the probability density  $|\psi|^2$  are not zero. There is some probability of finding the particle at an indefinitely large value of  $x$ . For a classical-mechanical harmonic oscillator with energy  $(v + \frac{1}{2})h\nu$ , Eq. (17.74) gives  $(v + \frac{1}{2})h\nu = \frac{1}{2}kA^2$ , and  $A = [(2v + 1)h\nu/k]^{1/2}$ . A classical oscillator is confined to the region  $-A \leq x \leq A$ . However, a quantum-mechanical oscillator has some probability of being found in the *classically forbidden* regions  $x > A$  and  $x < -A$ , where the potential energy is greater than the particle's total energy. This penetration into classically forbidden regions is called **tunneling**. Tunneling occurs more readily the smaller the particle's mass and is most important in chemistry for electrons, protons, and H atoms. Tunneling influences the rates of reactions involving these species (see Secs. 22.3 and 22.4). Electron tunneling is the basis for the scanning tunneling microscope, a remarkable device that gives pictures of the atoms on the surface of a solid (Sec. 23.10). Tunneling makes possible the fusion of hydrogen nuclei to helium nuclei in the sun, despite the electrical repulsion between two hydrogen nuclei.



**Figure 17.17**

Energy levels of a one-dimensional harmonic oscillator.

**Figure 17.18**

Wave functions for the lowest four harmonic-oscillator stationary states.

## 17.13 TWO-PARTICLE PROBLEMS

Consider a two-particle system where the coordinates of the particles are  $x_1, y_1, z_1$  and  $x_2, y_2, z_2$ . The **relative** (or **internal**) **coordinates**  $x, y, z$  are defined by

$$x \equiv x_2 - x_1, \quad y \equiv y_2 - y_1, \quad z \equiv z_2 - z_1 \quad (17.77)$$

These are the coordinates of particle 2 in a coordinate system whose origin is attached to particle 1 and moves with it.

In most cases, the potential energy  $V$  of the two-particle system depends only on the relative coordinates  $x, y$ , and  $z$ . For example, if the particles are electrically charged, the Coulomb's law potential energy of interaction between the particles depends only on the distance  $r$  between them, and  $r = (x^2 + y^2 + z^2)^{1/2}$ . Let us assume that  $V = V(x, y, z)$ . Let  $X, Y$ , and  $Z$  be the coordinates of the center of mass of the system;  $X$  is given by  $(m_1 x_1 + m_2 x_2)/(m_1 + m_2)$ , where  $m_1$  and  $m_2$  are the masses of the particles (*Halliday and Resnick*, sec. 9-1). If one expresses the classical energy (that is, the classical Hamiltonian) of the system in terms of the internal coordinates  $x, y$ , and  $z$  and the center-of-mass coordinates  $X, Y$ , and  $Z$ , instead of  $x_1, y_1, z_1, x_2, y_2$ , and  $z_2$ , it turns out (see Prob. 17.55) that

$$H = \left[ \frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z) \right] + \left[ \frac{1}{2M} (p_X^2 + p_Y^2 + p_Z^2) \right] \quad (17.78)$$

where  $M$  is the system's total mass ( $M = m_1 + m_2$ ), the **reduced mass**  $\mu$  is defined by

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad (17.79)^*$$



and the momenta in (17.78) are defined by

$$\begin{aligned} p_x &\equiv \mu v_x, & p_y &\equiv \mu v_y, & p_z &\equiv \mu v_z \\ p_X &\equiv M v_X, & p_Y &\equiv M v_Y, & p_Z &\equiv M v_Z \end{aligned} \quad (17.80)$$

where  $v_x = dx/dt$ , etc., and  $v_X = dX/dt$ , etc.

Equation (17.55) shows that the Hamiltonian (17.78) is the sum of a Hamiltonian for a fictitious particle of mass  $\mu$  and coordinates  $x$ ,  $y$ , and  $z$  that has the potential energy  $V(x, y, z)$  and a Hamiltonian for a second fictitious particle of mass  $M = m_1 + m_2$  and coordinates  $X$ ,  $Y$ , and  $Z$  that has  $V = 0$ . Moreover, there is no term for any interaction between these two fictitious particles. Hence, Eqs. (17.69) and (17.70) show that the quantum-mechanical energy  $E$  of the two-particle system is given by  $E = E_\mu + E_M$ , where  $E_\mu$  and  $E_M$  are found by solving

$$\hat{H}_\mu \psi_\mu(x, y, z) = E_\mu \psi_\mu(x, y, z) \quad \text{and} \quad \hat{H}_M \psi_M(X, Y, Z) = E_M \psi_M(X, Y, Z)$$

The Hamiltonian operator  $\hat{H}_\mu$  is formed from the terms in the first pair of brackets in (17.78), and  $\hat{H}_M$  is formed from the terms in the second pair of brackets.

Introduction of the relative coordinates  $x$ ,  $y$ , and  $z$  and the center-of-mass coordinates  $X$ ,  $Y$ , and  $Z$  reduces the two-particle problem to two separate one-particle problems. We solve a Schrödinger equation for a fictitious particle of mass  $\mu$  moving subject to the potential energy  $V(x, y, z)$ , and we solve a separate Schrödinger equation for a fictitious particle whose mass is  $M (= m_1 + m_2)$  and whose coordinates are the system's center-of-mass coordinates  $X$ ,  $Y$ , and  $Z$ . The Hamiltonian  $\hat{H}_M$  involves only kinetic energy. If the two particles are confined to a box, we can use the particle-in-a-box energies (17.47) for  $E_M$ . The energy  $E_M$  is translational energy of the two-particle system as a whole. The Hamiltonian  $\hat{H}_\mu$  involves the kinetic energy and potential energy of motion of the particles relative to each other, so  $E_\mu$  is the energy associated with this relative or “internal” motion.

The system's total energy  $E$  is the sum of its translational energy  $E_M$  and its internal energy  $E_\mu$ . For example, the energy of a hydrogen atom in a box is the sum of the atom's translational energy through space and the atom's internal energy, which is composed of potential energy of interaction between the electron and the proton and kinetic energy of motion of the electron relative to the proton.

## 17.14 THE TWO-PARTICLE RIGID ROTOR

The **two-particle rigid rotor** consists of particles of masses  $m_1$  and  $m_2$  constrained to remain a fixed distance  $d$  from each other. This is a useful model for treating the rotation of a diatomic molecule; see Sec. 20.3. The system's energy is wholly kinetic, and  $V = 0$ . Since  $V = 0$  is a special case of  $V$  being a function of only the relative coordinates of the particles, the results of the last section apply. The quantum-mechanical energy is the sum of the translational energy of the system as a whole and the energy of internal motion of one particle relative to the other. The interparticle distance is constant, so the internal motion consists entirely of changes in the spatial orientation of the interparticle axis. The internal motion is a rotation of the two-particle system.

Solution of the Schrödinger equation for internal motion is complicated, so we shall just quote the results without proof. (For a derivation, see, for example, *Levine*, sec. 6.4.) The allowed rotational energies turn out to be

$$E_{\text{rot}} = J(J + 1) \frac{\hbar^2}{2I} \quad \text{where } J = 0, 1, 2, \dots \quad (17.81)^*$$

where the rotor's **moment of inertia**  $I$  is

$$I = \mu d^2 \quad (17.82)^*$$

with  $\mu = m_1 m_2 / (m_1 + m_2)$ . The spacing between adjacent rotational energy levels increases with increasing quantum number  $J$  (Fig. 17.19). There is no zero-point rotational energy.

The rotational wave functions are most conveniently expressed in terms of the angles  $\theta$  and  $\phi$  that give the spatial orientation of the rotor (Fig. 17.20). One finds  $\psi_{\text{rot}} = \Theta_{JM_J}(\theta)\Phi_{M_J}(\phi)$ , where  $\Theta_{JM_J}$  is a function of  $\theta$  whose form depends on the two quantum numbers  $J$  and  $M_J$ , and  $\Phi_{M_J}$  is a function of  $\phi$  whose form depends on  $M_J$ . These functions won't be given here but will be discussed in Sec. 18.3.

Ordinarily, the wave function for internal motion of a two-particle system is a function of three coordinates. However, since the interparticle distance is held fixed in this problem,  $\psi_{\text{rot}}$  is a function of only two coordinates,  $\theta$  and  $\phi$ . Since there are two coordinates, there are two quantum numbers,  $J$  and  $M_J$ . The possible values of  $M_J$  turn out to range from  $-J$  to  $J$  in steps of 1:

$$M_J = -J, -J + 1, \dots, J - 1, J \quad (17.83)^*$$

For example, if  $J = 2$ , then  $M_J = -2, -1, 0, 1, 2$ . For a given  $J$ , there are  $2J + 1$  values of  $M_J$ . The quantum numbers  $J$  and  $M_J$  determine the rotational wave function, but  $E_{\text{rot}}$  depends only on  $J$ . Hence, each rotational level is  $(2J + 1)$ -fold degenerate. For example, the value  $J = 1$  corresponds to one energy level ( $E_{\text{rot}} = \hbar^2/I$ ) and corresponds to the three  $M_J$  values  $-1, 0, 1$ . Therefore for  $J = 1$  there are three different  $\psi_{\text{rot}}$  functions, that is, three different rotational states.

### EXAMPLE 17.7 Rotational energy levels

Find the two lowest rotational energy levels of the  $^1\text{H}^{35}\text{Cl}$  molecule, treating it as a rigid rotor. The bond distance is 1.28 Å in HCl. Atomic masses are listed in a table inside the back cover.

The rotational energy [Eqs. (17.81) and (17.82)] depends on the reduced mass  $\mu$  of Eq. (17.79). The atomic mass  $m_1$  in  $\mu$  equals the molar mass  $M_1$  divided by the Avogadro constant  $N_A$ . Using the table of atomic masses, we have

$$\begin{aligned} \mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{[(1.01 \text{ g/mol})/N_A][(35.0 \text{ g/mol})/N_A]}{[(1.01 \text{ g/mol}) + (35.0 \text{ g/mol})]/N_A} = \frac{0.982 \text{ g/mol}}{6.02 \times 10^{23}/\text{mol}} \\ &= 1.63 \times 10^{-24} \text{ g} \end{aligned}$$

$$I = \mu d^2 = (1.63 \times 10^{-27} \text{ kg})(1.28 \times 10^{-10} \text{ m})^2 = 2.67 \times 10^{-47} \text{ kg m}^2$$

The two lowest rotational levels have  $J = 0$  and  $J = 1$ , and (17.81) gives  $E_{J=0} = 0$  and

$$E_{J=1} = \frac{J(J+1)\hbar^2}{2I} = \frac{1(2)(6.63 \times 10^{-34} \text{ J s})^2}{2(2\pi)^2(2.67 \times 10^{-47} \text{ kg m}^2)} = 4.17 \times 10^{-22} \text{ J}$$

#### Exercise

The separation between the two lowest rotational levels of  $^{12}\text{C}^{32}\text{S}$  is  $3.246 \times 10^{-23} \text{ J}$ . Calculate the bond distance in  $^{12}\text{C}^{32}\text{S}$ . (Answer: 1.538 Å.)

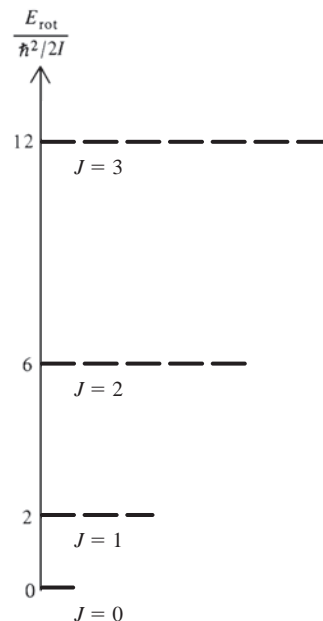


Figure 17.19

Lowest four energy levels of a two-particle rigid rotor. Each energy level consists of  $2J + 1$  states.

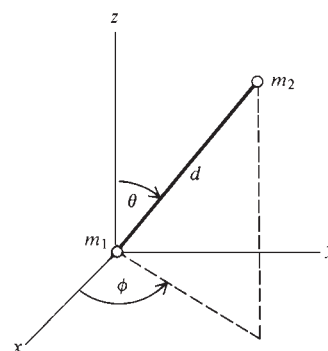
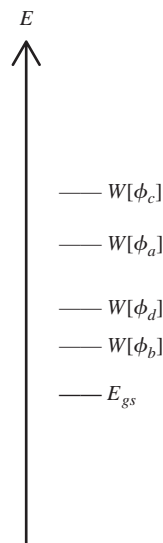


Figure 17.20

A two-particle rigid rotor.

## 17.15 APPROXIMATION METHODS

For a many-electron atom or molecule, the interelectronic repulsion terms in the potential energy  $V$  make it impossible to solve the Schrödinger equation (17.24) exactly. One must resort to approximation methods.

**Figure 17.21**

The variational integral cannot be less than the true ground-state energy  $E_{gs}$ . The quantities  $W[\phi_a]$ ,  $W[\phi_b]$ ,  $W[\phi_c]$ , and  $W[\phi_d]$  are the values of the variational integral in (17.84) for the normalized functions  $\phi_a$ ,  $\phi_b$ ,  $\phi_c$ , and  $\phi_d$ . Of these functions,  $\phi_b$  gives the lowest  $W$  and so its  $W$  is closest to  $E_{gs}$ .

## The Variation Method

The most widely used approximation method is the **variation method**. From the postulates of quantum mechanics, one can deduce the following theorem (for the proof, see Prob. 17.68). Let  $\hat{H}$  be the time-independent Hamiltonian operator of a quantum-mechanical system. If  $\phi$  is any *normalized, well-behaved* function of the coordinates of the particles of the system, then

$$\int \phi^* \hat{H} \phi \, d\tau \geq E_{gs} \quad \text{for } \phi \text{ normalized} \quad (17.84)$$

where  $E_{gs}$  is the system's true ground-state energy and the definite integral goes over all space. (Do not confuse the variation *function*  $\phi$  with the *angle*  $\phi$  in Fig. 17.20.)

To apply the variation method, one takes many different normalized, well-behaved functions  $\phi_1, \phi_2, \dots$ , and for each of them one computes the **variational integral**  $\int \phi^* \hat{H} \phi \, d\tau$ . The variation theorem (17.84) shows that the function giving the lowest value of  $\int \phi^* \hat{H} \phi \, d\tau$  provides the closest approximation to the ground-state energy (Fig. 17.21). This function can serve as an approximation to the true ground-state wave function and can be used to compute approximations to ground-state molecular properties in addition to the energy (for example, the dipole moment).

Suppose we were lucky enough to guess the true ground-state wave function  $\psi_{gs}$ . Substitution of  $\phi = \psi_{gs}$  in (17.84) and the use of (17.61) and (17.17) give the variational integral as  $\int \psi_{gs}^* \hat{H} \psi_{gs} \, d\tau = \int \psi_{gs}^* E_{gs} \psi_{gs} \, d\tau = E_{gs} \int \psi_{gs}^* \psi_{gs} \, d\tau = E_{gs}$ . We would then get the true ground-state energy.

If the variation function  $\phi$  is not normalized, it must be multiplied by a normalization constant  $N$  before being used in (17.84). The normalization condition is  $1 = \int |N\phi|^2 \, d\tau = |N|^2 \int |\phi|^2 \, d\tau$ . Hence,

$$|N|^2 = \frac{1}{\int |\phi|^2 \, d\tau} \quad (17.85)$$

Use of the normalized function  $N\phi$  in place of  $\phi$  in (17.84) gives  $\int N^* \phi^* \hat{H} (N\phi) \, d\tau = |N|^2 \int \phi^* \hat{H} \phi \, d\tau \geq E_{gs}$ , where we used the linearity of  $\hat{H}$  (Sec. 17.11) to write  $\hat{H}(N\phi) = N\hat{H}\phi$ . Substitution of (17.85) into the last inequality gives

$$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_{gs} \quad (17.86)^*$$

where  $\phi$  need not be normalized but must be well behaved.

## EXAMPLE 17.8 Trial variation function

Devise a trial variation function for the particle in a one-dimensional box and use it to estimate  $E_{gs}$ .

The particle in a box is exactly solvable, and there is no need to resort to an approximate method. For instructional purposes, let's pretend we don't know how to solve the particle-in-a-box Schrödinger equation. We know that the true ground-state wave function is zero outside the box, so we take the variation function  $\phi$  to be zero outside the box. Equations (17.84) and (17.86) are valid only if  $\phi$  is a well-behaved function, and this requires that  $\phi$  be continuous. For  $\phi$  to be continuous at the ends of the box, it must be zero at  $x = 0$  and at  $x = a$ , where  $a$  is the box length. Perhaps the simplest way to get a function that vanishes at 0 and  $a$  is to take  $\phi = x(a - x)$  for the region inside the box. As noted above,  $\phi = 0$

outside the box. Since we did not normalize  $\phi$ , Eq. (17.86) must be used. For the particle in a box,  $V = 0$  and  $\hat{H} = -(\hbar^2/2m) d^2/dx^2$  inside the box. We have

$$\begin{aligned}\int \phi^* \hat{H} \phi d\tau &= \int_0^a x(a-x) \left( \frac{-\hbar^2}{2m} \right) \frac{d^2}{dx^2} [x(a-x)] dx \\ &= \frac{-\hbar^2}{2m} \int_0^a x(a-x)(-2) dx = \frac{\hbar^2 a^3}{6m}\end{aligned}$$

Also,  $\int \phi^* \phi d\tau = \int_0^a x^2(a-x)^2 dx = a^5/30$ . The variation theorem (17.86) becomes  $(\hbar^2 a^3/6m) \div (a^5/30) \geq E_{gs}$ , or

$$E_{gs} \leq 5\hbar^2/4\pi^2 m a^2 = 0.12665\hbar^2/ma^2$$

From (17.34), the true ground-state energy is  $E_{gs} = \hbar^2/8ma^2 = 0.125\hbar^2/ma^2$ . The variation function  $x(a-x)$  gives a 1.3% error in  $E_{gs}$ .

Figure 17.22 plots the normalized variation function  $(30/a^5)^{1/2}x(a-x)$  and the true ground-state wave function  $(2/a)^{1/2} \sin(\pi x/a)$ . Figure 17.22 also plots the percent deviation of the variation function from the true wave function versus  $x$ .

### Exercise

Which of the following functions could be used as trial variation functions for the particle in a box? All functions are zero outside the box and the expression given applies only inside the box. (a)  $-x^2(a-x)^2$ ; (b)  $x^2$ ; (c)  $x^3$ ; (d)  $\sin(\pi x/a)$ ; (e)  $\cos(\pi x/a)$ ; (f)  $x(a-x) \sin(\pi x/a)$ . [Answer: (a), (d), (f).]

If the normalized variation function  $\phi$  contains the parameter  $c$ , then the variational integral  $W \equiv \int \phi^* \hat{H} \phi d\tau$  will be a function of  $c$ , and one minimizes  $W$  by setting  $\partial W/\partial c = 0$ .

### EXAMPLE 17.9 Variation function with a parameter

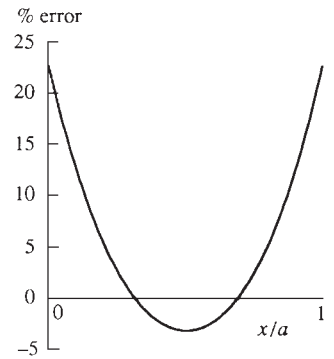
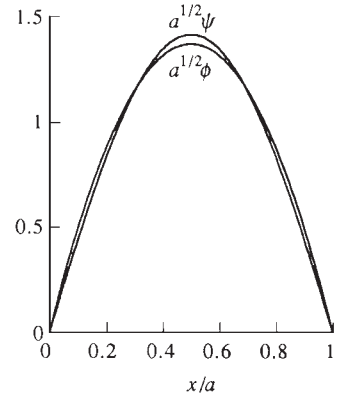
Apply the variation function  $e^{-cx^2}$  to the harmonic oscillator, where  $c$  is a parameter whose value is chosen to minimize the variational integral.

The harmonic-oscillator potential energy (17.71) is  $\frac{1}{2}kx^2$  and the Hamiltonian operator (17.56) is  $\hat{H} = -(\hbar^2/2m) (d^2/dx^2) + \frac{1}{2}kx^2$ . We have

$$\begin{aligned}\hat{H}\phi &= -\frac{\hbar^2}{2m} \frac{d^2(e^{-cx^2})}{dx^2} + \frac{1}{2}kx^2 e^{-cx^2} = -\frac{\hbar^2}{2m} (4c^2x^2 - 2c) e^{-cx^2} + \frac{1}{2}kx^2 e^{-cx^2} \\ \int \phi^* \hat{H} \phi d\tau &= \int_{-\infty}^{\infty} \left[ -\frac{\hbar^2}{2m} (4c^2x^2 - 2c) e^{-2cx^2} + \frac{1}{2}kx^2 e^{-2cx^2} \right] dx \\ &= \frac{\hbar^2}{m} \left( \frac{\pi c}{8} \right)^{1/2} + \frac{k}{4} \left( \frac{\pi}{8c^3} \right)^{1/2}\end{aligned}$$

where Table 14.1 of Sec. 14.4 was used to evaluate the integrals. Also,

$$\begin{aligned}\int \phi^* \phi d\tau &= \int_{-\infty}^{\infty} e^{-2cx^2} dx = \left( \frac{\pi}{2c} \right)^{1/2} \\ W &\equiv \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} = \frac{\hbar^2 c}{2m} + \frac{k}{8c}\end{aligned}$$



**Figure 17.22**

The upper figure plots the variation function  $\phi = (30/a^5)^{1/2}x(a-x)$  and the true ground-state wave function  $\psi_{gs}$  for the particle in a one-dimensional box. The lower figure plots the percent deviation of this  $\phi$  from the true  $\psi_{gs}$ .

We now find the value of  $c$  that minimizes  $W$ :

$$0 = \frac{\partial W}{\partial c} = \frac{\hbar^2}{2m} - \frac{k}{8c^2}$$

We have  $c^2 = mk/4\hbar^2$  and  $c = \pm(mk)^{1/2}/2\hbar$ . The negative value for  $c$  would give a positive exponent in the variation function  $\phi = e^{-cx^2}$ ;  $\phi$  would go to infinity as  $x$  goes to  $\pm\infty$  and  $\phi$  would not be quadratically integrable. We therefore reject the negative value of  $c$ . With  $c = (mk)^{1/2}/2\hbar$ , the variational integral  $W$  becomes

$$W = \frac{\hbar^2 c}{2m} + \frac{k}{8c} = \frac{\hbar k^{1/2}}{4m^{1/2}} + \frac{\hbar k^{1/2}}{4m^{1/2}} = \frac{hk^{1/2}}{4\pi m^{1/2}} = \frac{h\nu}{2}$$

where  $\nu = (1/2\pi)(k/m)^{1/2}$  [Eq. (17.73)] was used. The value  $h\nu/2$  is the true ground-state energy of the harmonic oscillator [Eq. (17.76)], and with  $c = (mk)^{1/2}/2\hbar = \pi\nu m/\hbar$ , the trial function  $e^{-cx^2}$  is the same as the unnormalized ground-state wave function of the harmonic oscillator (Fig. 17.18).

### Exercise

Verify the integration results in this example.

A common form for variational functions in quantum mechanics is the **linear variation function**

$$\phi = c_1 f_1 + c_2 f_2 + \cdots + c_n f_n$$

where  $f_1, \dots, f_n$  are functions and  $c_1, \dots, c_n$  are variational parameters whose values are determined by minimizing the variational integral. Let  $W$  be the left side of (17.86). Then the conditions for a minimum in  $W$  are  $\partial W/\partial c_1 = 0$ ,  $\partial W/\partial c_2 = 0$ ,  $\dots$ ,  $\partial W/\partial c_n = 0$ . These conditions lead to a set of equations that allows the  $c$ 's to be found. It turns out that there are  $n$  different sets of coefficients  $c_1, \dots, c_n$  that satisfy  $\partial W/\partial c_1 = \cdots = \partial W/\partial c_n = 0$ , so we end up with  $n$  different variational functions  $\phi_1, \dots, \phi_n$  and  $n$  different values for the variational integral  $W_1, \dots, W_n$ , where  $W_1 = \int \phi_1^* \hat{H} \phi_1 d\tau / \int \phi_1^* \phi_1 d\tau$ , etc. If these  $W$ 's are numbered in order of increasing energy, it can be shown that  $W_1 \geq E_{gs}$ ,  $W_2 \geq E_{gs+1}$ , etc., where  $E_{gs}, E_{gs+1}, \dots$  are the true energies of the ground state, the next-lowest state, etc. Thus, use of the linear variation function  $c_1 f_1 + \cdots + c_n f_n$  gives us approximations to the energies and wave functions of the lowest  $n$  states in the system. (In using this method, one deals separately with wave functions of different symmetry.)

### Perturbation Theory

In recent years, the perturbation-theory approximation method has become important in molecular electronic structure calculations. Let  $\hat{H}$  be the time-independent Hamiltonian operator of a system whose Schrödinger equation  $\hat{H}\psi_n = E_n\psi_n$  we seek to solve. In the perturbation-theory approximation, one divides  $\hat{H}$  into two parts:

$$\hat{H} = \hat{H}^0 + \hat{H}' \quad (17.87)$$

where  $\hat{H}^0$  is the Hamiltonian operator of a system whose Schrödinger equation can be solved exactly and  $\hat{H}'$  is a term whose effects one hopes are small. The system with Hamiltonian  $\hat{H}^0$  is called the *unperturbed system*,  $\hat{H}'$  is called the *perturbation*, and the system with Hamiltonian  $\hat{H} = \hat{H}^0 + \hat{H}'$  is called the *perturbed system*. One finds that the energy  $E_n$  of state  $n$  of the perturbed system can be written as

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots \quad (17.88)$$

where  $E_n^{(0)}$  is the energy of state  $n$  of the unperturbed system, and  $E_n^{(1)}, E_n^{(2)}, \dots$  are called the first-order, second-order,  $\dots$  corrections to the energy. (For derivations of

this and other perturbation-theory equations, see a quantum chemistry text.) If the problem is suitable for perturbation theory, the quantities  $E_n^{(1)}$ ,  $E_n^{(2)}$ ,  $E_n^{(3)}$ , ... decrease as the order of the perturbation correction increases.

To find  $E_n^{(0)}$  we solve the Schrödinger equation  $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$  of the unperturbed system.

Perturbation theory shows that the first-order energy correction  $E_n^{(1)}$  is given by

$$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau \quad (17.89)$$

Since  $\psi_n^{(0)}$  is known,  $E_n^{(1)}$  is easily calculated. The formulas for  $E_n^{(2)}$ ,  $E_n^{(3)}$ , ... are complicated and are omitted.

### EXAMPLE 17.10 Perturbation theory

Suppose a one-particle, one-dimensional system has

$$\hat{H} = -(\hbar^2/2m) d^2/dx^2 + \frac{1}{2}kx^2 + bx^4$$

where  $b$  is small. Apply perturbation theory to obtain an approximation to the stationary-state energies of this system.

If we take  $\hat{H}^0 = -(\hbar^2/2m) d^2/dx^2 + \frac{1}{2}kx^2$  and  $\hat{H}' = bx^4$ , then the unperturbed system is a harmonic oscillator, whose energies and wave functions are known (Sec. 17.12). From (17.76), we have  $E_n^{(0)} = (n + \frac{1}{2})h\nu$ , with  $n = 0, 1, 2, \dots$  and  $\nu = (1/2\pi)(k/m)^{1/2}$ , where the quantum-number symbol was changed from  $\nu$  to  $n$  to conform with the notation of this section. Including only the first-order correction to  $E_n$ , we have from (17.76) and (17.89)

$$E_n \approx E_n^{(0)} + E_n^{(1)} = (n + \frac{1}{2})h\nu + b \int_{-\infty}^{\infty} \psi_{n,\text{ho}}^* x^4 \psi_{n,\text{ho}} dx \quad (17.90)$$

where  $\psi_{n,\text{ho}}$  is the harmonic-oscillator wave function with quantum number  $n$ . Substitution of the known  $\psi_{n,\text{ho}}$  functions (Fig. 17.18) enables  $E_n^{(1)}$  to be found.

#### Exercise

Evaluate  $E_n^{(1)}$  in (17.90) for the ground state. Use Table 14.1. (Answer:  $3b\hbar^2/64\pi^4\nu^2m^2$ .)

## 17.16 HERMITIAN OPERATORS

Section 17.11 noted that operators in quantum mechanics are linear. Quantum-mechanical operators that correspond to a physical property must have another property besides linearity, namely, they must be Hermitian. This section discusses Hermitian operators and their properties. The material of this section is important for a thorough understanding of quantum mechanics, but is not essential to understanding the material in the remaining chapters of this book and so may be omitted if time does not allow its inclusion. The abstract material of this section can induce dizziness in susceptible individuals and is best studied in small doses.

### Hermitian Operators

The quantum-mechanical average value  $\langle M \rangle$  of the physical quantity  $M$  must be a real number. To take the complex conjugate of a number, we replace  $i$  by  $-i$  wherever it occurs. A real number does not contain  $i$ , so a real number equals its complex conjugate:  $z = z^*$  if  $z$  is real. Hence  $\langle M \rangle = \langle M \rangle^*$ . We have  $\langle M \rangle = \int \Psi^* \hat{M} \Psi d\tau$  [Eq. (17.62)] and

$\langle M \rangle^* = \int (\Psi^* \hat{M} \Psi)^* d\tau = \int (\Psi^*)^* (\hat{M} \Psi)^* d\tau = \int \Psi (\hat{M} \Psi)^* d\tau$ , where the result of Prob. 17.19 was used. Therefore

$$\int \Psi^* \hat{M} \Psi d\tau = \int \Psi (\hat{M} \Psi)^* d\tau \quad (17.91)$$

Equation (17.91) must hold for all possible state functions  $\Psi$ , that is, for all functions that are continuous, single-valued, and quadratically integrable. A linear operator that obeys (17.91) for all well-behaved functions is called a **Hermitian operator**. If  $\hat{M}$  is a Hermitian operator, it follows from (17.91) that (Prob. 17.63)

$$\int f^* \hat{M} g d\tau = \int g (\hat{M} f)^* d\tau \quad (17.92)^*$$

where  $f$  and  $g$  are arbitrary well-behaved functions (not necessarily eigenfunctions of any operator) and the integrals are definite integrals over all space. Although (17.92) looks like a more stringent requirement than (17.91), it is actually a consequence of (17.91). Thus a Hermitian operator obeys (17.92). The Hermitian property (17.92) is readily verified for the quantum-mechanical operators  $x \cdot$  and  $(\hbar/i)(\partial/\partial x)$  (Prob. 17.64).

### Eigenvalues of Hermitian Operators

Section 17.11 noted that when  $\Psi$  is an eigenfunction of  $\hat{M}$  with eigenvalue  $c$ , a measurement of  $M$  will give the value  $c$ . Since measured values are real, we expect  $c$  to be a real number. We now prove that *the eigenvalues of a Hermitian operator are real numbers*. To prove the theorem, we take the special case of (17.92) where  $f$  and  $g$  are the same function and this function is an eigenfunction of  $\hat{M}$  with eigenvalue  $b$ . With  $f = g$  and  $\hat{M}f = bf$ , (17.92) becomes

$$\int f^* bf d\tau = \int f (bf)^* d\tau$$

Using  $(bf)^* = b^* f^*$  and taking the constants outside the integrals, we get  $b \int f^* f d\tau = b^* \int f^* f d\tau$  or

$$(b - b^*) \int |f|^2 d\tau = 0 \quad (17.93)$$

The quantity  $|f|^2$  is never negative. The only way the definite integral  $\int |f|^2 d\tau$  (which is the infinite sum of the nonnegative infinitesimal quantities  $|f|^2 d\tau$ ) could be zero would be if the function  $f$  were zero everywhere. However, the function  $f = 0$  is not allowed as an eigenfunction (Sec. 17.11). Therefore (17.93) requires that  $b - b^* = 0$  and  $b = b^*$ . Only a real number is equal to its complex conjugate, so the eigenvalue  $b$  must be real.

### Orthogonality of Eigenfunctions

We noted in Eq. (17.36) that the particle-in-a-one-dimensional-box stationary-state wave functions, which are eigenfunctions of  $\hat{H}$ , are orthogonal, meaning that  $\int \psi_i^* \psi_j d\tau = 0$  when  $i \neq j$ . This is an example of the theorem that *two eigenfunctions of a Hermitian operator that correspond to different eigenvalues are orthogonal*. The proof is as follows.

The Hermitian property (17.92) holds for all well-behaved functions. In particular, it holds if we take  $f$  and  $g$  as two of the eigenfunctions of the Hermitian operator  $\hat{M}$ . With  $\hat{M}f = bf$  and  $\hat{M}g = cg$ , the Hermitian property  $\int f^* \hat{M} g d\tau = \int g (\hat{M} f)^* d\tau$  becomes

$$c \int f^* g d\tau = \int g (bf)^* d\tau = \int g b^* f^* d\tau = b^* \int g f^* d\tau$$

since a Hermitian operator has real eigenvalues. We have

$$(c - b) \int f^* g \, d\tau = 0$$

If the eigenvalues  $c$  and  $b$  are different ( $c \neq b$ ), then  $\int f^* g \, d\tau = 0$ , and the theorem is proved.

If the eigenvalues  $b$  and  $c$  happen to be equal, then orthogonality need not necessarily hold. Recall that we saw examples of different eigenfunctions of  $\hat{H}$  having the same eigenvalue when we discussed the degenerate energy levels of the particle in a three-dimensional cubic box and the rigid two-particle rotor (Secs. 17.10 and 17.14). Because the quantum-mechanical operator  $\hat{M}$  is linear, one can show (Prob. 17.65) that if the functions  $f_1$  and  $f_2$  are eigenfunctions of  $\hat{M}$  with the same eigenvalue, that is, if  $\hat{M}f_1 = bf_1$  and  $\hat{M}f_2 = bf_2$ , then any linear combination  $c_1f_1 + c_2f_2$  (where  $c_1$  and  $c_2$  are constants) is an eigenfunction of  $\hat{M}$  with eigenvalue  $b$ . This freedom to take linear combinations of eigenfunctions with the same eigenvalue enables us to choose the constants  $c_1$  and  $c_2$  so as to give orthogonal eigenfunctions (Prob. 17.66). From here on, we shall assume that this has been done, so that all eigenfunctions of a Hermitian operator that we deal with will be orthogonal.

Let the set of functions  $g_1, g_2, g_3, \dots$  be the eigenfunctions of a Hermitian operator. Since these functions are (or can be chosen to be) orthogonal, we have  $\int g_j^* g_k \, d\tau = 0$  when  $j \neq k$  (that is, when  $g_j$  and  $g_k$  are different eigenfunctions). We shall always normalize eigenfunctions of operators, so  $\int g_j^* g_j \, d\tau = 1$ . These two equations expressing orthogonality and normalization can be written as the single equation

$$\int g_j^* g_k \, d\tau = \delta_{jk} \quad (17.94)$$

where the **Kronecker delta**  $\delta_{jk}$  is a special symbol defined to equal 1 when  $j = k$  and to equal 0 when  $j$  and  $k$  differ:

$$\delta_{jk} \equiv 1 \quad \text{when } j = k, \quad \delta_{jk} \equiv 0 \quad \text{when } j \neq k \quad (17.95)$$

A set of functions that are orthogonal and normalized is an **orthonormal set**.

### Complete Sets of Eigenfunctions

A set of functions  $g_1, g_2, g_3, \dots$  is said to be a **complete set** if every well-behaved function that depends on the same variables as the  $g$ 's and obeys the same boundary conditions as the  $g$ 's can be expressed as the sum  $\sum_i c_i g_i$ , where the  $c$ 's are constants whose values depend on the function being expressed. The sets of eigenfunctions of many of the Hermitian operators that occur in quantum mechanics have been proved to be complete, and quantum mechanics assumes that *the set of eigenfunctions of a Hermitian operator that represents a physical quantity is a complete set*. If  $F$  is a well-behaved function and the set  $g_1, g_2, g_3, \dots$  is the set of eigenfunctions of the Hermitian operator  $\hat{R}$  that corresponds to the physical property  $R$ , then

$$F = \sum_k c_k g_k \quad (17.96)$$

and one says that  $F$  has been *expanded* in terms of the set of  $g$ 's.

How do we find the coefficients  $c_k$  in the expansion (17.96)? Multiplication of (17.96) by  $g_j^*$  gives  $g_j^* F = \sum_k c_k g_j^* g_k$ . Integration of this equation over the full range of all the coordinates gives

$$\int g_j^* F \, d\tau = \int \sum_k c_k g_j^* g_k \, d\tau = \sum_k \int c_k g_j^* g_k \, d\tau = \sum_k c_k \int g_j^* g_k \, d\tau = \sum_k c_k \delta_{jk}$$

where the orthonormality of the eigenfunctions of a Hermitian operator [Eq. (17.94)] and the fact that the integral of a sum equals the sum of the integrals were used. The



Kronecker delta  $\delta_{jk}$  is always zero except when  $k$  equals  $j$ . Therefore every term in the sum  $\sum_k c_k \delta_{jk}$  is zero except for the one term where  $k$  becomes equal to  $j$ : thus,  $\sum_k c_k \delta_{jk} = c_j \delta_{jj} = c_j$  [Eq. (17.95)]. Therefore

$$c_j = \int g_j^* F d\tau$$

Changing  $j$  to  $k$  in this equation and substituting in the expansion (17.96), we have

$$F = \sum_k \left( \int g_k^* F d\tau \right) g_k \quad (17.97)$$

where the definite integrals  $\int g_j^* F d\tau$  are constants. Equation (17.97) shows how to expand any function  $F$  in terms of a known complete set of functions  $g_1, g_2, g_3, \dots$

Suppose we are unable to solve the Schrödinger equation for a system we are interested in. We can express the unknown ground-state wave function as  $\psi_{gs} = \sum_k c_k g_k$ , where the  $g$ 's are a known complete set of functions. We then use the linear variation method (Sec. 17.15) to solve for the coefficients  $c_k$ , thereby obtaining  $\psi_{gs}$ . The difficulty with this approach is that a complete set of functions usually contains an infinite number of functions. We are therefore forced to limit ourselves to a finite number of functions in the expansion sum, thereby introducing error into our determination of  $\psi_{gs}$ . Most methods of calculating wave functions for molecules use expansions, as we shall see in Chapter 19.

Consider an example. Let the function  $F$  be defined as  $F = x^2(a - x)$  for  $x$  between 0 and  $a$  and  $F = 0$  elsewhere. Could we use the particle-in-a-box stationary-state wave functions  $\psi_n = (2/a)^{1/2} \sin(n\pi x/a)$  [Eq. (17.35)] to expand  $F$ ? The function  $F$  is well-behaved and satisfies the same boundary conditions as  $\psi_n$ , namely,  $F$  is zero at the ends of the box. The functions  $\psi_n$  are the eigenfunctions of a Hermitian operator (the particle-in-a-box Hamiltonian  $\hat{H}$ ) and so are a complete set. Therefore we can express  $F$  as  $F = \sum_{n=1}^{\infty} c_n \psi_n$ , where the coefficients  $c_n$  are given in (17.97) as

$$c_n = \int \psi_n^* F d\tau = \int_0^a \left( \frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} x^2(a - x) dx \quad (17.98)$$

Problem 17.67 evaluates  $c_n$  and shows how the sum  $\sum_n c_n \psi_n$  becomes a more and more accurate representation of  $F$  as more terms are included in the sum.

The proof of the variation theorem (17.84) uses an expansion of the variation function  $\phi$ , as in Eq. (17.96). The proof is outlined in Prob. 17.68.

## Summary

Quantum-mechanical operators that correspond to physical properties are Hermitian, meaning that they satisfy (17.92) for all well-behaved functions  $f$  and  $g$ . The eigenvalues of a Hermitian operator are real. The eigenfunctions of a Hermitian operator are (or can be chosen to be) orthogonal. The eigenfunctions of a Hermitian operator form a complete set, meaning that any well-behaved function can be expanded in terms of them.

## 17.17 SUMMARY

Electromagnetic waves of frequency  $\nu$  and wavelength  $\lambda$  travel at speed  $c = \lambda\nu$  in vacuum. Processes involving absorption or emission of electromagnetic radiation (for example, blackbody radiation, the photoelectric effect, spectra of atoms and molecules) can be understood by viewing the electromagnetic radiation to be composed of photons, each photon having an energy  $h\nu$ , where  $h$  is Planck's constant. When an atom or molecule absorbs or emits a photon, it makes a transition between two energy levels  $E_a$  and  $E_b$  whose energy difference is  $h\nu$ ;  $E_a - E_b = h\nu$ .

De Broglie proposed that microscopic particles such as electrons have wavelike properties, and this was confirmed by observation of electron diffraction. Because

of this wave-particle duality, simultaneous measurement of the precise position and momentum of a microscopic particle is impossible (the Heisenberg uncertainty principle).

The state of a quantum-mechanical system is described by the state function  $\Psi$ , which is a function of the particles' coordinates and the time. The change in  $\Psi$  with time is governed by the time-dependent Schrödinger equation (17.10) [or (17.60)], which is the quantum-mechanical analog of Newton's second law in classical mechanics. The probability density for finding the system's particles is  $|\Psi|^2$ . For example, for a two-particle, one-dimensional system,  $|\Psi(x_1, x_2, t)|^2 dx_1 dx_2$  is the probability of simultaneously finding particle 1 between  $x_1$  and  $x_1 + dx_1$  and particle 2 between  $x_2$  and  $x_2 + dx_2$  at time  $t$ .

When the system's potential energy  $V$  is independent of time, the system can exist in one of many possible stationary states. For a stationary state, the state function is  $\Psi = e^{-iEt/\hbar}\psi$ . The (time-independent) wave function  $\psi$  is a function of the particles' coordinates and is one of the well-behaved solutions of the (time-independent) Schrödinger equation  $\hat{H}\psi = E\psi$ , where  $E$  is the energy and the Hamiltonian operator  $\hat{H}$  is the quantum-mechanical operator that corresponds to the classical quantity  $E$ . To find the operator corresponding to a classical quantity  $M$ , one writes down the classical-mechanical expression for  $M$  in terms of cartesian coordinates and momenta and then replaces the coordinates and momenta by their corresponding quantum-mechanical operators:  $\hat{x}_1 = x_1 \times$ ,  $\hat{p}_{x,1} = (\hbar/i) \partial/\partial x_1$ , etc. For a stationary state,  $|\Psi|^2 = |\psi|^2$  and the probability density and energy are independent of time.

In accord with the probability interpretation, the state function is normalized to satisfy  $\int |\Psi|^2 d\tau = 1$ , where  $\int d\tau$  denotes the definite integral over the full range of the particles' coordinates. For a stationary state, the normalization condition becomes  $\int |\psi|^2 d\tau = 1$ .

The average value of property  $M$  for a system in stationary state  $\psi$  is  $\langle M \rangle = \int \psi^* \hat{M} \psi d\tau$ , where  $\hat{M}$  is the quantum-mechanical operator for property  $M$ .

The stationary-state wave functions and energies were found for the following systems.

(a) Particle in a one-dimensional box ( $V = 0$  for  $x$  between 0 and  $a$ ;  $V = \infty$  elsewhere):  $E = n^2 h^2 / 8ma^2$ ,  $\psi = (2/a)^{1/2} \sin(n\pi x/a)$ ,  $n = 1, 2, 3, \dots$

(b) Particle in a three-dimensional rectangular box with dimensions  $a, b, c$ :  $E = (h^2/8m) \cdot (n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2)$ .

(c) One-dimensional harmonic oscillator ( $V = \frac{1}{2}kx^2$ ):  $E = (v + \frac{1}{2})h\nu$ ,  $\nu = (1/2\pi)(k/m)^{1/2}$ ,  $v = 0, 1, 2, \dots$

(d) Two-particle rigid rotor (particles at fixed distance  $d$  and energy entirely kinetic):  $E = J(J + 1)\hbar^2/2I$ ,  $I = \mu d^2$ ,  $J = 0, 1, 2, \dots$ ;  $\mu \equiv m_1 m_2 / (m_1 + m_2)$  is the reduced mass.

When more than one state function corresponds to the same energy level, that energy level is said to be degenerate. There is degeneracy for the particle in a cubic box and for the two-particle rigid rotor.

For a system of noninteracting particles, the stationary-state wave functions are products of wave functions for each particle and the energy is the sum of the energies of the individual particles.

The variation theorem states that for any well-behaved trial variation function  $\phi$ , one has  $\int \phi^* \hat{H} \phi d\tau / \int \phi^* \phi d\tau \geq E_{gs}$ , where  $\hat{H}$  is the system's Hamiltonian operator and  $E_{gs}$  is its true ground-state energy.

Important kinds of calculations discussed in this chapter include:

- Use of  $\lambda\nu = c$  to calculate the wavelength of light from the frequency, and vice versa.
- Use of  $E_{\text{upper}} - E_{\text{lower}} = h\nu$  to calculate the frequency of the photon emitted or absorbed when a quantum-mechanical system makes a transition between two states.

- Use of energy-level formulas such as  $E = n^2 h^2 / 8ma^2$  for the particle in a box or  $E = (v + \frac{1}{2})h\nu$  for the harmonic oscillator to calculate energy levels of quantum-mechanical systems.
- For a one-particle, one-dimensional, stationary-state system, use of  $|\psi|^2 dx$  to calculate the probability of finding the particle between  $x$  and  $x + dx$  and of  $\int_a^b |\psi|^2 dx$  to calculate the probability of finding the particle between  $a$  and  $b$ .
- Use of  $\langle M \rangle = \int \psi^* \hat{M} \psi d\tau$  to calculate average values.
- Use of the variation theorem to estimate the ground-state energy of a quantum-mechanical system.

## FURTHER READING

*Hanna*, chap. 3; *Karplus and Porter*, chap. 2; *Levine*, chaps. 1–4, 8, 9; *Lowe and Peterson*, chaps. 1–3, 7; *McQuarrie* (1983), chaps. 1–5; *Atkins and Friedman*, chaps. 1–3, 6.

## PROBLEMS

### Section 17.1

**17.1** (a) Let  $\nu_{\max}$  be the frequency at which the blackbody-radiation function (17.2) is a maximum. Show that  $\nu_{\max} = kTx/h$ , where  $x$  is the nonzero solution of  $x + 3e^{-x} = 3$ . Since  $x$  is a constant,  $\nu_{\max}$  increases linearly with  $T$ . (b) Use a calculator with an  $e^x$  key to solve the equation in (a) by trial and error. To save time, use interpolation after you have found the successive integers that  $x$  lies between. Alternatively, use the Solver in Excel. (c) Calculate  $\nu_{\max}$  for a blackbody at 300 K and at 3000 K. Refer to Fig. 20.2 to state in which portions of the electromagnetic spectrum these frequencies lie. (d) The light emitted by the sun conforms closely to the blackbody radiation law and has  $\nu_{\max} = 3.5 \times 10^{14} \text{ s}^{-1}$ . Estimate the sun's surface temperature. (e) The skin temperature of humans is 33°C, and the emission spectrum of human skin at this temperature conforms closely to blackbody radiation. Find  $\nu_{\max}$  for human skin at 33°C. What region of the electromagnetic spectrum is this in?

**17.2** (a) Use the fact that  $\int_0^\infty [z^3/(e^z - 1)] dz = \pi^4/15$  to show that the total radiant energy emitted per second by unit area of a blackbody is  $2\pi^5 k^4 T^4 / 15c^2 h^3$ . Note that this quantity is proportional to  $T^4$  (*Stefan's law*). (b) The sun's diameter is  $1.4 \times 10^9 \text{ m}$  and its effective surface temperature is 5800 K. Assume the sun is a blackbody and estimate the rate of energy loss by radiation from the sun. (c) Use  $E = mc^2$  to calculate the relativistic mass of the photons lost by radiation from the sun in 1 year.

### Section 17.2

**17.3** The work function of K is 2.2 eV and that of Ni is 5.0 eV, where  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ . (a) Calculate the threshold frequencies and wavelengths for these two metals. (b) Will violet light of wavelength 4000 Å cause the photoelectric effect in K? In Ni? (c) Calculate the maximum kinetic energy of the electrons emitted in (b).

**17.4** Calculate the energy of a photon of red light of wavelength 700 nm. ( $1 \text{ nm} = 10^{-9} \text{ m}$ .)

**17.5** A 100-W sodium-vapor lamp emits yellow light of wavelength 590 nm. Calculate the number of photons emitted per second.

**17.6** Millikan found the following data for the photoelectric effect in Na:

$10^{12} K_{\max}/\text{ergs}$	3.41	2.56	1.95	0.75
$\lambda/\text{\AA}$	3125	3650	4047	5461

where  $K_{\max}$  is the maximum kinetic energy of emitted electrons and  $\lambda$  is the wavelength of the incident radiation. Plot  $K_{\max}$  versus  $\nu$ . From the slope and intercept, calculate  $h$  and the work function for Na.

### Section 17.4

**17.7** Calculate the de Broglie wavelength of (a) a neutron moving at  $6.0 \times 10^6 \text{ cm/s}$ ; (b) a 50-g particle moving at 120 cm/s.

### Section 17.5

**17.8** A beam of electrons traveling at  $6.0 \times 10^8 \text{ cm/s}$  falls on a slit of width 2400 Å. The diffraction pattern is observed on a screen 40 cm from the slit. The  $x$  and  $y$  axes are defined as in Fig. 17.4. Find (a) the angle  $\theta$  to the first diffraction minimum; (b) the width of the central maximum of the diffraction pattern on the screen; (c) the uncertainty  $\Delta p_x$  at the slit.

**17.9** Estimate the minimum uncertainty in the  $x$  component of velocity of an electron whose position is measured to an uncertainty of  $1 \times 10^{-10} \text{ m}$ .

### Section 17.6

**17.10** For a system containing three particles, what are the variables on which the state function  $\Psi$  depends?

**17.11** True or false? (a) In the equation  $\int |\Psi|^2 d\tau = 1$ , the integral is an indefinite integral. (b) The state function  $\Psi$  takes on

only real values. (c) If  $z$  is a complex number, then  $zz^* = |z|^2$ . (d) If  $z$  is a complex number, then  $z + z^*$  is always a real number. (e) If  $z = a + bi$ , where  $a$  and  $b$  are real numbers, and we plot  $a$  on the  $x$  axis and  $b$  on the  $y$  axis, the distance of the point  $(a, b)$  from the origin in the  $xy$  plane is equal to  $|z|$ . (f) The absolute value  $|z|$  of a complex number must be a real nonnegative number.

**17.12** Find the complex conjugate and the absolute value of (a)  $-2$ ; (b)  $3 - 2i$ ; (c)  $\cos \theta + i \sin \theta$ ; (d)  $-3e^{-i\pi/5}$ .

**17.13** Verify that, if  $\Psi$  is a solution of the time-dependent Schrödinger equation (17.10), then  $c\Psi$  is also a solution, where  $c$  is any constant.

**17.14** Show that

$$\int_a^b \int_c^d \int_s^t f(r)g(\theta)h(\phi) dr d\theta d\phi = \int_s^t f(r) dr \int_c^d g(\theta) d\theta \int_a^b h(\phi) d\phi$$

where the limits are constants.

**17.15** Verify that  $\Psi$  in Example 17.1 is normalized.

## Section 17.7

**17.16** For a system consisting of three particles, on what variables does the time-independent wave function  $\psi$  depend?

**17.17** True or false? For a stationary state, (a)  $|\psi| = |\Psi|$ ; (b)  $\psi = \Psi$ ; (c) the probability density is independent of time; (d) the energy is a constant.

**17.18** Which is more general, the time-dependent Schrödinger equation or the time-independent Schrödinger equation?

**17.19** Prove that  $(fg)^* = f^*g^*$ , where  $f$  and  $g$  are complex quantities.

**17.20** Verify that if  $\psi$  is a solution of the time-independent Schrödinger equation (17.24), then  $k\psi$  is also a solution, where  $k$  is any constant.

**17.21** State whether each of the functions (a) to (d) is quadratically integrable. ( $a$  and  $b$  are positive constants.) (a)  $e^{-ax^2}$  (Hint: See Table 14.1.) (b)  $e^{-bx}$ . (c)  $1/x$ . (Hint: In (c) and (d), write the integral as the sum of two integrals.) (d)  $1/|x|^{1/4}$ . (e) True or false? A function that becomes infinite at a point must not be quadratically integrable.

## Section 17.8

**17.22** Calculate the wavelength of the photon emitted when a  $1.0 \times 10^{-27}$  g particle in a box of length  $6.0 \text{ Å}$  goes from the  $n = 5$  to the  $n = 4$  level.

**17.23** (a) For a particle in the stationary state  $n$  of a one-dimensional box of length  $a$ , find the probability that the particle is in the region  $0 \leq x \leq a/4$ . (b) Calculate this probability for  $n = 1, 2$ , and  $3$ .

**17.24** For a  $1.0 \times 10^{-26}$  g particle in a box whose ends are at  $x = 0$  and  $x = 2.000 \text{ Å}$ , calculate the probability that the particle's

$x$  coordinate is between  $1.6000$  and  $1.6001 \text{ Å}$  if (a)  $n = 1$ ; (b)  $n = 2$ .

**17.25** Sketch  $\psi$  and  $|\psi|^2$  for the  $n = 4$  and  $n = 5$  states of a particle in a one-dimensional box.

**17.26** Solve Eq. (17.28) for the special case  $E = 0$ . Then apply the continuity requirement at each end of the box to evaluate the two integration constants and thus show that  $\psi = 0$  for  $E = 0$ . From (17.32),  $E = 0$  corresponds to  $n = 0$ , so  $n = 0$  is not allowed.

**17.27** For an electron in a certain one-dimensional box, the lowest observed transition frequency is  $2.0 \times 10^{14} \text{ s}^{-1}$ . Find the length of the box.

**17.28** If the  $n = 3$  to  $4$  transition for a certain particle-in-a-box system occurs at  $4.00 \times 10^{13} \text{ s}^{-1}$ , find the frequency of the  $n = 6$  to  $9$  transition in this system.

**17.29** Verify the orthogonality equation (17.36) for particle-in-a-box wave functions.

**17.30** For the particle in a box, check that the wave functions (17.35) satisfy the Schrödinger equation (17.28) by substituting (17.35) into (17.28).

## Section 17.9

**17.31** For a particle in a two-dimensional box with sides of equal lengths, draw rough sketches of contours of constant  $|\psi|$  for the states (a)  $n_x = 2, n_y = 1$ ; (b)  $n_x = 2, n_y = 2$ . At what points in the box is  $|\psi|$  a maximum for each state? (Hint: The maximum value of  $|\sin \theta|$  is  $1$ .)

## Section 17.10

**17.32** For a particle in a cubic box of length  $a$ , give the degree of degeneracy of the energy level with energy (a)  $21h^2/8ma^2$ ; (b)  $24h^2/8ma^2$ .

**17.33** For a particle in a cubic box of edge  $a$ : (a) How many states have energies in the range  $0$  to  $16h^2/8ma^2$ ? (b) How many energy levels lie in this range?

## Section 17.11

**17.34** True or false? (a)  $(\hat{A} + \hat{B})f(x)$  is always equal to  $\hat{A}f(x) + \hat{B}f(x)$ . (b)  $\hat{A}[f(x) + g(x)]$  is always equal to  $\hat{A}f(x) + \hat{A}g(x)$ . (c)  $\hat{B}\hat{C}f(x)$  is always equal to  $\hat{C}\hat{B}f(x)$ . (d)  $[\hat{A}f(x)]/f(x)$  is always equal to  $\hat{A}$ , provided  $f(x) \neq 0$ . (e)  $3x$  is an eigenvalue of  $\hat{x}$ . (f)  $3x$  is an eigenfunction of  $\hat{x}$ . (g)  $e^{ikx/\hbar}$ , where  $k$  is a constant, is an eigenfunction of  $\hat{p}_x$  with eigenvalue  $k$ .

**17.35** If  $f$  is a function, state whether or not each of the following expressions is equal to  $f^*\hat{B}f$ . (a)  $f^*(\hat{B}f)$ . (b)  $\hat{B}(f^*f)$ . (c)  $(\hat{B}f)f^*$ . (d)  $f^*f\hat{B}$ .

**17.36** If the energy of a particle in the  $n = 5$  stationary state of a particle in a one-dimensional box of length  $a$  is measured, state the possible result(s).

**17.37** Let  $\hat{A} = d^2/dx^2$  and  $\hat{B} = x \times$ . (a) Find  $\hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x)$ . (b) Find  $(\hat{A} + \hat{B})(e^{x^2} + \cos 2x)$ .

**17.38** (a) Classify each of these operators as linear or nonlinear:  $\partial^2/\partial x^2$ ,  $2 \partial/\partial z$ ,  $3z^2 \times$ ,  $(\ )^2$ ,  $(\ )^*$ . (b) Verify that  $\hat{H}$  in (17.58) is linear.

**17.39** State whether each of the following entities is an operator or a function: (a)  $\hat{A}\hat{B}g(x)$ ; (b)  $\hat{A}\hat{B} + \hat{B}\hat{A}$ ; (c)  $\hat{B}^2f(x)$ ; (d)  $g(x)\hat{A}$ , (e)  $g(x)\hat{A}f(x)$ .

**17.40** Find the quantum-mechanical operator for (a)  $p_x^3$ ; (b)  $p_z^4$ .

**17.41** (a) Which of the functions  $\sin 3x$ ,  $6 \cos 4x$ ,  $5x^3$ ,  $1/x$ ,  $3e^{-5x}$ ,  $\ln 2x$  are eigenfunctions of  $d^2/dx^2$ ? (b) For each eigenfunction, state the eigenvalue.

**17.42** For a particle in a one-dimensional-box stationary state, show that (a)  $\langle p_x \rangle = 0$ ; (b)  $\langle x \rangle = a/2$ ; (c)  $\langle x^2 \rangle = a^2(1/3 - 1/2n^2\pi^2)$ .

**17.43** Verify the separation-of-variables equations of Sec. 17.11 as follows. For the Hamiltonian (17.64), write the time-independent Schrödinger equation. Assume solutions of the form (17.65) and substitute into the Schrödinger equation to derive (17.66) and (17.67).

**17.44** For a system of two noninteracting particles of masses  $m_1$  and  $m_2$  in a one-dimensional box of length  $a$ , give the formulas for the stationary-state wave functions and energies.

## Section 17.12

**17.45** For each of the following, state whether it is a nu or a vee and whether it is a quantum number or a frequency. (a)  $\nu$ ; (b)  $v$ .

**17.46** Calculate the frequency of radiation emitted when a harmonic oscillator of frequency  $6.0 \times 10^{13} \text{ s}^{-1}$  goes from the  $v = 8$  to the  $v = 7$  level.

**17.47** Draw rough sketches of  $\psi^2$  for the  $v = 0, 1, 2$ , and 3 harmonic-oscillator states.

**17.48** Find the most probable value(s) of  $x$  for a harmonic oscillator in the state (a)  $v = 0$ ; (b)  $v = 1$ .

**17.49** Verify that  $\psi_0$  in Fig. 17.18 is a solution of the Schrödinger equation (17.75).

**17.50** Verify that the harmonic-oscillator  $\psi_1$  in Fig. 17.18 is normalized. (See Table 14.1.)

**17.51** For the ground state of a harmonic oscillator, calculate (a)  $\langle x \rangle$ ; (b)  $\langle x^2 \rangle$ ; (c)  $\langle p_x \rangle$ . See Table 14.1.

**17.52** (a) Verify Eq. (17.74). (b) Verify by substitution that (17.72) satisfies the differential equation  $m d^2x/dt^2 = -kx$ .

**17.53** A mass of 45 g on a spring oscillates at the frequency of 2.4 vibrations per second with an amplitude 4.0 cm. (a) Calculate the force constant of the spring. (b) What would be the quantum number  $v$  if the system were treated quantum-mechanically?

**17.54** For a three-dimensional harmonic oscillator,  $V = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2$ , where the three force constants  $k_x$ ,  $k_y$ ,  $k_z$  are not necessarily equal. (a) Write down the expression for the energy levels of this system. Define all symbols. (b) What is the zero-point energy?

## Section 17.13

**17.55** Substitute (17.79), (17.80), and  $M = m_1 + m_2$  into (17.78) and verify that  $H$  reduces to  $p_1^2/2m_1 + p_2^2/2m_2 + V$ , where  $p_1$  is the momentum of particle 1.

## Section 17.14

**17.56** Consider the  $^{12}\text{C}^{16}\text{O}$  molecule to be a two-particle rigid rotor with  $m_1$  and  $m_2$  equal to the atomic masses and the interparticle distance fixed at the CO bond length 1.13 Å. (a) Find the reduced mass. (b) Find the moment of inertia. (c) Find the energies of the four lowest rotational levels and give the degeneracy of each of these levels. (d) Calculate the frequency of the radiation absorbed when a  $^{12}\text{C}^{16}\text{O}$  molecule goes from the  $J = 0$  level to the  $J = 1$  level. Repeat for  $J = 1$  to  $J = 2$ .

## Section 17.15

**17.57** The unnormalized particle-in-a-box variation function  $x(a - x)$  for  $x$  between 0 and  $a$  was used in Example 17.8. (a) Use work in that example to show that  $(30/a^5)^{1/2}x(a - x)$  is the normalized form of this function. (b) Calculate  $\langle x^2 \rangle$  using the normalized function in (a) and compare the result with the exact ground-state  $\langle x^2 \rangle$  (Prob. 17.42).

**17.58** For the particle in a one-dimensional box, one finds that use of the normalized variation function  $\phi = Nx^k(a - x)^k$ , where  $k$  is a parameter, gives  $\int \phi^* \hat{H} \phi d\tau = (\hbar^2/ma^2) \cdot (4k^2 + k)/(2k - 1)$ . Find the value of  $k$  that minimizes the variational integral  $W$  and find the value of  $W$  for this  $k$  value. Compare the percent error in the ground-state energy with that for the function  $Nx(a - x)$  used in Example 17.8.

**17.59** (a) Apply the variation function  $x^2(a - x)^2$  for  $x$  between 0 and  $a$  to the particle in a box and estimate the ground-state energy. Calculate the percent error in  $E_{gs}$ . (b) Explain why the function  $x^2$  (for  $x$  between 0 and  $a$ ) cannot be used as a variation function for the particle in a box.

**17.60** Consider a one-particle, one-dimensional system with  $V = \infty$  for  $x < 0$ ,  $V = \infty$  for  $x > a$ , and  $V = kx$  for  $0 \leq x \leq a$ , where  $k$  is small. Treat the system as a perturbed particle in a box and find  $E_n^{(0)} + E_n^{(1)}$  for the state with quantum number  $n$ . Use a table of integrals.

## Section 17.16

**17.61** True or false? (a) All the eigenvalues of a Hermitian operator are real numbers. (b) Two eigenfunctions of the same Hermitian operator are always orthogonal. (c)  $\delta_{jk} = \delta_{kj}$ . (d) A Hermitian operator cannot contain the imaginary number  $i$ . (e)  $\sum_n b_m c_m \delta_{mn} = b_n c_n$ .

**17.62** Prove that the sum of two Hermitian operators is a Hermitian operator.

**17.63** Use the following procedure to show that for the Hermitian operator  $\hat{M}$ , Eq. (17.92) is a consequence of (17.91). (a) Set  $\Psi = f + cg$  in (17.91), where  $c$  is an arbitrary constant. Use (17.91) to cancel some terms in the resulting equation, thereby getting

$$c^* \int g^* \hat{M} f d\tau + c \int f^* \hat{M} g d\tau = c \int g^* (\hat{M} f)^* d\tau + c^* \int f^* (\hat{M} g)^* d\tau \quad (17.99)$$

(b) First set  $c = 1$  in (17.99). Then set  $c = i$  in (17.99) and divide the resulting equation by  $i$ . Add these two equations, thereby proving (17.92).

**17.64** Verify that if  $f$  and  $g$  are functions of  $x$  and  $d\tau = dx$ , then (a) the Hermitian property (17.92) holds for  $\hat{x}$ ; (b) (17.92) holds for  $\hat{p}_x$ . [Hint: For part (b), use integration by parts and the fact that a quadratically integrable function must go to zero as  $x$  goes to  $\pm\infty$ .]

**17.65** Given that  $\hat{M}$  is a linear operator and that  $\hat{M}f_1 = bf_1$  and  $\hat{M}f_2 = bf_2$ , prove that  $c_1f_1 + c_2f_2$ , where  $c_1$  and  $c_2$  are constants, is an eigenfunction of  $\hat{M}$  with eigenvalue  $b$ .

**17.66** If  $\hat{M}$  is a linear operator with  $\hat{M}f_1 = bf_1$  and  $\hat{M}f_2 = bf_2$ , and we define  $g_1$  and  $g_2$  as  $g_1 \equiv f_1$  and  $g_2 \equiv f_2 + kf_1$ , where  $k \equiv -\int f_1^* f_2 d\tau / \int f_1^* f_1 d\tau$ , verify that  $g_1$  and  $g_2$  are orthogonal.

**17.67** Let  $F \equiv x^2(a - x)$  for  $x$  between 0 and  $a$ . Let  $G \equiv \sum_{n=1}^m c_n \psi_n$ , where  $\psi_n$  is a particle-in-a-one-dimensional box wave function with quantum number  $n$  and  $c_n$  is given by (17.98). To make things a bit simpler, take the length  $a$  as equal to 1. (a) Use a table of integrals to find  $c_n$ . (b) Use a spreadsheet to calculate  $F$  and  $G$  for  $m = 3$  and plot them on the same graph. (c) Repeat (b) for  $m = 5$  and comment on the results.

**17.68** For a system with Hamiltonian operator  $\hat{H}$  and stationary-state wave functions and energies  $\psi_n$  and  $E_n$ , we have  $\hat{H}\psi_n = E_n\psi_n$ , where  $n$  labels the various states. Let  $\phi$  be a normalized, well-behaved variation function that depends on the coordinates of the system's particles and let  $W \equiv \int \phi^* \hat{H} \phi d\tau$  be the variational integral. Since the eigenfunctions  $\psi_n$  form a complete set, we can use (17.96) to expand  $\phi$  as  $\phi = \sum_k c_k \psi_k$ . (a) Explain why  $\phi^* = \sum_j c_j^* \psi_j^*$ . (b) Substitute these expansions for  $\phi^*$  and  $\phi$  into the normalization condition  $\int \phi^* \phi d\tau = 1$  and use the orthonormality of the eigenfunctions  $\psi_n$  to show that  $1 = \sum_j \sum_k c_j^* c_k \delta_{jk}$ . Explain why this last equation becomes  $\sum_k |c_k|^2 = 1$ . (c) Substitute the expansions for  $\phi^*$  and  $\phi$  into  $W$  and show that  $W = \sum_k |c_k|^2 E_k$ . (d) We have  $E_k \geq E_{gs}$ , where  $E_{gs}$  is the ground-state energy. Since  $|c_k|^2$  is never negative, we can multiply the inequality by  $|c_k|^2$  to get  $|c_k|^2 E_k \geq |c_k|^2 E_{gs}$ . Explain why  $W \geq \sum_k |c_k|^2 E_{gs}$ . Then use the result of part (b) to conclude that  $W \geq E_{gs}$ . (e) In the expansions of  $\phi^*$  and  $\phi$ , we used different letters  $j$  and  $k$  for the summation indices. Explain why this was done. Hint: Express the product  $(a_1 + a_2)(b_1 + b_2)$  using summation notation and move both sum signs to the left of everything.

## General

**17.69** What are the SI units of a stationary-state wave function  $\psi$  for (a) a one-particle, one-dimensional system; (b) a one-particle, three-dimensional system; (c) a two-particle, three-dimensional system?

**17.70** By fitting experimental blackbody-radiation curves using Eq. (17.2), Planck not only obtained a value for  $h$ , but also obtained the first reasonably accurate values of  $k$ ,  $N_A$ , and the proton charge  $e$ . Explain how Planck obtained values for these constants.

**17.71** State quantitatively the effect on the system's energy levels of each of the following: (a) doubling the box length for

a particle in a one-dimensional box; (b) doubling the interparticle distance of a two-particle rigid rotor; (c) doubling the mass of a harmonic oscillator.

**17.72** True or false? (a) In classical mechanics, knowledge of the present state of an isolated system allows the future state to be predicted with certainty. (b) In quantum mechanics, knowledge of the present state of an isolated system allows the future state to be predicted with certainty. (c) For a stationary state,  $\Psi$  is the product of a function of time and a function of the coordinates. (d) An increase in the particle mass would decrease the ground-state energy of both the particle in a box and the harmonic oscillator. (e) For a system of noninteracting particles, each stationary-state wave function is equal to the sum of wave functions for each particle. (f) The one-dimensional harmonic-oscillator energy levels are nondegenerate. (g)  $\Psi$  must be real. (h) The energies of any two photons must be equal. (i) In the variation method, the variational function  $\phi$  must be an eigenfunction of  $\hat{H}$ .

**17.73** *Scientist trivia question.* Name the scientist referred to in each of the following descriptions. The same name can be used more than once and all names except (f) appear in Chapter 17. (a) On Christmas vacation in Arosa, Switzerland, this 38-year-old professor of theoretical physics at the University of Zurich began work on a series of papers titled "Quantisierung als Eigenwertproblem" ("Quantization as an Eigenvalue Problem"), papers described by Born as "of a grandeur unsurpassed in theoretical physics." (b) On the tiny North Sea island of Helgoland, where he had gone to recover from a severe attack of hay fever, this 23-year-old lecturer at the University of Göttingen conceived the ideas embodied in his paper "Über Quantentheoretische Umdeutung Kinematischer und Mechanischer Beziehungen" ("On a Quantum-Theoretical Interpretation of Kinematical and Mechanical Relations") that marks the birth of modern quantum mechanics. He later wrote: "it was almost three o'clock in the morning before the final result of my computations lay before me . . . I could no longer doubt the mathematical consistency and coherence of the kind of quantum mechanics to which my calculations pointed. At first, I was deeply alarmed. I had the feeling that, through the surface of atomic phenomena, I was looking at a strangely beautiful interior . . . I was far too excited to sleep, and so, as a new day dawned, I made for the southern tip of the island, where I had been longing to climb a rock jutting out into the sea. I now did so without too much trouble, and waited for the sun to rise." (c) He headed Germany's atom-bomb project during World War II. (d) In September 1943, under cover of darkness, he crossed the Öresund strait by boat from German-occupied Denmark to Sweden. A few days later, a British bomber flew him to Scotland. The plane had no passenger seat and he flew in the bomb bay. He failed to use the oxygen mask supplied him and lost consciousness during the flight, but recovered when the plane landed. (e) In a discussion with Bohr about quantum mechanics, he said "If we are still going to have to put up with these damn quantum jumps, I am sorry I ever had anything to do with quantum theory." (f) Besides founding a journal of physical chemistry, he also founded a journal of philosophy. When the philosopher Ludwig Wittgenstein had

trouble finding a publisher for his first book, this physical chemist published the book in 1921 in his philosophy journal. (Wittgenstein was chosen by *Time* magazine as one of the 100 most influential people of the 20th century.) (g) He spent 1940–1956 working mainly on a unified field theory at the Dublin Institute for Advanced Studies; during the early years of this period he lived in a two-story house with his wife Anny, his mistress Hilde March (wife of the physicist Arthur March), and his daughter Ruth (who did not find out she was his daughter until she was 17). (h) This nineteenth-century mathematician and physicist reformulated classical mechanics in a form especially suitable for formulating quantum mechanics. He was appointed Professor of Astronomy at Trinity College while still an undergraduate student. (i) He used the pseudonym **Nicholas Baker** when he worked on the atomic bomb in Los Alamos, New Mexico. (j) In a 1999 poll of physicists he was chosen as the greatest physicist of all time and was chosen by *Time* magazine as “Person of the Twentieth Century.” (k) His son Erwin was found guilty of complicity in the 1944 plot to kill Hitler and was executed in February 1945. Shortly thereafter, when the town he was living in became a battlefield, this 87-year-old physicist had to hide in the woods and sleep in haystacks.

(l) He believed in the Hindu philosophy of Vedanta, which he summarized as “we living beings all belong to one another . . . we are all actually members or aspects of a single being, which we may in western terminology call God, while in the Upanishads it is called Brahman.” (m) His 1919 divorce settlement with his first wife provided that in addition to providing child support, if he were to win a Nobel Prize, the prize money would be given to his ex-wife. She received the prize money in 1923. In a letter he praised a friend’s ability to have a happy, long-lasting marriage, “an undertaking in which I failed twice rather disgracefully.” (n) He helped develop quantum mechanics and from 1957 to 1961 was a member of West Germany’s parliament. (o) In a letter to a father whose child had died, he wrote: “A human being is a part of the whole, called by us “Universe,” a part limited in time and space. He experiences himself, his thoughts and feelings as something separated from the rest—a kind of optical delusion of his consciousness. This delusion is a prison for us, restricting us to our personal desires and to affection for a few persons nearest to us. Our task must be to free ourselves from this prison by widening our circle of compassion to embrace all living creatures and the whole of nature in its beauty.”

# Atomic Structure

## CHAPTER OUTLINE

- 18.1 Units
- 18.2 Historical Background
- 18.3 The Hydrogen Atom
- 18.4 Angular Momentum
- 18.5 Electron Spin
- 18.6 The Helium Atom and the Spin–Statistics Theorem
- 18.7 Total Orbital and Spin Angular Momenta
- 18.8 Many-Electron Atoms and the Periodic Table
- 18.9 Hartree–Fock and Configuration–Interaction Wave Functions
- 18.10 Summary

Chapter 17 introduced some of the main ideas of quantum chemistry and looked at the solutions of the time-independent Schrödinger equation for the particle in a box, the rigid two-particle rotor, and the harmonic oscillator. We now use quantum mechanics to discuss the electronic structure of atoms (Chapter 18) and molecules (Chapter 19).

## 18.1 UNITS

The forces acting between the particles in atoms and molecules are electrical (Prob. 18.69). To formulate the Hamiltonian operator of an atom or molecule, we need the expression for the potential energy of interaction between two charged particles. Equation (13.12) gives the electric potential  $\phi$  at a distance  $r$  from charge  $Q_1$  as  $\phi = Q_1/4\pi\epsilon_0 r$ . Equation (13.10) gives the potential energy  $V$  of interaction of a second charge  $Q_2$  with this electric potential as  $V = \phi Q_2 = (Q_1/4\pi\epsilon_0 r)Q_2$ . The potential energy of interaction between two charges separated by a distance  $r$  is therefore

$$V = \frac{1}{4\pi\epsilon_0} \frac{Q_1 Q_2}{r} \quad (18.1)^*$$

Equation (18.1) is in SI units, with  $Q_1$  and  $Q_2$  in coulombs (C),  $r$  in meters, and  $V$  in joules. The values of the constants  $\epsilon_0$  and  $1/4\pi\epsilon_0$  are listed in Eq. (13.2) and in the fundamental-constants table inside the back cover. The  $1/4\pi\epsilon_0$  factor in (18.1) is a bit of a pain, but if you learn the value of the speed of light  $c$ , you can avoid looking up  $1/4\pi\epsilon_0$  by using the relation (Prob. 18.3)

$$\frac{1}{4\pi\epsilon_0} = 10^{-7} c^2 \text{ N s}^2/\text{C}^2 \quad (18.2)$$

Atomic and molecular energies are very small. A convenient unit for these energies is the **electronvolt** (eV), defined as the kinetic energy acquired by an electron accelerated through a potential difference of one volt. From (13.10), the change in potential energy for this process is  $-e(1 \text{ V})$ , where  $-e$  is the electron's charge. This loss in potential energy is matched by a gain of kinetic energy equal to  $e(1 \text{ V})$ . Substitution of (18.4) for  $e$  gives  $1 \text{ eV} = (1.6022 \times 10^{-19} \text{ C})(1 \text{ V})$ ; the use of  $1 \text{ V} = 1 \text{ J/C}$  [Eq. (13.8)] gives

$$1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J} \quad (18.3)$$

## 18.2 HISTORICAL BACKGROUND

In a low-pressure gas-discharge tube, bombardment of the negative electrode (the cathode) by positive ions causes the cathode to emit what nineteenth-century physicists called *cathode rays*. In 1897, J. J. Thomson measured the deflection of cathode



rays in simultaneously applied electric and magnetic fields of known strengths. His experiment allowed calculation of the charge-to-mass ratio  $Q/m$  of the cathode-ray particles. Thomson found that  $Q/m$  was independent of the metal used for the cathode, and his experiments mark the discovery of the electron. [G. P. Thomson, who was one of the first people to observe diffraction effects with electrons (Sec. 17.4), was J. J.'s son. It has been said that J. J. Thomson got the Nobel Prize for proving the electron to be a particle, and G. P. Thomson got the Nobel Prize for proving the electron to be a wave.]

Let the symbol  $e$  denote the charge on the proton. The electron charge is then  $-e$ . Thomson found  $e/m_e = 1.7 \times 10^8$  C/g, where  $m_e$  is the electron's mass.

The first accurate measurement of the electron's charge was made by R. A. Millikan and Harvey Fletcher in the period 1909–1913 (see H. Fletcher, *Physics Today*, June 1982, p. 43). They observed the motion of charged oil drops in oppositely directed electric and gravitational fields and found that all observed values of the charge  $Q$  of a drop satisfied  $|Q| = ne$ , where  $n$  was a small integer and was clearly the number of extra or missing electrons on the charged oil drop. The smallest observed difference between values of  $|Q|$  could then be taken as the magnitude of the charge of the electron. The currently accepted value of the proton charge is

$$e = 1.6022 \times 10^{-19} \text{ C} \quad (18.4)$$

From the values of  $e$  and the Faraday constant  $F$ , an accurate value of the Avogadro constant  $N_A$  can be obtained. Equation (13.13) gives  $N_A = F/e = (96485 \text{ C mol}^{-1})/(1.6022 \times 10^{-19} \text{ C}) = 6.022 \times 10^{23} \text{ mol}^{-1}$ .

From the values of  $e$  and  $e/m_e$ , the electron mass  $m_e$  can be found. The modern value is  $9.1094 \times 10^{-28}$  g. The  $^1\text{H}$  atom mass is  $(1.0078 \text{ g})/(6.022 \times 10^{23}) = 1.6735 \times 10^{-24}$  g. This is 1837 times  $m_e$ , and so a proton is 1836 times as heavy as an electron. Nearly all the mass of an atom is in its nucleus.

The existence of the atomic nucleus was demonstrated by the 1909–1911 experiments of Rutherford, Geiger, and Marsden, who allowed a beam of alpha particles ( $\text{He}^{2+}$  nuclei) to fall on a very thin gold foil. Although most of the alpha particles passed nearly straight through the foil, a few were deflected through large angles. Since the very light electrons of the gold atoms cannot significantly deflect the alpha particles (in a collision between a truck and a bicycle, it is the bicycle that is deflected), one need consider only the force between the alpha particle and the positive charge of a gold atom. This force is given by Coulomb's law (13.1). To get a force large enough to produce the observed large deflections, Rutherford found that  $r$  in (13.1) had to be in the range  $10^{-12}$  to  $10^{-13}$  cm, which is much less than the known radius of an atom ( $10^{-8}$  cm). Rutherford therefore concluded in 1911 that the positive charge of an atom was not distributed throughout the atom but was concentrated in a tiny central region, the nucleus.

In 1913, Bohr proposed his theory of the hydrogen atom (Sec. 17.3). By the early 1920s, physicists realized that the Bohr theory was not correct.

In January 1926, Erwin Schrödinger formulated the Schrödinger equation. He solved the time-independent Schrödinger equation for the hydrogen atom in his first paper on quantum mechanics, obtaining energy levels in agreement with the observed spectrum. In 1929, Hylleraas used the quantum-mechanical variational method (Sec. 17.15) to obtain a ground-state energy for helium in accurate agreement with experiment.

### 18.3 THE HYDROGEN ATOM

The simplest atom is hydrogen. The Schrödinger equation can be solved exactly for the H atom but not for atoms with more than one electron. Ideas developed in treating the H atom provide a basis for dealing with many-electron atoms.

The hydrogen atom is a two-particle system in which a nucleus and an electron interact according to Coulomb's law. Instead of dealing only with the H atom, we shall consider the slightly more general problem of the **hydrogenlike atom**; this is an atom with one electron and  $Z$  protons in the nucleus. The values  $Z = 1, 2, 3, \dots$  give the species H,  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\dots$ . With the nuclear charge  $Q_1$  set equal to  $Ze$  and the electron charge  $Q_2$  set equal to  $-e$ , Eq. (18.1) gives the potential energy as  $V = -Ze^2/4\pi\epsilon_0 r$ , where  $r$  is the distance between the electron and the nucleus.

The potential-energy function depends only on the relative coordinates of the two particles, and so the conclusions of Sec. 17.13 apply. The total energy  $E_{\text{tot}}$  of the atom is the sum of its translational energy and the energy of internal motion of the electron relative to the proton. The translational energy levels can be taken as the particle-in-a-box levels (17.47). The box is the container holding the gas of H atoms. We now focus on the energy  $E$  of internal motion. The Hamiltonian  $H$  for the internal motion is given by the terms in the first pair of brackets in (17.78), and the corresponding Hamiltonian operator  $\hat{H}$  for the internal motion is

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (18.5)$$

where  $x$ ,  $y$ , and  $z$  are the coordinates of the electron relative to the nucleus and  $r = (x^2 + y^2 + z^2)^{1/2}$ . The reduced mass  $\mu$  is  $\mu = m_1 m_2 / (m_1 + m_2)$  [Eq. (17.79)], where  $m_1$  and  $m_2$  are the nuclear and electron masses. For a hydrogen atom,  $m_{\text{nucleus}} = m_{\text{proton}} = 1836.15m_e$  and

$$\mu_{\text{H}} = \frac{1836.15m_e}{1837.15m_e} = 0.999456m_e \quad (18.6)$$

which differs only slightly from  $m_e$ .

The H-atom Schrödinger equation  $\hat{H}\psi = E\psi$  is difficult to solve in cartesian coordinates but is relatively easy to solve in spherical coordinates. The spherical coordinates  $r$ ,  $\theta$ , and  $\phi$  of the electron relative to the nucleus are defined in Fig. 18.1. (Math books usually interchange  $\theta$  and  $\phi$ .) The projection of  $r$  on the  $z$  axis is  $r \cos \theta$ , and its projection on the  $xy$  plane is  $r \sin \theta$ . The relation between cartesian and spherical coordinates is therefore

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta \quad (18.7)$$

Note that  $x^2 + y^2 + z^2 = r^2$ . The ranges of the coordinates are

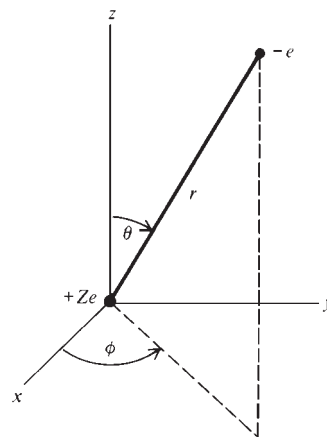
$$0 \leq r \leq \infty, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi \leq 2\pi \quad (18.8)^*$$

To solve the H-atom Schrödinger equation, one transforms the partial derivatives in the Hamiltonian operator (18.5) to derivatives with respect to  $r$ ,  $\theta$ , and  $\phi$  and then uses the separation-of-variables procedure (Sec. 17.11). The details (which can be found in quantum chemistry texts) are omitted, and only an outline of the solution process will be given. The H-atom Schrödinger equation in spherical coordinates is found to be separable when the substitution

$$\psi = R(r)\Theta(\theta)\Phi(\phi)$$

is made, where  $R$ ,  $\Theta$ , and  $\Phi$  are functions of  $r$ ,  $\theta$ , and  $\phi$ , respectively. One obtains three separate differential equations, one for each coordinate.

The differential equation for  $\Phi(\phi)$  is found to have solutions of the form  $\Phi(\phi) = Ae^{im\phi}$ , where  $i = \sqrt{-1}$ ,  $A$  is an integration constant whose value is chosen to normalize  $\Phi$ , and  $m$  (not to be confused with a mass) is a constant introduced in the process of separating the  $\phi$  differential equation (recall the introduction of the separation constants  $E_x$ ,  $E_y$ , and  $E_z$  in solving the problem of the particle in a three-dimensional box



**Figure 18.1**

Coordinates of the electron relative to the nucleus in a hydrogenlike atom.

in Sec. 17.9). Since addition of  $2\pi$  to the coordinate  $\phi$  brings us back to the same point in space, the requirement that the wave function be single-valued (Sec. 17.7) means that we must have  $\Phi(\phi) = \Phi(\phi + 2\pi)$ . One finds (Prob. 18.18) that this equation is satisfied only if  $m$  is an integer (positive, negative, or zero).

The solution to the differential equation for  $\Theta(\theta)$  is a complicated function of  $\theta$  that involves a separation constant  $l$  and also the integer  $m$  that occurs in the  $\phi$  equation. The  $\Theta(\theta)$  solutions are not quadratically integrable except for values of  $l$  that satisfy  $l = |m|, |m| + 1, |m| + 2, \dots$ , where  $|m|$  is the absolute value of the integer  $m$ . Thus  $l$  is an integer with minimum possible value 0, since this is the minimum possible value of  $|m|$ . The condition  $l \geq |m|$  means that  $m$  ranges from  $-l$  to  $+l$  in steps of 1.

The differential equation for  $R(r)$  for the H atom contains the energy  $E$  of internal motion as a parameter and also contains the quantum number  $l$ . The choice of zero level of energy is arbitrary. The potential energy  $V = -Ze^2/4\pi\epsilon_0 r$  in (18.5) takes the zero level to correspond to infinite separation of the electron and nucleus, which is an ionized atom. If the internal energy  $E$  is less than zero, the electron is bound to the nucleus. If the internal energy is positive, the electron has enough energy to escape the attraction of the nucleus and is free. One finds that for negative  $E$ , the function  $R(r)$  is not quadratically integrable except for values of  $E$  that satisfy  $E = -Z^2 e^4 \mu / (4\pi\epsilon_0)^2 2n^2 \hbar^2$ , where  $n$  is an integer such that  $n \geq l + 1$ . Since the minimum  $l$  is zero, the minimum  $n$  is 1. Also,  $l$  cannot exceed  $n - 1$ . Further, one finds that all positive values of  $E$  are allowed. When the electron is free, its energy is continuous rather than quantized.

In summary, the hydrogenlike-atom wave functions have the form

$$\psi = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi) \quad (18.9)$$

where the radial function  $R_{nl}(r)$  is a function of  $r$  whose form depends on the quantum numbers  $n$  and  $l$ , the theta factor depends on  $l$  and  $m$ , and the phi factor is

$$\Phi_m(\phi) = (2\pi)^{-1/2} e^{im\phi}, \quad i \equiv \sqrt{-1} \quad (18.10)$$

Since there are three variables, the solutions involve three quantum numbers: the **principal quantum number**  $n$ , the **angular-momentum quantum number**  $l$ , and the **magnetic quantum number**  $m$  (often symbolized by  $m_l$ ). For  $\psi$  to be well behaved, the quantum numbers are restricted to the values

$$n = 1, 2, 3, \dots \quad (18.11)^*$$

$$l = 0, 1, 2, \dots, n - 1 \quad (18.12)^*$$

$$m = -l, -l + 1, \dots, l - 1, l \quad (18.13)^*$$

For example, for  $n = 2$ ,  $l$  can be 0 or 1. For  $l = 0$ ,  $m$  is 0. For  $l = 1$ ,  $m$  can be  $-1, 0$ , or  $1$ . The allowed bound-state energy levels are

$$E = -\frac{Z^2}{n^2} \frac{e^2}{(4\pi\epsilon_0)2a} \quad \text{where } a \equiv \frac{\hbar^2(4\pi\epsilon_0)}{\mu e^2} \quad (18.14)$$

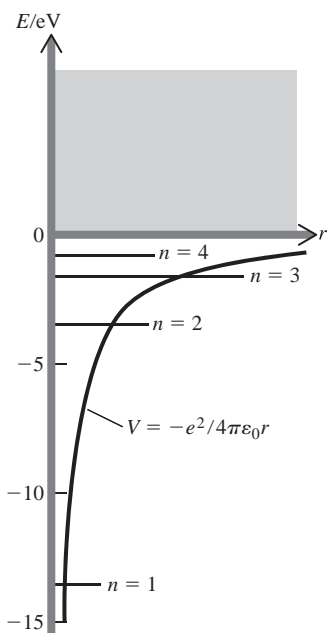
where  $n = 1, 2, 3, \dots$ . Also, all values  $E \geq 0$  are allowed, corresponding to an ionized atom. Figure 18.2 shows some of the allowed energy levels and the potential-energy function.

The following letter code is often used to specify the  $l$  value of an electron:

$l$ value	0	1	2	3	4	5
Code letter	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>

(18.15)\*

The value of  $n$  is given as a prefix to the  $l$  code letter, and the  $m$  value is added as a subscript. Thus,  $2s$  denotes the  $n = 2, l = 0$  state;  $2p_{-1}$  denotes the  $n = 2, l = 1, m = -1$  state.



**Figure 18.2**

Energy levels and potential-energy function of the hydrogen atom. The shading indicates that all positive energies are allowed.

The hydrogenlike-atom energy levels (18.14) depend only on  $n$ , but the wave functions (18.9) depend on all three quantum numbers  $n$ ,  $l$ , and  $m$ . Therefore, there is degeneracy. For example, the  $n = 2$  H-atom level is fourfold degenerate (spin considerations omitted), the wave functions (states)  $2s$ ,  $2p_1$ ,  $2p_0$ , and  $2p_{-1}$  all having the same energy.

The defined quantity  $a$  in (18.14) has the dimensions of length. For a hydrogen atom, substitution of numerical values gives (Prob. 18.13)  $a = 0.5295 \text{ \AA}$ .

If the reduced mass  $\mu$  in the definition of  $a$  is replaced by the electron mass  $m_e$ , we get the **Bohr radius**  $a_0$ :

$$a_0 = \hbar^2(4\pi\epsilon_0)/m_e e^2 = 0.5292 \text{ \AA} \quad (18.16)$$

$a_0$  was the radius of the  $n = 1$  circle in the Bohr theory.

### EXAMPLE 18.1 Ground-state energy of H

Calculate the ground-state hydrogen-atom energy  $E_{gs}$ . Also, express  $E_{gs}$  in electronvolts.

Setting  $n = 1$  and  $Z = 1$  in (18.14), we get

$$\begin{aligned} E_{gs} &= -\frac{e^2}{(4\pi\epsilon_0)2a} = -\frac{(1.6022 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})2(0.5295 \times 10^{-10} \text{ m})} \\ &= -2.179 \times 10^{-18} \text{ J} \end{aligned}$$

The use of the conversion factor (18.3) gives for an H atom

$$E_{gs} = -e^2/(4\pi\epsilon_0)(2a) = -13.60 \text{ eV} \quad (18.17)$$

#### Exercise

Find the wavelength of the longest-wavelength absorption line for a gas of ground-state hydrogen atoms. (Answer: 121.6 nm.)

$|E_{gs}|$  is the minimum energy needed to remove the electron from an H atom and is the **ionization energy** of H. The **ionization potential** of H is 13.60 V.

From (18.17), the energy levels (18.14) can be written as

$$E = -(Z^2/n^2)(13.60 \text{ eV}) \quad \text{H-like atom} \quad (18.18)^*$$

Although the reduced mass  $\mu$  in (18.14) differs for different hydrogenlike species (H,  $\text{He}^+$ ,  $\text{Li}^{2+}$ , ...), the differences are very slight and have been ignored in (18.18).

Quantum chemists often use a system called **atomic units**, in which energies are reported in **hartrees** and distances in **bohrs**. These quantities are defined as

$$1 \text{ bohr} \equiv a_0 = 0.52918 \text{ \AA}, \quad 1 \text{ hartree} \equiv e^2/(4\pi\epsilon_0)a_0 = 27.211 \text{ eV}$$

The ground-state energy (18.17) of H would be  $-\frac{1}{2}$  hartree if  $a$  were approximated by  $a_0$ .

The first few  $R_{nl}(r)$  and  $\Theta_{lm}(\theta)$  factors in the wave functions (18.9) are

$$R_{1s} = 2(Z/a)^{3/2} e^{-Zr/a} \quad (18.19)$$

$$R_{2s} = 2^{-1/2}(Z/a)^{3/2}(1 - Zr/2a)e^{-Zr/2a} \quad (18.20)$$

$$R_{2p} = (24)^{-1/2}(Z/a)^{5/2}re^{-Zr/2a} \quad (18.21)$$

$$\Theta_{s_0} = 1/\sqrt{2}, \quad \Theta_{p_0} = \frac{1}{2}\sqrt{6} \cos \theta, \quad \Theta_{p_1} = \Theta_{p_{-1}} = \frac{1}{2}\sqrt{3} \sin \theta \quad (18.22)$$

where the code (18.15) was used for  $l$ . The general form of  $R_{nl}$  is

$$R_{nl}(r) = r^l e^{-Zr/na} (b_0 + b_1 r + b_2 r^2 + \cdots + b_{n-l-1} r^{n-l-1})$$

where  $b_0, b_1, \dots$  are certain constants whose values depend on  $n$  and  $l$ . As  $n$  increases,  $e^{-Zr/na}$  dies off more slowly as  $r$  increases, so the average radius  $\langle r \rangle$  of the atom increases as  $n$  increases. For the ground state, one finds (Prob. 18.15)  $\langle r \rangle = 3a/2Z$ , which is  $0.79 \text{ \AA}$  for H. In (18.19) and (18.10),  $e$  is the base of natural logarithms, and not the proton charge.

Figure 18.3 shows some plots of  $R_{nl}(r)$ . The radial factor in  $\psi$  has  $n - l - 1$  nodes (not counting the node at the origin for  $l \neq 0$ ).

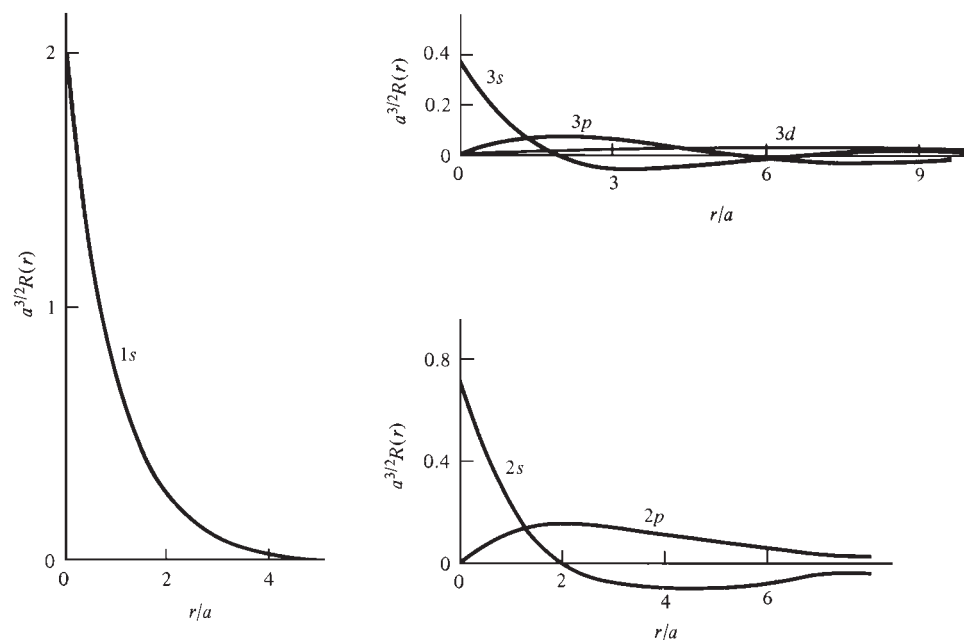
For  $s$  states ( $l = 0$ ), Eqs. (18.10) and (18.22) give the angular factor in  $\psi$  as  $1/\sqrt{4\pi}$ , which is independent of  $\theta$  and  $\phi$ . For  $s$  states,  $\psi$  depends only on  $r$  and is therefore said to be **spherically symmetric**. For  $l \neq 0$ , the angular factor is not constant, and  $\psi$  is not spherically symmetric. Note from Fig. 18.3 that  $R_{nl}$ , and hence  $\psi$ , is nonzero at the nucleus ( $r = 0$ ) for  $s$  states.

The ground-state wave function is found by multiplying  $R_{1s}$  in (18.19) by the  $s$ -state angular factor  $(4\pi)^{-1/2}$  to give

$$\psi_{1s} = \pi^{-1/2} (Z/a)^{3/2} e^{-Zr/a} \quad (18.23)$$

### Wave Functions of a Degenerate Energy Level

To deal with the  $2p$  wave functions of the H atom, we need to use a quantum-mechanical theorem about wave functions of a degenerate level. By a **linear combination** of the functions  $g_1, g_2, \dots, g_k$ , one means a function of the form  $c_1 g_1 + c_2 g_2 + \cdots + c_k g_k$ , where the  $c$ 's are constants. Any linear combination of two or more stationary-state wave functions that belong to the same degenerate energy level is an eigenfunction of the Hamiltonian operator with the same energy value as that of the degenerate level. In other words, if  $\hat{H}\psi_1 = E_1\psi_1$  and  $\hat{H}\psi_2 = E_1\psi_2$ , then  $\hat{H}(c_1\psi_1 + c_2\psi_2) = E_1(c_1\psi_1 + c_2\psi_2)$ . The linear combination  $c_1\psi_1 + c_2\psi_2$  (when multiplied by a normalization constant) is therefore also a valid wave function, meaning that



**Figure 18.3**

Radial factors in some hydrogen-atom wave functions.

it is an eigenfunction of  $\hat{H}$  and therefore a solution of the Schrödinger equation. The proof follows from the fact that  $\hat{H}$  is a linear operator (Sec. 17.11).

$$\begin{aligned}\hat{H}(c_1\psi_1 + c_2\psi_2) &= \hat{H}(c_1\psi_1) + \hat{H}(c_2\psi_2) = c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 \\ &= c_1E_1\psi_1 + c_2E_1\psi_2 = E_1(c_1\psi_1 + c_2\psi_2)\end{aligned}$$

Note that this theorem does not apply to wave functions belonging to two different energy levels. If  $\hat{H}\psi_5 = E_5\psi_5$  and  $\hat{H}\psi_6 = E_6\psi_6$  with  $E_5 \neq E_6$ , then  $c_1\psi_5 + c_2\psi_6$  is not an eigenfunction of  $\hat{H}$ .

## Real Wave Functions

The  $\Phi$  factor (18.10) in the H-atom wave function (18.9) contains  $i$  and so is complex. Chemists often find it convenient to work with real wave functions instead. To get real functions, we use the theorem just stated.

From (18.9), (18.10), and (18.21), the complex  $2p$  functions are

$$\begin{aligned}2p_{+1} &= be^{-Zr/2a}r \sin \theta e^{i\phi}, & 2p_{-1} &= be^{-Zr/2a}r \sin \theta e^{-i\phi} \\ 2p_0 &= ce^{-Zr/2a}r \cos \theta\end{aligned}$$

where  $b \equiv (1/8\pi^{1/2})(Z/a)^{5/2}$  and  $c \equiv \pi^{-1/2}(Z/2a)^{5/2}$ . The  $2p_0$  function is real as it stands. Equation (18.7) gives  $r \cos \theta = z$ , so the  $2p_0$  function is also written as

$$2p_z \equiv 2p_0 = cze^{-Zr/2a}$$

(Don't confuse the nuclear charge  $Z$  with the  $z$  spatial coordinate.) The  $2p_{+1}$  and  $2p_{-1}$  functions are each eigenfunctions of  $\hat{H}$  with the same energy eigenvalue, so we can take any linear combination of them and have a valid wave function.

As a preliminary, we note that

$$e^{i\phi} = \cos \phi + i \sin \phi \quad (18.24)^*$$

and  $e^{-i\phi} = (e^{i\phi})^* = \cos \phi - i \sin \phi$ . For a proof of (18.24), see Prob. 18.16.

We define the linear combinations  $2p_x$  and  $2p_y$  as

$$2p_x \equiv (2p_{+1} + 2p_{-1})/\sqrt{2}, \quad 2p_y \equiv (2p_{+1} - 2p_{-1})/i\sqrt{2} \quad (18.25)$$

The  $1/\sqrt{2}$  factors normalize these functions. Using (18.24) and its complex conjugate, we find (Prob. 18.17) that

$$2p_x = cxe^{-Zr/2a}, \quad 2p_y = cye^{-Zr/2a} \quad (18.26)$$

where  $c \equiv \pi^{-1/2}(Z/2a)^{5/2}$ . The  $2p_x$  and  $2p_y$  functions have the same  $n$  and  $l$  values as the  $2p_{+1}$  and  $2p_{-1}$  functions (namely,  $n = 2$  and  $l = 1$ ) but do not have a definite value of  $m$ . Similar linear combinations give real wave functions for higher H-atom states. The real functions (which have directional properties) are more suitable than the complex functions for use in treating the bonding of atoms to form molecules. Table 18.1 lists the  $n = 1$  and  $n = 2$  real hydrogenlike functions.

## Orbitals

An **orbital** is a one-electron spatial wave function. Since a hydrogenlike atom has one electron, all the hydrogenlike wave functions are orbitals. The use of (one-electron) orbitals in many-electron atoms is considered later in this chapter.

The **shape** of an orbital is defined as a surface of constant probability density that encloses some large fraction (say 90%) of the probability of finding the electron. The probability density is  $|\psi|^2$ . When  $|\psi|^2$  is constant, so is  $|\psi|$ . Hence  $|\psi|$  is constant on the surface of an orbital.

**TABLE 18.1****Real Hydrogenlike Wave Functions for  $n = 1$  and  $n = 2$** 

$$\begin{aligned}
 1s &= \pi^{-1/2} (Z/a)^{3/2} e^{-Zr/a} \\
 2s &= \frac{1}{4} (2\pi)^{-1/2} (Z/a)^{3/2} (2 - Zr/a) e^{-Zr/2a} \\
 2p_x &= \frac{1}{4} (2\pi)^{-1/2} (Z/a)^{5/2} r e^{-Zr/2a} \sin \theta \cos \phi \\
 2p_y &= \frac{1}{4} (2\pi)^{-1/2} (Z/a)^{5/2} r e^{-Zr/2a} \sin \theta \sin \phi \\
 2p_z &= \frac{1}{4} (2\pi)^{-1/2} (Z/a)^{5/2} r e^{-Zr/2a} \cos \theta
 \end{aligned}$$

For an  $s$  orbital,  $\psi$  depends only on  $r$ , and  $|\psi|$  is constant on the surface of a sphere with center at the nucleus. An  $s$  orbital has a spherical shape.

The volume element in spherical coordinates (see any calculus text) is

$$d\tau = r^2 \sin \theta \, dr \, d\theta \, d\phi \quad (18.27)^*$$

This is the volume of an infinitesimal solid for which the spherical coordinates lie in the ranges  $r$  to  $r + dr$ ,  $\theta$  to  $\theta + d\theta$ , and  $\phi$  to  $\phi + d\phi$ .

**EXAMPLE 18.2**  $1s$  orbital radius

Find the radius of the  $1s$  orbital in H using the 90 percent probability definition.

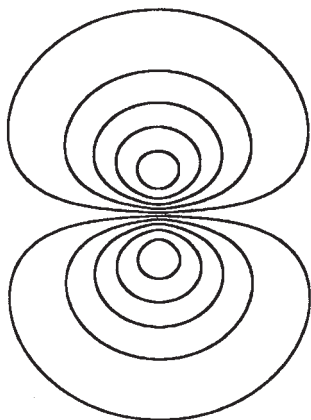
The probability that a particle will be in a given region is found by integrating the probability density  $|\psi|^2$  over the volume of the region. The region being considered here is a sphere of radius  $r_{1s}$ . For this region,  $\theta$  and  $\phi$  go over their full ranges 0 to  $\pi$  and 0 to  $2\pi$ , respectively, and  $r$  goes from 0 to  $r_{1s}$ . Also,  $\psi_{1s} = \pi^{-1/2} (Z/a)^{3/2} e^{-Zr/a}$  (Table 18.1). Using (18.27) for  $d\tau$ , we have as the probability that the electron is within distance  $r_{1s}$  from the nucleus:

$$\begin{aligned}
 0.90 &= \int_0^{2\pi} \int_0^\pi \int_0^{r_{1s}} \pi^{-1} \left( \frac{Z}{a} \right)^3 e^{-2Zr/a} r^2 \sin \theta \, dr \, d\theta \, d\phi \\
 0.90 &= \frac{Z^3}{\pi a^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \int_0^{r_{1s}} e^{-2Zr/a} r^2 \, dr
 \end{aligned}$$

where the integral identity of Prob. 17.14 was used. One next evaluates the integrals and uses trial and error or the Excel Solver or a calculator with equation-solving capability to find the value of  $r_{1s}$  that satisfies this equation with  $Z = 1$ . The remaining work is left as an exercise. One finds  $r_{1s} = 1.4 \text{ \AA}$  for H.

**Exercise**

Evaluate the integrals in this example (use a table of integrals for the  $r$  integral) and show that the result for  $Z = 1$  is  $e^{-2w}(2w^2 + 2w + 1) - 0.1 = 0$ , where  $w \equiv r_{1s}/a$ . Solve this equation to show that  $r_{1s} = 1.41 \text{ \AA}$ .

**Figure 18.4**

Contours of the  $2p_z$  orbital in the  $yz$  plane. The  $z$  axis is vertical.

Consider the shapes of the real  $2p$  orbitals. The  $2p_z$  orbital is  $2p_z = cze^{-Zr/2a}$ , where  $c$  is a constant. The  $2p_z$  function is zero in the  $xy$  plane (where  $z = 0$ ), is positive above this nodal plane (where  $z$  is positive), and is negative below this plane. A detailed investigation (Prob. 18.70) gives the curves shown in Fig. 18.4 as the contours of

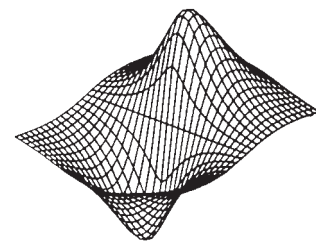
constant  $|\psi_{2p_z}|$  in the  $yz$  plane. The curves shown are for  $|\psi/\psi_{\max}| = 0.9$  (the two innermost ovals), 0.7, 0.5, 0.3, and 0.1, where  $\psi_{\max}$  is the maximum value of  $\psi_{2p_z}$ . The three-dimensional shape of the  $2p_z$  orbital is obtained by rotating a cross section around the  $z$  axis. This gives two distorted ellipsoids, one above and one below the  $xy$  plane. The ellipsoids do not touch each other. This is obvious from the fact that  $\psi$  has opposite signs on each ellipsoid. The absolute value  $|\psi|$  is the same on each ellipsoid of the  $2p_z$  orbital. The  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals have the same shape but different orientations in space. The two distorted ellipsoids are located on the  $x$  axis for the  $2p_x$  orbital, on the  $y$  axis for the  $2p_y$  orbital, and on the  $z$  axis for the  $2p_z$  orbital.

The  $2p_z$  wave function is a function of the three spatial coordinates:  $\psi_{2p_z} = \psi_{2p_z}(x, y, z)$ . Just as two dimensions are needed to graph a function of one variable, it would require four dimensions to graph  $\psi_{2p_z}(x, y, z)$ . Figure 18.5 shows a three-dimensional graph of  $\psi_{2p_z}(0, y, z)$ . In this graph, the value of  $\psi_{2p_z}$  at each point in the  $yz$  plane is given by the height of the graph above this plane. Note the resemblance to Fig. 17.13 for the  $n_x = 1, n_y = 2$  particle-in-a-two-dimensional-box state.

Figure 18.6 shows some hydrogen-atom orbital shapes. The plus and minus signs in Fig. 18.6 give the algebraic signs of  $\psi$  and have nothing to do with electric charge. The  $3p_z$  orbital has a spherical node (shown by the dashed line in Fig. 18.6). The  $3d_{z^2}$  orbital has two nodal cones (dashed lines). The other four  $3d$  orbitals have the same shape as one another but different orientations; each of these orbitals has two nodal planes separating the four lobes.

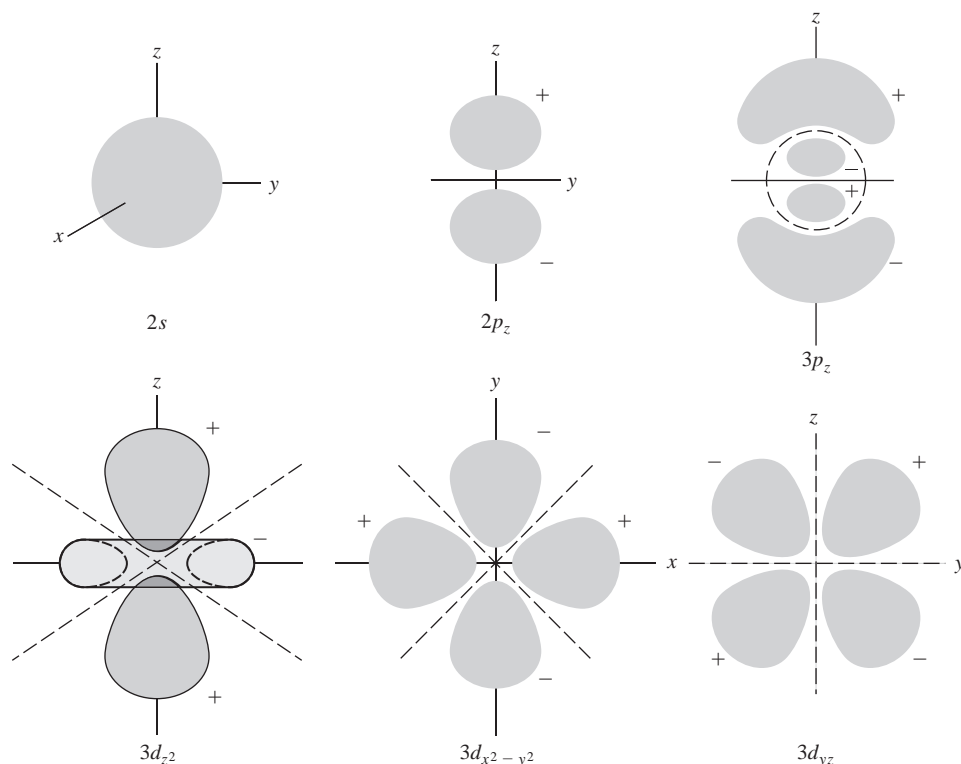
### Probability Density

The electron probability density for the hydrogenlike-atom ground state (Table 18.1) is  $|\psi_{1s}|^2 = (Z^3/\pi a^3)e^{-2Zr/a}$ . The  $1s$  probability density is a maximum at the nucleus ( $r = 0$ ). Figure 18.7 is a schematic indication of this, the density of the dots indicating the relative probability densities in various regions. Since  $|\psi_{1s}|^2$  is nonzero everywhere, the



**Figure 18.5**

Three-dimensional graph of values of  $\psi_{2p_z}$  in the  $yz$  plane.



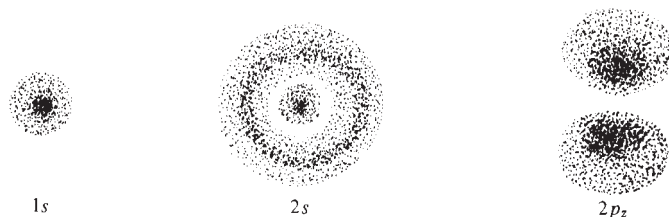
**Figure 18.6**

Shapes of some hydrogen-atom orbitals. (Not drawn to scale.) Note the different orientation of the axes in the  $3d_{x^2-y^2}$  figure compared with the others. Not shown are the  $3d_{xy}$  and  $3d_{xz}$  orbitals; these have their lobes between the  $x$  and  $y$  axes and between the  $x$  and  $z$  axes, respectively.



**Figure 18.7**

Probability densities in three hydrogen-atom states. (Not drawn to scale.)



electron can be found at any location in the atom (in contrast to the Bohr theory, where it had to be at a fixed  $r$ ). Figure 18.7 also indicates the variation in probability density for the  $2s$  and  $2p_z$  states. Note the nodal sphere in the  $2s$  function.

### Radial Distribution Function

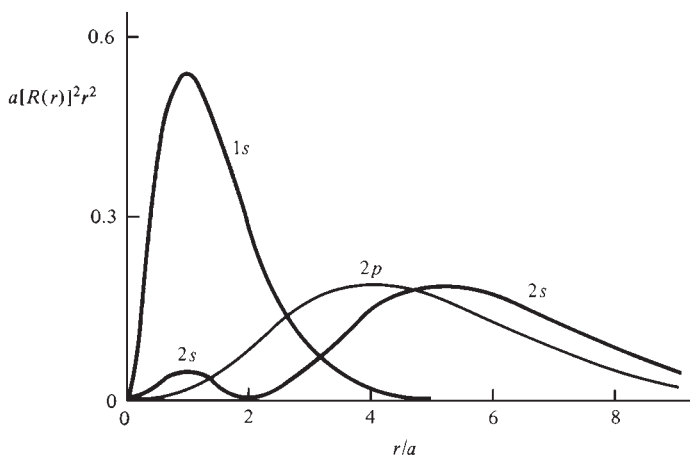
Suppose we want the probability  $\text{Pr}(r \rightarrow r + dr)$  that the electron–nucleus distance is between  $r$  and  $r + dr$ . This is the probability of finding the electron in a thin spherical shell whose center is at the nucleus and whose inner and outer radii are  $r$  and  $r + dr$ . For an  $s$  orbital,  $\psi$  is independent of  $\theta$  and  $\phi$  and so is essentially constant in the thin shell. Hence, the desired probability is found by multiplying  $|\psi_s|^2$  (the probability per unit volume) by the volume of the thin shell. This volume is  $\frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3 = 4\pi r^2 dr$ , where the terms in  $(dr)^2$  and  $(dr)^3$  are negligible. Therefore, for an  $s$  state  $\text{Pr}(r \rightarrow r + dr) = 4\pi r^2 |\psi_s|^2 dr$ .

For a non- $s$  state,  $\psi$  depends on the angles, so  $|\psi|^2$  is not constant in the thin shell. Let us divide the shell into tiny volume elements such that the spherical coordinates range from  $r$  to  $r + dr$ , from  $\theta$  to  $\theta + d\theta$ , and from  $\phi$  to  $\phi + d\phi$  in each tiny element. The volume  $d\tau$  of each such element is given by (18.27), and the probability that the electron is in an element is  $|\psi|^2 d\tau = |\psi|^2 r^2 \sin \theta dr d\theta d\phi$ . To find  $\text{Pr}(r \rightarrow r + dr)$ , we must sum these infinitesimal probabilities over the thin shell. Since the shell goes over the full range of  $\theta$  and  $\phi$ , the desired sum is the definite integral over the angles. Hence,  $\text{Pr}(r \rightarrow r + dr) = \int_0^{2\pi} \int_0^\pi |\psi|^2 r^2 \sin \theta dr d\theta d\phi$ . The use of  $\psi = R\Theta\Phi$  [Eq. (18.9)] and a result similar to that in Prob. 17.14 gives

$$\begin{aligned} \text{Pr}(r \rightarrow r + dr) &= |R|^2 r^2 dr \int_0^\pi |\Theta|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi \\ \text{Pr}(r \rightarrow r + dr) &= [R_n(r)]^2 r^2 dr \end{aligned} \quad (18.28)$$

since the multiplicative constants in the  $\Theta$  and  $\Phi$  functions have been chosen to normalize  $\Theta$  and  $\Phi$ ;  $\int_0^\pi |\Theta|^2 \sin \theta d\theta = 1$  and  $\int_0^{2\pi} |\Phi|^2 d\phi = 1$  (Prob. 18.26). Equation (18.28) holds for both  $s$  and non- $s$  states. The function  $[R(r)]^2 r^2$  in (18.28) is the **radial distribution function** and is plotted in Fig. 18.8 for several states. For the ground state, the radial distribution function is a maximum at  $r = a/Z$  (Prob. 18.24), which is  $0.53 \text{ \AA}$  for H.

For the hydrogen-atom ground state, the probability density  $|\psi|^2$  is a maximum at the origin (nucleus), but the radial distribution function  $R^2 r^2$  is zero at the nucleus because of the  $r^2$  factor; the most probable value of  $r$  is  $0.53 \text{ \AA}$ . A little thought shows that these facts are not contradictory. In finding  $\text{Pr}(r \rightarrow r + dr)$ , we find the probability that the electron is in a thin shell. This thin shell ranges over all values of  $\theta$  and  $\phi$  and so is composed of many volume elements. As  $r$  increases, the thin-shell volume  $4\pi r^2 dr$  increases. This increase, combined with the decrease in the probability density  $|\psi|^2$  as  $r$  increases, gives a maximum in  $\text{Pr}(r \rightarrow r + dr)$  for a value of  $r$  between 0 and  $\infty$ . The radial distribution function is zero at the nucleus because the thin-shell volume  $4\pi r^2 dr$  is zero here. (Note the resemblance to the discussion of the distribution function for speeds in a gas; Sec. 14.4.)

**Figure 18.8**

Radial distribution functions for some hydrogen-atom states.

### Average Values

To find the average value of any property  $M$  of a stationary-state hydrogen atom, one uses  $\langle M \rangle = \int \psi^* \hat{M} \psi d\tau$ , Eq. (17.63).

### EXAMPLE 18.3 Finding $\langle r \rangle$

Find the average value of the electron–nucleus separation in a hydrogenlike atom in the  $2p_z$  state.

We have  $\langle r \rangle = \int \psi^* \hat{r} \psi d\tau$ . The  $2p_z$  wave function is given in Table 18.1 and is real, so  $\psi^* = \psi$ . The operator  $\hat{r}$  is multiplication by  $r$ . Thus,  $\psi^* \hat{r} \psi = \psi^2 r$ . The volume element is  $d\tau = r^2 \sin \theta dr d\theta d\phi$  [Eq. (18.27)], and (18.8) gives the coordinate limits. Therefore

$$\begin{aligned} \langle r \rangle &= \int \psi^* \hat{r} \psi d\tau \\ \langle r \rangle &= \frac{1}{16(2\pi)} \left( \frac{Z}{a} \right)^5 \int_0^{2\pi} \int_0^\pi \int_0^\infty r^2 e^{-Zr/a} \cos^2 \theta (r) r^2 \sin \theta dr d\theta d\phi \\ &= \frac{1}{32\pi} \left( \frac{Z}{a} \right)^5 \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty r^5 e^{-Zr/a} dr \end{aligned}$$

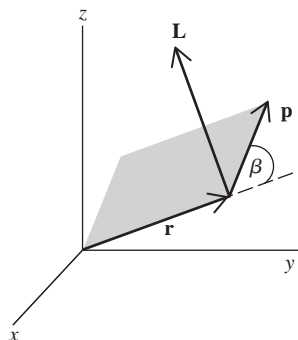
where the integral identity of Prob. 17.14 was used. A table of definite integrals gives  $\int_0^\infty x^n e^{-bx} dx = n!/b^{n+1}$  for  $b > 0$  and  $n$  a positive integer. Evaluation of the integrals (Prob. 18.23) gives  $\langle r \rangle = 5a/Z$ , where  $a$  is defined by (18.14) and equals  $0.53 \text{ \AA}$ . As a partial check, note that  $5a/Z$  has units of length.

### Exercise

Find  $\langle z^2 \rangle$  for the  $2p_z$  H-atom state. (Answer:  $18a^2 = 5.05 \text{ \AA}^2$ .)

## 18.4 ANGULAR MOMENTUM

The H-atom quantum numbers  $l$  and  $m$  are related to the angular momentum of the electron. The (linear) momentum  $\mathbf{p}$  of a particle of mass  $m$  and velocity  $\mathbf{v}$  is defined classically by  $\mathbf{p} = m\mathbf{v}$ . Don't confuse the mass  $m$  with the  $m$  quantum number. Let  $\mathbf{r}$  be the

**Figure 18.9**

The angular-momentum vector  $\mathbf{L}$  of a particle is perpendicular to the vectors  $\mathbf{r}$  and  $\mathbf{p}$  and has magnitude  $rp \sin \beta$ .

vector from the origin of a coordinate system to the particle. The particle's **angular momentum**  $\mathbf{L}$  with respect to the coordinate origin is defined classically as a vector of length  $rp \sin \beta$  (where  $\beta$  is the angle between  $\mathbf{r}$  and  $\mathbf{p}$ ) and direction perpendicular to both  $\mathbf{r}$  and  $\mathbf{p}$ ; see Fig. 18.9. More concisely,  $\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}$ , where  $\times$  indicates the vector cross-product.

To deal with angular momentum in quantum mechanics, one uses the quantum-mechanical operators for the components of the  $\mathbf{L}$  vector. We shall omit the quantum-mechanical treatment (see *Levine*, chaps. 5 and 6) and simply state the results. There are two kinds of angular momentum in quantum mechanics. **Orbital angular momentum** is the quantum-mechanical analog of the classical quantity  $\mathbf{L}$  and is due to the motion of a particle through space. In addition to orbital angular momentum, many particles have an intrinsic angular momentum called *spin* angular momentum; this will be discussed in the next section.

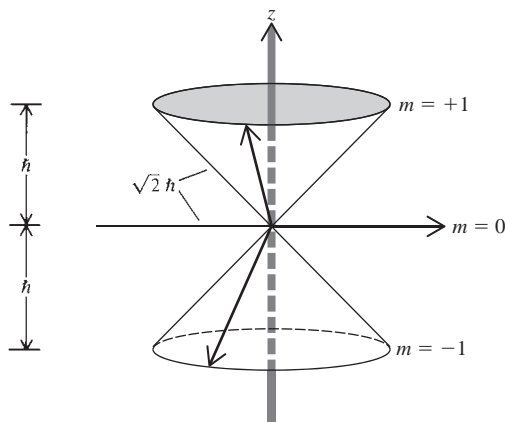
The H-atom stationary-state wave functions  $\psi_{nlm} = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi)$  [Eq. (18.9)] are eigenfunctions of the energy operator  $\hat{H}$  with eigenvalues given by Eq. (18.14);  $\hat{H}\psi_{nlm} = E_n\psi_{nlm}$  [Eq. (17.61)], where  $E_n = -(Z^2/n^2)(e^2/8\pi\epsilon_0 a)$ . This means that a measurement of the energy of an H atom in the state  $\psi_{nlm}$  must give the result  $E_n$  (see Sec. 17.11). One can show that the H-atom functions  $\psi_{nlm}$  are also eigenfunctions of the angular-momentum operators  $\hat{L}^2$  and  $\hat{L}_z$ , where  $\hat{L}^2$  is the operator for the square of the magnitude of the electron's orbital angular momentum  $\mathbf{L}$  with respect to the nucleus, and  $\hat{L}_z$  is the operator for the  $z$  component of  $\mathbf{L}$ . The eigenvalues are  $l(l+1)\hbar^2$  for  $\hat{L}^2$  and  $m\hbar$  for  $\hat{L}_z$ :

$$\hat{L}^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm}, \quad \hat{L}_z\psi_{nlm} = m\hbar\psi_{nlm} \quad (18.29)$$

where the quantum numbers  $l$  and  $m$  are given by (18.12) and (18.13). These eigenvalue equations mean that the magnitude  $|\mathbf{L}|$  and the  $z$  component  $L_z$  of the electron's orbital angular momentum in the H-atom state  $\psi_{nlm}$  are

$$|\mathbf{L}| = \sqrt{l(l+1)}\hbar, \quad L_z = m\hbar \quad (18.30)^*$$

For  $s$  states ( $l = 0$ ), the electronic orbital angular momentum is zero (a result hard to understand classically). For  $p$  states ( $l = 1$ ), the magnitude of  $\mathbf{L}$  is  $\sqrt{2}\hbar$ , and  $L_z$  can be  $\hbar$ , 0, or  $-\hbar$ . The possible orientations of  $\mathbf{L}$  for  $l = 1$  and  $m = 1, 0$ , and  $-1$  are shown in Fig. 18.10. The quantum number  $l$  specifies the magnitude  $|\mathbf{L}|$  of  $\mathbf{L}$ , and  $m$  specifies the  $z$  component  $L_z$  of  $\mathbf{L}$ . When  $|\mathbf{L}|$  and  $L_z$  are specified in a quantum-mechanical system, it turns out that  $L_x$  and  $L_y$  cannot be specified, so  $\mathbf{L}$  can lie anywhere on the surface of a cone about the  $z$  axis. For  $m = 0$ , the cone becomes a circle in the  $xy$  plane. Each of the three  $\mathbf{L}$  vectors in Fig. 18.10 has length  $|\mathbf{L}| = 2^{1/2}\hbar$ ; the  $z$  component of the  $m = 1$  vector has length  $m\hbar = \hbar$ .

**Figure 18.10**

Allowed spatial orientations of the electronic orbital-angular-momentum vector  $\mathbf{L}$  for  $l = 1$  and  $m = -1, 0$ , and  $1$ .

When an external magnetic field is applied to a hydrogen atom, the energies of the states depend on the  $m$  quantum number as well as on  $n$ .

The H-atom quantum numbers  $l$  and  $m$  are analogous to the two-particle-rigid-rotor quantum numbers  $J$  and  $M_J$  (Sec. 17.14). The functions  $\Theta$  and  $\Phi$  in the two-particle-rigid-rotor wave functions  $\psi_{\text{rot}}$  are the same functions as  $\Theta$  and  $\Phi$  in the H-atom wave functions (18.9).

The H-atom wave functions  $\psi_{nlm}$  are simultaneously eigenfunctions of the H-atom Hamiltonian operator  $\hat{H}$  and of the angular-momentum operators  $\hat{L}^2$  and  $\hat{L}_z$  [Eq. (18.29)]. A theorem of quantum mechanics shows this is possible because the operators  $\hat{H}$ ,  $\hat{L}^2$ , and  $\hat{L}_z$  all **commute** with one another, meaning that the commutators (Example 17.4)  $[\hat{H}, \hat{L}^2]$ ,  $[\hat{H}, \hat{L}_z]$ , and  $[\hat{L}^2, \hat{L}_z]$  are all equal to zero. However, one finds that  $[\hat{L}_z, \hat{L}_x] \neq 0$  and  $[\hat{L}_z, \hat{L}_y] \neq 0$ . Hence the  $\psi_{nlm}$  functions are not eigenfunctions of  $\hat{L}_x$  and  $\hat{L}_y$ , and the quantities  $L_x$  and  $L_y$  cannot be specified for the states  $\psi_{nlm}$ . The  $l = 0$  states are an exception. When  $l = 0$ , the orbital-angular-momentum magnitude  $|\mathbf{L}|$  in (18.30) is zero and every component  $L_x$ ,  $L_y$ , and  $L_z$  has the definite value of zero.

## 18.5 ELECTRON SPIN

The Schrödinger equation is a nonrelativistic equation and fails to account for certain relativistic phenomena. In 1928, the British physicist P. A. M. Dirac discovered the correct relativistic quantum-mechanical equation for a one-electron system. Dirac's relativistic equation predicts the existence of electron spin. Electron spin was first proposed by Uhlenbeck and Goudsmit in 1925 to explain certain observations in atomic spectra. In the nonrelativistic Schrödinger version of quantum mechanics that we are using, the existence of electron spin must be added to the theory as an additional postulate.

What is spin? **Spin** is an intrinsic (built-in) angular momentum possessed by elementary particles. This intrinsic angular momentum is in addition to the orbital angular momentum (Sec. 18.4) the particle has as a result of its motion through space. In a crude way, one can think of this intrinsic (or spin) angular momentum as being due to the particle's spinning about its own axis, but this picture should not be considered to represent reality. Spin is a nonclassical effect.

Quantum mechanics shows that the magnitude of the orbital angular momentum  $\mathbf{L}$  of any particle can take on only the values  $[l(l+1)]^{1/2}\hbar$ , where  $l = 0, 1, 2, \dots$ ; the  $z$  component  $L_z$  can take on only the values  $m\hbar$ , where  $m = -l, \dots, +l$ . We mentioned this for the electron in the H atom, Eq. (18.30).

Let  $\mathbf{S}$  be the spin-angular-momentum vector of an elementary particle. By analogy to orbital angular momentum [Eqs. (18.13) and (18.30)], we postulate that the magnitude of  $\mathbf{S}$  is

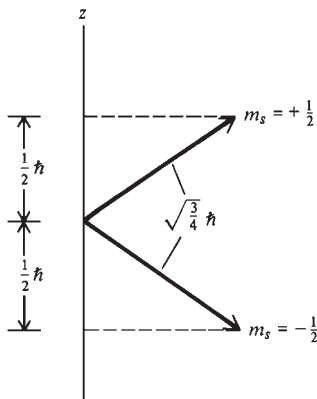
$$|\mathbf{S}| = [s(s+1)]^{1/2}\hbar \quad (18.31)^*$$

and that  $S_z$ , the component of the spin angular momentum along the  $z$  axis, can take on only the values

$$S_z = m_s\hbar \quad \text{where } m_s = -s, -s+1, \dots, s-1, s \quad (18.32)^*$$

The spin-angular-momentum quantum numbers  $s$  and  $m_s$  are analogous to the orbital-angular-momentum quantum numbers  $l$  and  $m$ , respectively. The analogy is not complete, since one finds that a given kind of elementary particle can have only one value for  $s$  and this value may be half-integral ( $\frac{1}{2}, \frac{3}{2}, \dots$ ) as well as integral ( $0, 1, \dots$ ). Experiment shows that electrons, protons, and neutrons all have  $s = \frac{1}{2}$ . Therefore,  $m_s = -\frac{1}{2}$  or  $+\frac{1}{2}$  for these particles.

$$s = \frac{1}{2}, \quad m_s = +\frac{1}{2}, -\frac{1}{2} \quad \text{for an electron} \quad (18.33)^*$$

**Figure 18.11**

Orientations of the electron spin vector  $\mathbf{S}$  with respect to the  $z$  axis. For  $m_s = +\frac{1}{2}$ , the vector  $\mathbf{S}$  must lie on the surface of a cone about the  $z$  axis; similarly for  $m_s = -\frac{1}{2}$ .

With  $s = \frac{1}{2}$ , the magnitude of the electron spin-angular-momentum vector is  $|\mathbf{S}| = [s(s+1)]^{1/2}\hbar = (3/4)^{1/2}\hbar$  and the possible values of  $S_z$  are  $\frac{1}{2}\hbar$  and  $-\frac{1}{2}\hbar$ . Figure 18.11 shows the orientations of  $\mathbf{S}$  for these two spin states. Chemists often use the symbols  $\uparrow$  and  $\downarrow$  to indicate the  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$  states, respectively.

Photons have  $s = 1$ . However, because photons are relativistic entities traveling at speed  $c$ , it turns out that they don't obey (18.32). Instead, photons can have only  $m_s = +1$  or  $m_s = -1$ . These two  $m_s$  values correspond to left- and right-circularly polarized light.

The wave function is supposed to describe the state of the system as fully as possible. An electron has two possible spin states, namely,  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$ , and the wave function should indicate which spin state the electron is in. We therefore postulate the existence of two spin functions  $\alpha$  and  $\beta$  that indicate the electron's spin state:  $\alpha$  means that  $m_s$  is  $+\frac{1}{2}$ ;  $\beta$  means that  $m_s$  is  $-\frac{1}{2}$ . The spin functions  $\alpha$  and  $\beta$  can be considered to be functions of some hypothetical internal coordinate  $\omega$  (omega) of the electron:  $\alpha = \alpha(\omega)$  and  $\beta = \beta(\omega)$ . Since nothing is known of the internal structure of an electron (or even whether it has an internal structure),  $\omega$  is purely hypothetical.

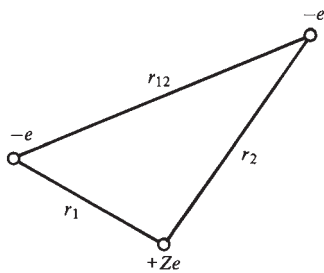
Since the spin function  $\alpha$  has  $m_s = \frac{1}{2}$  and  $\beta$  has  $m_s = -\frac{1}{2}$  and both have  $s = \frac{1}{2}$ , by analogy to (18.29), we write

$$\hat{S}^2\alpha = \frac{3}{4}\hbar^2\alpha, \quad \hat{S}^2\beta = \frac{3}{4}\hbar^2\beta, \quad \hat{S}_z\alpha = \frac{1}{2}\hbar\alpha, \quad \hat{S}_z\beta = -\frac{1}{2}\hbar\beta \quad (18.34)$$

where these equations are purely symbolic, in that we have not specified forms for the spin functions  $\alpha$  and  $\beta$  or for the operators  $\hat{S}^2$  and  $\hat{S}_z$ .

For a one-electron system, the spatial wave function  $\psi(x, y, z)$  is multiplied by either  $\alpha$  or  $\beta$  to form the complete wave function including spin. To a very good approximation, the spin has no effect on the energy of a one-electron system. For the hydrogen atom, the electron spin simply doubles the degeneracy of each level. For the H-atom ground level, there are two possible wave functions,  $1s\alpha$  and  $1s\beta$ , where  $1s = \pi^{-1/2}(Z/a)^{3/2}e^{-Zr/a}$ . A one-electron wave function like  $1s\alpha$  or  $1s\beta$  that includes both spatial and spin functions is called a **spin-orbital**.

With inclusion of electron spin in the wave function,  $\psi$  of an  $n$ -electron system becomes a function of  $4n$  variables:  $3n$  spatial coordinates and  $n$  **spin variables** or **spin coordinates**. The normalization condition (17.17) must be modified to include an integration or summation over the spin variables as well as an integration over the spatial coordinates. If one uses the hypothetical spin coordinate  $\omega$ , one integrates over  $\omega$ . A common alternative is to take the spin quantum number  $m_s$  of each electron as being the spin variable of that electron. In this case, one sums over the two possible  $m_s$  values of each electron in the normalization equation. Such sums or integrals over the spin variables are, like (18.34), purely symbolic.

**Figure 18.12**

Interparticle distances in the heliumlike atom.

## 18.6 THE HELIUM ATOM AND THE SPIN-STATISTICS THEOREM

### The Helium Atom

The helium atom consists of two electrons and a nucleus (Fig. 18.12). Separation of the translational energy of the atom as a whole from the internal motion is more complicated than for a two-particle problem and won't be gone into here. We shall just assume that it is possible to separate the translational motion from the internal motions.

The Hamiltonian operator for the internal motions in a heliumlike atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (18.35)$$

The first term is the operator for the kinetic energy of electron 1. In this term,  $\nabla_1^2 \equiv \partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2$  (where  $x_1, y_1, z_1$  are the coordinates of electron 1, the origin being taken at the nucleus) and  $m_e$  is the electron mass. It would be more accurate to replace  $m_e$  by the reduced mass  $\mu$ , but  $\mu$  differs almost negligibly from  $m_e$  for He and heavier atoms. The second term is the operator for the kinetic energy of electron 2, and  $\nabla_2^2 \equiv \partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2$ . The third term is the potential energy of interaction between electron 1 and the nucleus and is obtained by putting  $Q_1 = -e$  and  $Q_2 = Ze$  in  $V = Q_1 Q_2 / 4\pi\epsilon_0 r$  [Eq. (18.1)]. For helium, the atomic number  $Z$  is 2. In the third term,  $r_1$  is the distance between electron 1 and the nucleus:  $r_1^2 = x_1^2 + y_1^2 + z_1^2$ . The fourth term is the potential energy of interaction between electron 2 and the nucleus. The last term is the potential energy of interaction between electrons 1 and 2 separated by distance  $r_{12}$  and is found by putting  $Q_1 = Q_2 = -e$  in  $V = Q_1 Q_2 / 4\pi\epsilon_0 r$ . There is no term for kinetic energy of the nucleus, because we are considering only the internal motion of the electrons relative to the nucleus.

The Schrödinger equation is  $\hat{H}\psi = E\psi$ , where  $\psi$  is a function of the spatial coordinates of the electrons relative to the nucleus:  $\psi = \psi(x_1, y_1, z_1, x_2, y_2, z_2)$ , or  $\psi = \psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$  if spherical coordinates are used. Electron spin is being ignored for now and will be taken care of later.

Because of the interelectronic repulsion term  $e^2/4\pi\epsilon_0 r_{12}$ , the helium-atom Schrödinger equation can't be solved exactly. As a crude approximation, we can ignore the  $e^2/4\pi\epsilon_0 r_{12}$  term. The Hamiltonian (18.35) then has the approximate form  $\hat{H}_{\text{approx}} = \hat{H}_1 + \hat{H}_2$ , where  $\hat{H}_1 \equiv -(\hbar^2/2m_e)\nabla_1^2 - Ze^2/4\pi\epsilon_0 r_1$  is a hydrogenlike Hamiltonian for electron 1 and  $\hat{H}_2 \equiv -(\hbar^2/2m_e)\nabla_2^2 - Ze^2/4\pi\epsilon_0 r_2$  is a hydrogenlike Hamiltonian for electron 2. Since  $\hat{H}_{\text{approx}}$  is the sum of Hamiltonians for two noninteracting particles, the approximate energy is the sum of energies of each particle and the approximate wave function is the product of wave functions for each particle [Eqs. (17.68) to (17.70)]:

$$E \approx E_1 + E_2 \quad \text{and} \quad \psi \approx \psi_1(r_1, \theta_1, \phi_1)\psi_2(r_2, \theta_2, \phi_2) \quad (18.36)$$

where  $\hat{H}_1\psi_1 = E_1\psi_1$  and  $\hat{H}_2\psi_2 = E_2\psi_2$ . Since  $\hat{H}_1$  and  $\hat{H}_2$  are hydrogenlike Hamiltonians,  $E_1$  and  $E_2$  are hydrogenlike energies and  $\psi_1$  and  $\psi_2$  are hydrogenlike wave functions (orbitals).

Let us check the accuracy of this approximation. Equations (18.14) and (18.18) give  $E_1 = -(Z^2/n_1^2)(e^2/8\pi\epsilon_0 a) = -(Z^2/n_1^2)(13.6 \text{ eV})$ , where  $n_1$  is the principal quantum number of electron 1 and  $a$  has been replaced by the Bohr radius  $a_0$ , since the reduced mass  $\mu$  was replaced by the electron mass in (18.35). A similar equation holds for  $E_2$ . For the helium-atom ground state, the principal quantum numbers of the electrons are  $n_1 = 1$  and  $n_2 = 1$ ; also,  $Z = 2$ . Hence,

$$E \approx E_1 + E_2 = -4(13.6 \text{ eV}) - 4(13.6 \text{ eV}) = -108.8 \text{ eV}$$

The experimental first and second ionization energies of He are 24.6 eV and 54.4 eV, so the true ground-state energy is  $-79.0 \text{ eV}$ . (The first and second ionization energies are the energy changes for the processes  $\text{He} \rightarrow \text{He}^+ + e^-$  and  $\text{He}^+ \rightarrow \text{He}^{2+} + e^-$ , respectively.) The approximate result  $-108.8 \text{ eV}$  is grossly in error, as might be expected from the fact that the  $e^2/4\pi\epsilon_0 r_{12}$  term we ignored is not small.

The approximate ground-state wave function is given by Eq. (17.68) and Table 18.1 as

$$\psi \approx (Z/a_0)^{3/2} \pi^{-1/2} e^{-Zr_1/a_0} \cdot (Z/a_0)^{3/2} \pi^{-1/2} e^{-Zr_2/a_0} \quad (18.37)$$

with  $Z = 2$ . We shall abbreviate (18.37) as

$$\psi \approx 1s(1)1s(2) \quad (18.38)$$

where  $1s(1)$  indicates that electron 1 is in a  $1s$  hydrogenlike orbital (one-electron spatial wave function). We have the familiar He ground-state configuration  $1s^2$ .

## Two-Electron Spin Functions

To be fully correct, electron spin must be included in the wave function. One's first impulse might be to write down the following four spin functions for two-electron systems:

$$\alpha(1)\alpha(2), \quad \beta(1)\beta(2), \quad \alpha(1)\beta(2), \quad \beta(1)\alpha(2) \quad (18.39)$$

where the notation  $\beta(1)\alpha(2)$  means electron 1 has its spin quantum number  $m_{s1}$  equal to  $-\frac{1}{2}$  and electron 2 has  $m_{s2} = +\frac{1}{2}$ . However, the last two functions in (18.39) are not valid spin functions because they distinguish between the electrons. Electrons are identical to one another, and there is no way of experimentally determining which electron has  $m_s = +\frac{1}{2}$  and which has  $m_s = -\frac{1}{2}$ . In classical mechanics, we can distinguish two identical particles from each other by following their paths. However, the Heisenberg uncertainty principle makes it impossible to follow the path of a particle in quantum mechanics. Therefore, the wave function must not distinguish between the electrons. Thus, the fourth spin function in (18.39), which says that electron 1 has spin  $\beta$  and electron 2 has spin  $\alpha$ , cannot be used. Instead of the third and fourth spin functions in (18.39), it turns out (see below for the justification) that one must use the functions  $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$  and  $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ . For each of these functions, electron 1 has both spin  $\alpha$  and spin  $\beta$ , and so does electron 2. The  $2^{-1/2}$  in these functions is a normalization constant.

The proper two-electron spin functions are therefore

$$\alpha(1)\alpha(2), \quad \beta(1)\beta(2), \quad 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad (18.40)*$$

$$2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (18.41)*$$

The three spin functions in (18.40) are unchanged when electrons 1 and 2 are interchanged. For example, interchanging the electrons in the third function gives  $2^{-1/2}[\alpha(2)\beta(1) + \beta(2)\alpha(1)]$ , which equals the original function. These three spin functions are said to be **symmetric** with respect to electron interchange. The spin function (18.41) is multiplied by  $-1$  when the electrons are interchanged, since interchange gives

$$2^{-1/2}[\alpha(2)\beta(1) - \beta(2)\alpha(1)] = -2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The function (18.41) is **antisymmetric**, meaning that interchange of the coordinates of two particles multiplies the function by  $-1$ .

## The Spin–Statistics Theorem

Since two identical particles cannot be distinguished from each other in quantum mechanics, interchange of two identical particles in the wave function must leave all physically observable properties unchanged. In particular, the probability density  $|\psi|^2$  must be unchanged. We therefore expect that  $\psi$  itself would be multiplied by either  $+1$  or  $-1$  by such an interchange or relabeling. It turns out that only one of these possibilities occurs, depending on the spin of the particles. A particle whose spin quantum number  $s$  is an integer ( $s = 0$  or  $1$  or  $2$  or  $\dots$ ) is said to have **integral spin**, whereas a particle with  $s = \frac{1}{2}$  or  $\frac{3}{2}$  or  $\frac{5}{2}$  or  $\dots$  has **half-integral spin**. Experimental evidence shows the validity of the following statement:

**The complete wave function (including both spatial and spin coordinates) of a system of identical particles with half-integral spin must be antisymmetric with respect to interchange of all the coordinates (spatial and spin) of any two particles. For a system of identical particles with integral spin, the complete wave function must be symmetric with respect to such interchange.**

This fact is called the **spin–statistics theorem**. (The word statistics is used because the symmetry or antisymmetry requirement of the wave function of identical particles leads to different results for integral-spin particles versus half-integral-spin particles as to how many particles can occupy a given state and this affects the statistical mechanics of systems of such particles; see Secs. 18.8 and 21.5, and Prob. 21.22.) In 1940, Pauli proved the spin–statistics theorem using relativistic quantum field theory. In the nonrelativistic quantum mechanics that we are using, the spin–statistics theorem must be regarded as an additional postulate.

Particles requiring antisymmetric wave functions and having half-integral spin are called **fermions** (after the Italian–American physicist Enrico Fermi). Particles requiring symmetric wave functions and having integral spin are called **bosons** (after the Indian physicist S. N. Bose). Electrons have  $s = \frac{1}{2}$  and are fermions.

We are now ready to include spin in the ground-state He wave function. The approximate ground-state spatial function  $1s(1)1s(2)$  of (18.38) is symmetric with respect to electron interchange, since  $1s(2)1s(1) = 1s(1)1s(2)$ . Since electrons have  $s = \frac{1}{2}$ , the spin–statistics theorem demands that the complete wave function be antisymmetric. To get an antisymmetric  $\psi$ , we must multiply  $1s(1)1s(2)$  by the antisymmetric spin function (18.41). Use of the symmetric spin functions in (18.40) would give a symmetric wave function, which is forbidden for fermions. With inclusion of spin, the approximate ground-state He wave function becomes

$$\psi \approx 1s(1)1s(2) \cdot 2^{-1/2} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (18.42)$$

Interchange of the electrons multiplies  $\psi$  by  $-1$ , so (18.42) is antisymmetric. Note that the two electrons in the  $1s$  orbital have opposite spins.

The wave function (18.42) can be written as the determinant

$$\psi \approx \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \quad (18.43)$$

A second-order determinant is defined by

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} \equiv ad - bc \quad (18.44)^*$$

The use of (18.44) in (18.43) gives (18.42).

The justification for replacing the third and fourth spin functions in (18.39) by the linear combinations in (18.40) and (18.41) is that the latter two functions are the only normalized linear combinations of  $\alpha(1)\beta(2)$  and  $\beta(1)\alpha(2)$  that are either symmetric or antisymmetric with respect to electron interchange and that therefore do not distinguish between the electrons.

## Improved Ground-State Wave Functions for Helium

For one- and two-electron systems, the wave function is a product of a spatial factor and a spin factor. The atomic Hamiltonian (to a very good approximation) contains no terms involving spin. Because of these facts, the spin part of the wave function need not be explicitly included in calculating the energy of one- and two-electron systems and will be omitted in the calculations in this section.

We saw above that ignoring the  $e^2/4\pi\epsilon_0 r_{12}$  term in  $\hat{H}$  and taking  $E$  as the sum of two hydrogenlike energies gave a 38% error in the ground-state He energy. To improve on this dismal result, we can use the variation method. The most obvious choice of variational function is the  $1s(1)1s(2)$  function of (18.37) and (18.38), which is a normalized product of hydrogenlike  $1s$  orbitals. The variational integral in (17.84) is then  $W = \int 1s(1)1s(2) \hat{H} 1s(1)1s(2) d\tau$ , where  $\hat{H}$  is the true Hamiltonian (18.35) and



$d\tau = d\tau_1 d\tau_2$ , with  $d\tau_1 = r_1^2 \sin \theta_1 dr_1 d\theta_1 d\phi_1$ . Since  $e^2/4\pi\epsilon_0 r_{12}$  is part of  $\hat{H}$ , the effect of the interelectronic repulsion will be included in an average way, rather than being ignored as it was in (18.36). Evaluation of the variational integral is complicated and is omitted here. The result is  $W = -74.8$  eV, which is reasonably close to the true ground-state energy  $-79.0$  eV.

A further improvement is to use a variational function having the same form as (18.37) and (18.38) but with the nuclear charge  $Z$  replaced by a variational parameter  $\zeta$  (zeta). We then vary  $\zeta$  to minimize the variational integral  $W = \int \phi^* \hat{H} \phi d\tau$ , where the normalized variation function  $\phi$  is  $(\zeta/a_0)^3 \pi^{-1} e^{-\zeta r_1/a_0} e^{-\zeta r_2/a_0}$ . Substitution of the He Hamiltonian (18.35) with  $Z = 2$  and evaluation of the integrals leads to

$$W = (\zeta^2 - 27\zeta/8)e^2/4\pi\epsilon_0 a$$

(See *Levine*, sec. 9.4, for the details.) The minimization condition  $\partial W/\partial \zeta = 0$  then gives  $0 = (2\zeta - 27/8)e^2/4\pi\epsilon_0 a$  and the optimum value of  $\zeta$  is  $27/16 = 1.6875$ . This value of  $\zeta$  gives  $W = -2.848(e^2/4\pi\epsilon_0 a) = -2.848(2 \times 13.6 \text{ eV}) = -77.5$  eV, where (18.17) was used. This result is only 2% above the true ground-state energy  $-79.0$  eV.

The parameter  $\zeta$  is called an *orbital exponent*. The fact that  $\zeta$  is less than the atomic number  $Z = 2$  can be attributed to the **shielding** or **screening** of one electron from the nucleus by the other electron. When electron 1 is between electron 2 and the nucleus, the repulsion between electrons 1 and 2 subtracts from the attraction between electron 2 and the nucleus. Thus,  $\zeta$  can be viewed as the “effective” nuclear charge for the  $1s$  electrons. Since both electrons are in the same orbital, the screening effect is not great and  $\zeta$  is only 0.31 less than  $Z$ .

By using complicated variational functions, workers have obtained agreement to 1 part in 2 million between the theoretical and the experimental ionization energies of ground-state He. [C. L. Pekeris, *Phys. Rev.*, **115**, 1216 (1959); C. Schwartz, *Phys. Rev.*, **128**, 1146 (1962).]

### Excited-State Wave Functions for Helium

We saw that the approximation of ignoring the interelectronic repulsion in the Hamiltonian gives the helium wave functions as products of two hydrogenlike functions [Eq. (18.36)]. The hydrogenlike  $2s$  and  $2p$  orbitals have the same energy, and we might expect the approximate spatial wave functions for the lowest excited energy level of He to be  $1s(1)2s(2)$ ,  $1s(2)2s(1)$ ,  $1s(1)2p_x(2)$ ,  $1s(2)2p_x(1)$ ,  $1s(1)2p_y(2)$ ,  $1s(2)2p_y(1)$ ,  $1s(1)2p_z(2)$ , and  $1s(2)2p_z(1)$ , where  $1s(2)2p_z(1)$  is a function with electron 2 in the  $1s$  orbital and electron 1 in the  $2p_z$  orbital. Actually, these functions are incorrect, in that they distinguish between the electrons. As we did above with the spin functions, we must take linear combinations to give functions that don't distinguish between the electrons. Analogous to the linear combinations in (18.40) and (18.41), the correct normalized approximate spatial functions are

$$2^{-1/2}[1s(1)2s(2) + 1s(2)2s(1)] \quad (18.45)$$

$$2^{-1/2}[1s(1)2s(2) - 1s(2)2s(1)] \quad (18.46)$$

$$2^{-1/2}[1s(1)2p_x(2) + 1s(2)2p_x(1)] \quad \text{etc.} \quad (18.47)$$

$$2^{-1/2}[1s(1)2p_x(2) - 1s(2)2p_x(1)] \quad \text{etc.} \quad (18.48)$$

where each “etc.” indicates two similar functions with  $2p_x$  replaced by  $2p_y$  or  $2p_z$ .

If  $\psi_k$  is the true wave function of state  $k$  of a system, then  $\hat{H}\psi_k = E_k\psi_k$ , where  $E_k$  is the energy of state  $k$ . We therefore have  $\int \psi_k^* \hat{H} \psi_k d\tau = \int \psi_k^* E_k \psi_k d\tau = E_k \int \psi_k^* \psi_k d\tau = E_k$ , since  $\psi_k$  is normalized. This result suggests that if we have an approximate wave



Figure 18.13 shows the energies and some of the approximate wave functions for the states arising from the  $1s2s$  and  $1s2p$  configurations. The labels  $^3S$ ,  $^1S$ ,  $^3P$ , and  $^1P$  and the  $S$  and  $M_S$  values are explained shortly. The atomic energies shown in Fig. 18.13 are called **terms**, rather than energy levels, for a reason to be explained in Sec. 18.7. The  $^3S$  term of the  $1s2s$  configuration is threefold degenerate, because of the three symmetric spin functions. The  $^1S$  term is onefold degenerate (that is, nondegenerate), since there is only one wave function for this term. The approximate wave functions for the  $^3P$  term are obtained from those of the  $^3S$  term by replacing  $2s$  by  $2p_x$ , by  $2p_y$ , and by  $2p_z$ . Each of these replacements gives three wave functions (due to the three symmetric spin functions), so the  $^3P$  term is ninefold degenerate. The  $^1P$  term is threefold degenerate, since three functions are obtained by replacement of  $2s$  in the  $^1S$  function with  $2p_x$ , with  $2p_y$ , and with  $2p_z$ .

Note that the helium wave functions (18.42) and (18.45) to (18.48) are only approximations, since at best they take account of the interelectronic repulsion in only an average way. Thus, to say that the helium ground state has the electron configuration  $1s^2$  is only approximately true. The use of orbitals (one-electron wave functions) in many-electron atoms is only an approximation.

## 18.7 TOTAL ORBITAL AND SPIN ANGULAR MOMENTA

The magnitude of the orbital angular momentum of the electron in a one-electron atom is given by (18.30) as  $[l(l+1)]^{1/2}\hbar$ , where  $l = 0, 1, 2, \dots$ . For an atom with more than one electron, the orbital angular momentum vectors  $\mathbf{L}_i$  of the individual electrons add to give a **total electronic orbital angular momentum**  $\mathbf{L}$ , given by  $\mathbf{L} = \sum_i \mathbf{L}_i$ . Quantum mechanics shows that the magnitude of  $\mathbf{L}$  is given by

$$|\mathbf{L}| = [L(L+1)]^{1/2}\hbar, \quad \text{where } L = 0, 1, 2, \dots \quad (18.50)$$

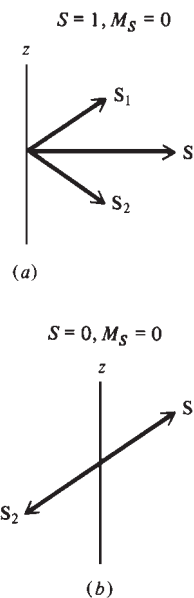
The value of the total electronic orbital-angular-momentum quantum number  $L$  is indicated by a code letter similar to (18.15), except that capital letters are used:

$L$ value	0	1	2	3	4	5
Code letter	$S$	$P$	$D$	$F$	$G$	$H$

For the  $1s2s$  configuration of the He atom, both electrons have  $l = 0$ . Hence, the total orbital angular momentum is zero, and the code letter  $S$  is used for each of the two terms that arise from the  $1s2s$  configuration (Fig. 18.13). For the  $1s2p$  configuration, one electron has  $l = 0$  and one has  $l = 1$ . Hence, the total-orbital-angular-momentum quantum number  $L$  equals 1, and the code letter  $P$  is used.

The **total electronic spin angular momentum**  $\mathbf{S}$  of an atom (or molecule) is the vector sum of the spin angular momenta of the individual electrons:  $\mathbf{S} = \sum_i \mathbf{S}_i$ . The magnitude of  $\mathbf{S}$  has the possible values  $[S(S+1)]^{1/2}\hbar$ , where the total electronic spin quantum number  $S$  can be  $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$  (Don't confuse the spin quantum number  $S$  with the orbital-angular-momentum code letter  $S$ .) The component of  $\mathbf{S}$  along the  $z$  axis has the possible values  $M_S\hbar$ , where  $M_S = -S, -S+1, \dots, S-1, S$ .

For a two-electron system such as He, each electron has spin quantum number  $s = \frac{1}{2}$ , and the total spin quantum number  $S$  can be 0 or 1, depending on whether the two electron spin vectors point in opposite directions or in approximately the same direction. (See Prob. 18.46.) For  $S = 1$ , the total spin angular momentum is  $[S(S+1)]^{1/2}\hbar = (1 \cdot 2)^{1/2}\hbar = 1.414\hbar$ . The spin angular momentum of each electron is  $(\frac{1}{2} \cdot \frac{3}{2})^{1/2}\hbar = 0.866\hbar$ . The algebraic sum of the spin angular momenta of the individual electrons is  $0.866\hbar + 0.866\hbar = 1.732\hbar$ , which is greater than the magnitude of the total spin angular momentum. Hence, the two spin-angular-momentum vectors of the electrons cannot be exactly parallel; see, for example, Fig. 18.14a.



**Figure 18.14**

Spin orientations corresponding to the spin functions  
 (a)  $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$  and  
 (b)  $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ .  
 $\mathbf{S}$  is the total electronic spin angular momentum.

For spin quantum number  $S = 0$ ,  $M_S$  must be zero, and there is only one possible spin state. This spin state corresponds to the antisymmetric spin function (18.41).

For  $S = 1$ ,  $M_S$  can be  $-1$ ,  $0$ , or  $+1$ . The  $M_S = -1$  spin state arises when each electron has  $m_s = -\frac{1}{2}$  and so corresponds to the symmetric spin function  $\beta(1)\beta(2)$  in (18.40). The  $M_S = +1$  spin state corresponds to the function  $\alpha(1)\alpha(2)$ . For the  $M_S = 0$  state, one electron must have  $m_s = +\frac{1}{2}$  and the other  $m_s = -\frac{1}{2}$ . This is the function  $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$  in (18.40). Although the  $z$  components of the two electron spins are in opposite directions, the two spin vectors can still add to give a total electronic spin with  $S = 1$ , as shown in Fig. 18.14a. The three symmetric spin functions in (18.40) thus correspond to  $S = 1$ .

The quantity  $2S + 1$  (where  $S$  is the total spin quantum number) is called the **spin multiplicity** of an atomic term and is written as a left superscript to the code letter for  $L$ . The lowest term in Fig. 18.13 has spin wave functions that correspond to total spin quantum number  $S = 1$ . Hence,  $2S + 1$  equals 3 for this term, and the term is designated  $^3S$  (read as “triplet ess”). The second-lowest term in Fig. 18.13 has the  $S = 0$  spin function and so has  $2S + 1 = 1$ . This is a  $^1S$  (“singlet ess”) term. The  $S$  and  $M_S$  total spin quantum numbers are listed in Fig. 18.13 for each state (wave function) of the  $^1S$  and  $^3S$  terms.

Note that the triplet term of the  $1s2s$  configuration lies lower than the singlet term. The same is true for the terms of the  $1s2p$  configuration. This illustrates **Hund’s rule**: *For a set of terms arising from a given electron configuration, the lowest-lying term is generally the one with the maximum spin multiplicity.* There are several exceptions to Hund’s rule. The theoretical basis for Hund’s rule is discussed in R. L. Snow and J. L. Bills, *J. Chem. Educ.*, **51**, 585 (1974); I. Shim and J. P. Dahl, *Theor. Chim. Acta*, **48**, 165 (1978); J. W. Warner and R. S. Berry, *Nature*, **313**, 160 (1985).

The maximum spin multiplicity is produced by having the maximum number of electrons with parallel spins. Two electrons are said to have **parallel** spins when their spin-angular-momentum vectors point in approximately the same direction, as, for example, in Fig. 18.14a. Two electrons have **antiparallel** spins when their spin vectors point in opposite directions to give a net spin angular momentum of zero, as in Fig. 18.14b. The  $^3S$  and  $^1S$  terms of the  $1s2s$  configuration can be represented by the diagrams

$$^3S: \begin{array}{cc} \uparrow & \uparrow \\ 1s & 2s \end{array} \quad ^1S: \begin{array}{cc} \uparrow & \downarrow \\ 1s & 2s \end{array}$$

where the spins are parallel in  $^3S$  and antiparallel in  $^1S$ .

Electrons in a filled subshell (for example, the electrons in  $2p^6$ ) have all their spins paired and contribute zero to the total electronic spin angular momentum. For each electron in a closed subshell with a positive value for the  $m$  quantum number, there is an electron with the corresponding negative value of  $m$ . (For example, in  $2p^6$ , there are two electrons with  $m = +1$  and two with  $m = -1$ .) Therefore, electrons in a filled subshell contribute zero to the total electronic orbital angular momentum. Hence, electrons in closed subshells can be ignored when finding the possible values of the quantum numbers  $L$  and  $S$  for the total orbital and spin angular momenta. For example, the  $1s^2 2s^2 2p^6 3s 3p$  electron configuration of Mg gives rise to the same terms as the  $1s2p$  configuration of He, namely,  $^3P$  and  $^1P$ .

The He-atom Hamiltonian (18.35) is not quite complete in that it omits a term called the *spin-orbit interaction* arising from the interaction between the spin and orbital motions of the electrons. The spin-orbit interaction is very small (except in heavy atoms), but it partly removes the degeneracy of a term, splitting an atomic term into a number of closely spaced **energy levels**. (See Prob. 18.47.) For example, the  $^3P$  term in Fig. 18.13 is split into three closely spaced levels; the other three terms are each slightly shifted in energy by the spin-orbit interaction but are not split. Because of this

spin-orbit splitting, the energies shown in Fig. 18.13 do not quite correspond to the actual pattern of atomic energy levels, and the energies in this figure are therefore called terms rather than energy levels.

An atomic term corresponds to definite values of the total orbital angular-momentum quantum number  $L$  and the total spin angular-momentum quantum number  $S$ . The  $L$  value is indicated by a code letter ( $S, P, D, \dots$ ), and the  $S$  value is indicated by writing the value of  $2S + 1$  as a left superscript to the  $L$  code letter.

For further discussion on the addition of angular momenta and on the way the terms arising from a given atomic electron configuration are found, see Probs. 18.46 and 18.47.

## 18.8 MANY-ELECTRON ATOMS AND THE PERIODIC TABLE

### Lithium and the Pauli Exclusion Principle

As we did with helium, we can omit the interelectronic repulsion terms  $(e^2/4\pi\epsilon_0) \cdot (1/r_{12} + 1/r_{13} + 1/r_{23})$  from the Li-atom Hamiltonian to give an approximate Hamiltonian that is the sum of three hydrogenlike Hamiltonians. The approximate wave function is then the product of hydrogenlike (one-electron) wave functions. For the ground state, we might expect the approximate wave function  $1s(1)1s(2)1s(3)$ . However, we have not taken account of electron spin or the spin-statistics theorem (Sec. 18.6). Electrons, which have  $s = \frac{1}{2}$  and are fermions, require a complete wave function that is antisymmetric. Therefore, the symmetric spatial function  $1s(1)1s(2)1s(3)$  must be multiplied by an antisymmetric three-electron spin function. One finds, however, that it is impossible to write an antisymmetric spin function for three electrons. With three or more electrons, the antisymmetry requirement cannot be satisfied by writing a wave function that is the product of separate spatial and spin factors.

The clue to constructing an antisymmetric wave function for three or more electrons lies in Eq. (18.43), which shows that the ground-state wave function of helium can be written as a determinant. The reason a determinant gives an antisymmetric wave function follows from the theorem: *Interchange of two rows of a determinant changes the sign of the determinant.* (For a proof, see *Sokolnikoff and Redheffer*, app. A.) Interchange of rows 1 and 2 of the determinant in (18.43) amounts to interchanging the electrons. Thus a determinantal  $\psi$  is multiplied by  $-1$  by such an interchange and therefore satisfies the antisymmetry requirement.

Let  $f$ ,  $g$ , and  $h$  be three spin-orbitals. (Recall that a spin-orbital is the product of a spatial orbital and a spin factor; Sec. 18.5.) We can get an antisymmetric three-electron wave function by writing the following determinant (called a **Slater determinant**)

$$\frac{1}{\sqrt{6}} \begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix} \quad (18.51)$$

The  $1/\sqrt{6}$  is a normalization constant; there are six terms in the expansion of this determinant.

A third-order determinant is defined by

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} \equiv a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix} \\ = aei - ahf - bdi + bgf + cdh - cge \quad (18.52)$$

where (18.44) was used. The second-order determinant that multiplies  $a$  in the expansion is found by striking out the row and the column that contains  $a$  in the third-order

determinant; similarly for the multipliers of  $-b$  and  $c$ . The reader can verify that interchange of two rows multiplies the determinant's value by  $-1$ .

To get an antisymmetric approximate wave function for Li, we use (18.51). Let us try to put all three electrons into the  $1s$  orbital by taking the spin-orbitals to be  $f = 1s\alpha$ ,  $g = 1s\beta$ , and  $h = 1s\alpha$ . The determinant (18.51) becomes

$$\frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\alpha(3) \end{vmatrix} \quad (18.53)$$

Expansion of this determinant using (18.52) shows it to equal zero. This can be seen without multiplying out the determinant by using the following theorem (*Sokolnikoff and Redheffer*, app. A): *If two columns of a determinant are identical, the determinant equals zero.* The first and third columns of (18.53) are identical, and so (18.53) vanishes. If any two of the spin-orbitals  $f$ ,  $g$ , and  $h$  in (18.51) are the same, two columns of the determinant are the same and the determinant vanishes. Of course, zero is ruled out as a possible wave function, since there would then be no probability of finding the electrons.

The requirement that the electronic wave function be antisymmetric thus leads to the conclusion:

### No more than one electron can occupy a given spin-orbital.

This is the **Pauli exclusion principle**, first stated by Pauli in 1925. An orbital (or one-electron spatial wave function) is defined by giving its three quantum numbers ( $n$ ,  $l$ ,  $m$  in an atom). A spin-orbital is defined by giving the three quantum numbers of the orbital and the  $m_s$  quantum number ( $+\frac{1}{2}$  for spin function  $\alpha$ ,  $-\frac{1}{2}$  for  $\beta$ ). Thus, in an atom, the exclusion principle requires that no two electrons have the same values for all four quantum numbers  $n$ ,  $l$ ,  $m$ , and  $m_s$ .

“There is no one fact in the physical world which has a greater impact on the way things are, than the Pauli Exclusion Principle. To this great Principle we credit the very existence of the hierarchy of matter, both nuclear and atomic, as ordered in Mendelejev’s Periodic Table of the chemical elements, which makes possible all of nuclear and atomic physics, chemistry, biology, and the macroscopic world that we see.” (I. Duck and E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem*, World Scientific, 1997, p. 21.)

Some physicists have speculated that small violations of the Pauli exclusion principle might occur. To test this, physicists passed a large current through a copper strip and searched for x-rays that would occur if an electron in the current dropped into the  $1s$  orbital of a Cu atom to give a  $1s^3$  atom. No such x-rays were found, and the experiment showed that the probability that a new electron introduced into copper would violate the Pauli principle is less than  $5 \times 10^{-28}$  [S. Bartalucci et al., *Phys. Lett. B*, **641**, 18 (2006)].

The antisymmetry requirement holds for any system of identical fermions (Sec. 18.6), so *in a system of identical fermions each spin-orbital can hold no more than one fermion*. In contrast,  $\psi$  is symmetric for bosons, so *there is no limit to the number of bosons that can occupy a given spin-orbital*.

Coming back to the Li ground state, we can put two electrons with opposite spins in the  $1s$  orbital ( $f = 1s\alpha$ ,  $g = 1s\beta$ ), but to avoid violating the exclusion principle, the third electron must go in the  $2s$  orbital ( $h = 2s\alpha$  or  $2s\beta$ ). The approximate Li ground-state wave function is therefore

$$\psi \approx \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} \quad (18.54)$$

When (18.54) is multiplied out, it becomes a sum of six terms, each containing a spatial and a spin factor, so  $\psi$  cannot be written as a single spatial factor times a single spin factor. Because the  $2s$  electron could have been given spin  $\beta$ , the ground state is doubly degenerate. The elements in each row of the Slater determinant (18.54) involve the same electron. The elements in each column involve the same spin-orbital.

Since all the electrons are  $s$  electrons with  $l = 0$ , the total-orbital-angular-momentum quantum number  $L$  is 0. The  $1s$  electrons have antiparallel spins, so the total electronic spin of the atom is due to the  $2s$  electron and the total-electronic-spin quantum number  $S$  is  $\frac{1}{2}$ . The spin multiplicity  $2S + 1$  is 2, and the ground term of Li is designated  $^2S$ .

A variational treatment using (18.54) would replace  $Z$  in the  $1s$  function in Table 18.1 by a parameter  $\zeta_1$  and  $Z$  in the  $2s$  function by a parameter  $\zeta_2$ . These parameters are “effective” atomic numbers that allow for electron screening. One finds the optimum values to be  $\zeta_1 = 2.69$  and  $\zeta_2 = 1.78$ . As expected, the  $2s$  electron is much better screened from the  $Z = 3$  nucleus than the  $1s$  electrons. The calculated variational energy turns out to be  $-201.2$  eV, compared with the true ground-state energy  $-203.5$  eV.

## The Periodic Table

A qualitative and semiquantitative understanding of atomic structure can be obtained from the orbital approximation. As we did with He and Li, we write an approximate wave function that assigns the electrons to hydrogenlike spin-orbitals. In each orbital, the nuclear charge is replaced by a variational parameter that represents an effective nuclear charge  $Z_{\text{eff}}$  and allows for electron screening. To satisfy the antisymmetry requirement, the wave function is written as a Slater determinant. For some atomic states, the wave function must be written as a linear combination of a few Slater determinants, but we won't worry about this complication.

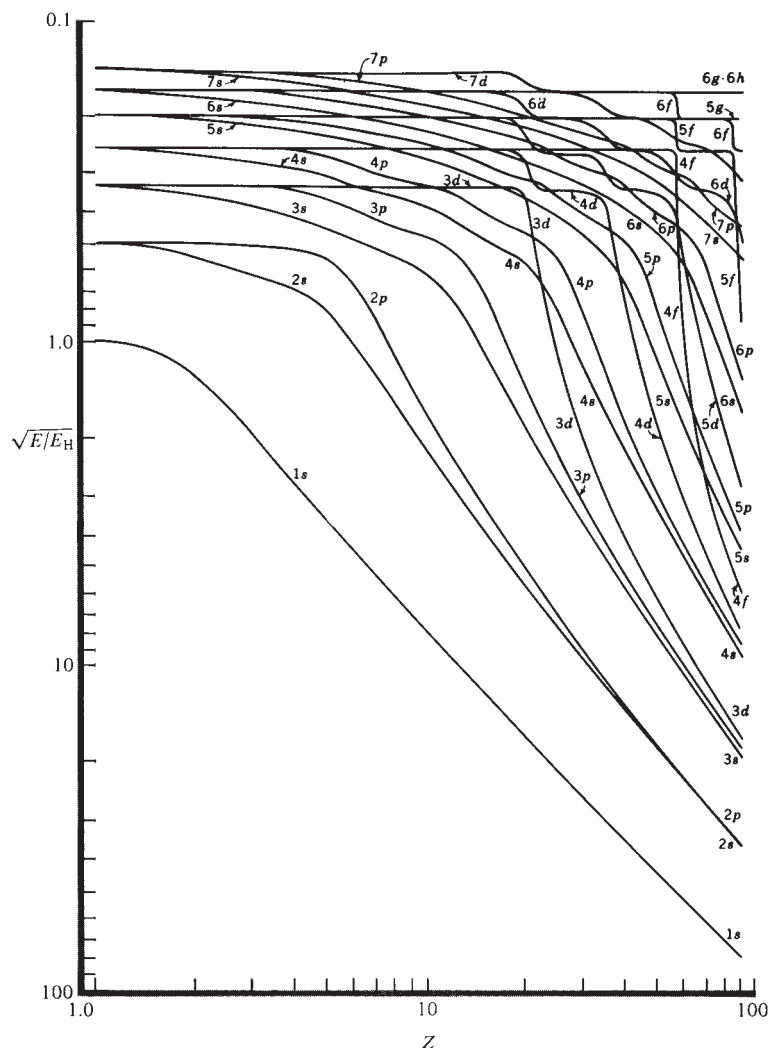
Since an electron has two possible spin states ( $\alpha$  or  $\beta$ ), the exclusion principle requires that no more than two electrons occupy the same orbital in an atom or molecule. Two electrons in the same orbital must have antiparallel spins, and such electrons are said to be **paired**. A set of orbitals with the same  $n$  value and the same  $l$  value constitutes a **subshell**. The lowest few subshells are  $1s, 2s, 2p, 3s, \dots$ . An  $s$  subshell has  $l = 0$  and  $m = 0$  and hence can hold at most two electrons without violating the exclusion principle. A  $p$  subshell has  $l = 1$  and the three possible  $m$  values  $-1, 0, +1$ ; hence, a  $p$  subshell has a capacity of 6 electrons;  $d$  and  $f$  subshells hold a maximum of 10 and 14 electrons, respectively.

The hydrogenlike energy formula (18.18) can be modified to approximate crudely the energy  $\varepsilon$  of a given atomic orbital as

$$\varepsilon \approx -(Z_{\text{eff}}^2/n^2)(13.6 \text{ eV}) \quad (18.55)$$

where  $n$  is the principal quantum number and the effective nuclear charge  $Z_{\text{eff}}$  differs for different subshells in the same atom. We write  $Z_{\text{eff}} = Z - s$ , where  $Z$  is the atomic number and the **screening constant**  $s$  for a given subshell is the sum of contributions from other electrons in the atom.

Figure 18.15 shows orbital energies for neutral atoms calculated using an approximate method. The scales in this figure are logarithmic. Note that the energy of an orbital depends strongly on the atomic number, decreasing with increasing  $Z$ , as would be expected from Eq. (18.55). Note the square-root sign on the vertical axis. Because  $Z_{\text{eff}}$  for the  $1s$  electrons in Ne ( $Z = 10$ ) is almost 10 times as large as  $Z_{\text{eff}}$  for the  $1s$  electron in H, the  $1s$  orbital energy  $\varepsilon_{1s}$  for Ne is roughly 100 times  $\varepsilon_{1s}$  for H. (Of course,  $\varepsilon_{1s}$  is negative.) As mentioned earlier, the  $l$  degeneracy that exists for  $Z = 1$  is removed in many-electron atoms. For most values of  $Z$ , the  $3s$  and  $3p$  orbitals are much closer together than the  $3p$  and  $3d$  orbitals, and we get the familiar stable octet

**Figure 18.15**

Approximate orbital energies versus atomic number  $Z$  in neutral atoms.  $E_H = -13.6$  eV, the ground-state H-atom energy. [Redrawn by M. Kasha from R. Latter, *Phys. Rev.*, **99**, 510 (1955).]

of outer electrons ( $ns^2np^6$ ). For  $Z$  between 7 and 21, the  $4s$  orbital lies below the  $3d$  ( $s$  orbitals are more penetrating than  $d$  orbitals), but for  $Z > 21$ , the  $3d$  lies lower.

We saw that the ground-state configuration of Li is  $1s^22s$ , where the superscripts give the numbers of electrons in each subshell and a superscript of 1 is understood for the  $2s$  subshell. We expect Li to readily lose one electron (the  $2s$  electron) to form the  $\text{Li}^+$  ion, and this is the observed chemical behavior.

The ground-state configurations of Be and B are  $1s^22s^2$  and  $1s^22s^22p$ , respectively. For C, the ground-state configuration is  $1s^22s^22p^2$ . A given electron configuration can give rise to more than one atomic term. For example, the He  $1s2s$  configuration produces the two terms  $^3S$  and  $^1S$  (Fig. 18.13). Figuring out the terms arising from the  $1s^22s^22p^2$  configuration is complicated and is omitted. Hund's rule tells us that the lowest-lying term will have the two  $2p$  spins parallel:

$$\begin{array}{ccccccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow & & & \\ 1s & 2s & & 2p & & & \end{array}$$

Putting the two  $2p$  electrons in different orbitals minimizes the electrostatic repulsion between them. The  $2p$  subshell is filled at  $_{10}\text{Ne}$ , whose electron configuration is  $1s^22s^22p^6$ . Like helium, neon does not form chemical compounds.



Sodium has the ground-state configuration  $1s^2 2s^2 2p^6 3s$ , and its chemical and physical properties resemble those of Li (ground-state configuration  $1s^2 2s$ ), its predecessor in group 1 of the periodic table. The periodic table is a consequence of the hydrogen-like energy-level pattern, the allowed electronic quantum numbers, and the exclusion principle. The third period ends with Ar, whose ground-state configuration is  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

For  $Z = 19$  and 20, the  $4s$  subshell lies below the  $3d$  (Fig. 18.15) and K and Ca have the outer electron configurations  $4s$  and  $4s^2$ , respectively. With  $Z = 21$ , the  $3d$  subshell begins to fill, giving the first series of *transition elements*. The  $3d$  subshell is filled at  $_{30}\text{Zn}$ , outer electron configuration  $3d^{10} 4s^2$  ( $3d$  now lies lower than  $4s$ ). Filling the  $4p$  subshell then completes the fourth period. For discussion of the electron configurations of transition-metal atoms and ions, see L. G. Vanquickenborne et al., *J. Chem. Educ.*, **71**, 469 (1994); Levine, sec. 11.2.

The rare earths (lanthanides) and actinides in the sixth and seventh periods correspond to filling the  $4f$  and  $5f$  subshells.

The order of filling of subshells in the periodic table is given by the  $n + l$  rule: Subshells fill in order of increasing  $n + l$  values; for subshells with equal  $n + l$  values, the one with the lower  $n$  fills first.

Niels Bohr rationalized the periodic table in terms of filling the atomic energy levels, and the familiar long form of the periodic table is due to him.

### Atomic Properties

The **first, second, third, . . . ionization energies** of atom A are the energies required for the processes  $A \rightarrow A^+ + e^-$ ,  $A^+ \rightarrow A^{2+} + e^-$ ,  $A^{2+} \rightarrow A^{3+} + e^-$ , . . . , where A,  $A^+$ , etc., are isolated atoms or ions in their ground states. Ionization energies are traditionally expressed in eV. The corresponding numbers in volts are called the **ionization potentials**. Some first, second, and third ionization energies in eV are (C. E. Moore, Ionization Potentials and Ionization Limits, *Nat. Bur. Stand. U.S. Publ. NSRDS-NBS 34*, 1970):

H	He	Li	Be	B	C	N	O	F	Ne	Na
13.6	24.6	5.4	9.3	8.3	11.3	14.5	13.6	17.4	21.6	5.1
	54.4	75.6	18.2	25.2	24.4	29.6	35.1	35.0	41.0	47.3
		122.5	153.9	37.9	47.9	47.4	54.9	62.7	63.4	71.6

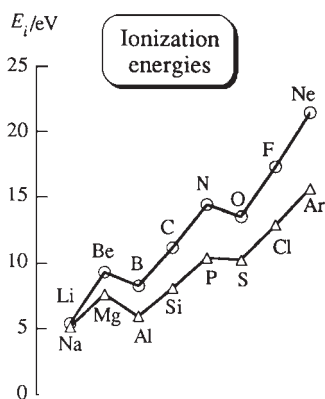
Note the low value for removal of the  $2s$  electron from Li and the high value for removal of a  $1s$  electron from  $\text{Li}^+$ . Ionization energies clearly show the “shell” structure of atoms.

The first ionization energy decreases going down a group in the periodic table because the increase in quantum number  $n$  of the valence electron increases the average distance of the electron from the nucleus, making it easier to remove. The first ionization energy generally increases going across a period (Fig. 18.16). As we go across a period, the nuclear charge increases, but the electrons being added have the same or a similar value of  $n$  and so don’t screen one another very effectively; the effective nuclear charge  $Z_{\text{eff}} = Z - s$  in (18.55) increases across a period, since  $Z$  is increasing faster than  $s$ , and the valence electrons become more tightly bound. Metals have lower ionization energies than nonmetals.

The **electron affinity** of atom A is the energy released in the process  $A + e^- \rightarrow A^-$ . Some values in eV are [T. Andersen et al., *J. Phys. Chem. Ref. Data*, **28**, 1511 (1999)]:

H	He	Li	Be	B	C	N	O	F	Ne	Na
0.8	<0	0.6	<0	0.3	1.3	−0.1	1.5	3.4	<0	0.5

Note the opposite convention in the definitions of ionization energy and electron affinity. The ionization energy is  $\Delta E$  accompanying loss of an electron. The electron affinity is  $-\Delta E$  accompanying gain of an electron.



**Figure 18.16**

Ionization energies of second- and third-period elements.

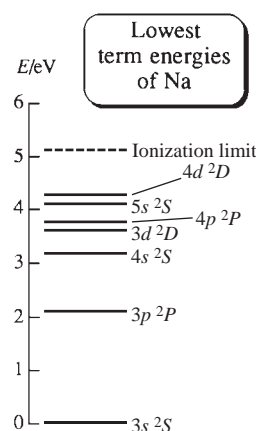
The motion of an electric charge produces a magnetic field. The orbital angular momentum of atomic electrons with  $l \neq 0$  therefore produces a magnetic field. The “spinning” of an electron about its own axis is a motion of electric charge and also produces a magnetic field. Because of the existence of electron spin, an electron acts like a tiny magnet. (Magnetic interactions between electrons are much smaller than the electrical forces and can be neglected in the Hamiltonian except in very precise calculations.) The magnetic fields of electrons with opposite spins cancel each other. It follows that an atom in a state with  $L \neq 0$  and/or  $S \neq 0$  produces a magnetic field and is said to be **paramagnetic**. In a magnetized piece of iron, the majority of electron spins are aligned in the same direction to produce the observed magnetic field.

The **radius** of an atom is not a well-defined quantity, as is obvious from Figs. 18.7 and 18.8. From observed bond lengths in molecules and interatomic distances in crystals, various kinds of atomic radii can be deduced. (See Secs. 19.1 and 23.6.) Atomic radii decrease going across a given period because of the increase in  $Z_{\text{eff}}$  and increase going down a given group because of the increase in  $n$ .

The energies of excited states of most atoms of the periodic table have been determined from atomic spectral data and are tabulated in C. E. Moore, *Atomic Energy Levels*, *Nat. Bur. Stand. U.S. Circ.* 467, vols. I, II, and III, 1949, 1952, and 1958; C. E. Moore, *Atomic Energy Levels*, *Nat. Bur. Stand. Publ. NSRDS-NBS* 35, vols. I, II, and III, 1971. For online atomic-energy-level data, see [physics.nist.gov/PhysRefData/ASD/index.html](http://physics.nist.gov/PhysRefData/ASD/index.html).

Figure 18.17 shows some of the term energies (as determined from emission and absorption spectra) of the Na atom, whose ground-state electron configuration is  $1s^2 2s^2 2p^6 3s$ . The zero level of energy has been taken at the ground state. This choice differs from the convention used in Fig. 18.2 and Eq. (18.5), where the zero level of energy corresponds to all charges being infinitely far from one another. (Each  $^2P$ ,  $^2D$ ,  $^2F$ , . . . term in Na is split by spin–orbit interaction into two closely spaced energy levels, which are not shown.)

Each excited term in Fig. 18.17 arises from an electron configuration with the  $3s$  valence electron excited to a higher orbital, which is written preceding the term symbol. Terms that correspond to electron configurations with an inner-shell Na electron excited have energies higher than the first ionization energy of Na (the dashed line), and such terms are not readily observed spectroscopically. Because Na has only one valence electron, each electron configuration with filled inner shells gives rise to only one term, and the Na term-energy diagram is simple. Note from Fig. 18.17 that the  $4s\ ^2S$  term of Na lies below the  $3d\ ^2D$  term, as might be expected from Fig. 18.15.



**Figure 18.17**

Some term energies of Na. The orbital of the excited electron is given preceding each term symbol.

## 18.9

## HARTREE–FOCK AND CONFIGURATION-INTERACTION WAVE FUNCTIONS

### Hartree–Fock Wave Functions

Wave functions like (18.42) for He and (18.54) for Li are approximations. How can these approximate wave functions be improved? One way is by not restricting the one-electron spatial functions to hydrogenlike functions. Instead, for the He ground state, we take as a trial variation function

$$\phi(1)\phi(2) \cdot 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (18.56)$$

and we look for the function  $\phi$  that minimizes the variational integral, where  $\phi$  need not be a hydrogenlike  $1s$  orbital but can have any form. For the Li ground state, we use a function like (18.54) but with the  $1s$  and  $2s$  functions replaced by unknown functions  $f$  and  $g$ , and we look for those functions  $f$  and  $g$  that minimize the variational

integral. These variation functions are still antisymmetrized products of one-electron spin-orbitals, so the functions  $\phi$ ,  $f$ , and  $g$  are still atomic orbitals.

In the period 1927–1930, the English physicist Hartree and the Russian physicist Fock developed a systematic procedure for finding the best possible forms for the orbitals. A variational wave function that is an antisymmetrized product of the best possible orbitals is called a **Hartree–Fock wave function**. For each state of a given system, there is a single Hartree–Fock wave function. Hartree and Fock showed that the Hartree–Fock orbitals  $\phi_i$  satisfy the equation

$$\hat{F}\phi_i = \varepsilon_i\phi_i \quad (18.57)$$

where the Hartree–Fock operator  $\hat{F}$  is a complicated operator whose form is discussed later in this section. Each of the spatial orbitals  $\phi_i$  is a function of the three spatial coordinates;  $\varepsilon_i$  is the energy of orbital  $i$ .

The Hartree–Fock operator  $\hat{F}$  in (18.57) is peculiar in that its form depends on what the eigenfunctions  $\phi_i$  are. Since the orbitals  $\phi_i$  are not known before the Hartree–Fock equations (18.57) are solved, the operator  $\hat{F}$  is initially unknown. To solve (18.57), one starts with an initial guess for the orbitals  $\phi_i$ , which allows one to calculate an initial guess for  $\hat{F}$ . One uses this initial estimate of  $\hat{F}$  to solve (18.57) for an improved set of orbitals, and then uses these orbitals to calculate an improved  $\hat{F}$ , which is then used to solve for further improved orbitals, etc. The process is continued until no further significant change in the orbitals occurs from one iteration to the next.

Each spatial orbital in (18.57) is a function of the three spatial coordinates of a single electron. Likewise, the Hartree–Fock operator  $\hat{F}$  contains the coordinates of a single electron and derivatives with respect to those coordinates. If we use the number 1 to label the electron in (18.57), we can write (18.57) as  $\hat{F}(1)\phi_i(1) = \varepsilon_i\phi_i(1)$ . The operator  $\hat{F}(1)$  for an atom is the sum of the following terms: (a) The kinetic-energy operator  $-(\hbar^2/2m_e)\nabla_1^2$  for electron 1. (b) The potential energy  $-Ze^2/4\pi\epsilon_0r_1$  of attraction between electron 1 and the nucleus. (c) The potential energy of repulsion between electron 1 and a hypothetical continuous spatial distribution of negative charge whose charge density (charge per unit volume) is calculated by imagining that each of the other electrons in the atom is smeared out into a charge cloud whose charge density at each point is  $-e|\phi_j|^2$ , where  $\phi_j$  is the orbital occupied by the hypothetical smeared-out electron. One adds the charge densities of the smeared-out electrons to get a charge cloud whose interaction with electron 1 is calculated. Part c of  $\hat{F}(1)$  is called the *Coulomb operator*. (d) An *exchange operator* that involves the occupied orbitals and is present so as to make the overall wave function antisymmetric with respect to exchange of electrons. Parts c and d of  $\hat{F}$  depend on the occupied orbitals, which are unknown at the start of the calculation.

Originally, Hartree–Fock orbitals were calculated numerically, and the results expressed as a table of values of  $\phi_i$  at various points in space. In 1951, Roothaan showed that the most convenient way to express Hartree–Fock orbitals is as linear combinations of a set of functions called **basis functions**. A set of functions is said to be a **complete set** if every well-behaved function can be written as a linear combination of the members of the complete set. If the functions  $g_1, g_2, g_3, \dots$  form a complete set, then every well-behaved function  $f$  that depends on the same variables as the  $g$  functions can be expressed as

$$f = \sum_k c_k g_k \quad (18.58)$$

where the coefficients  $c_k$  are constants that depend on what the function  $f$  is. (More details on complete sets are given in Sec. 17.16.) It generally requires an infinite number

of functions  $g_1, g_2, \dots$  to have a complete set (but not every infinite set of functions is complete). The basis functions  $g_k$  used to express the Hartree–Fock orbitals  $\phi_i$  must be a complete set. We have

$$\phi_i = \sum_k b_k g_k \quad (18.59)$$

An orbital  $\phi_i$  is specified by stating what the set of basis functions  $g_k$  is and giving the coefficients  $b_k$ . Roothaan showed how to calculate the  $b_k$ 's that give the best possible orbitals. A different set of coefficients in (18.59) is used to express each of the orbitals.

A complete set of basis functions commonly used in atomic Hartree–Fock calculations is the set of **Slater-type orbitals** (STOs). An STO has the form  $G_n(r)\Theta_{lm}(\theta)\Phi_m(\phi)$ , where  $\Theta_{lm}(\theta)$  and  $\Phi_m(\phi)$  are the same functions as in the hydrogenlike orbitals (18.9). The radial factor has the form  $G_n(r) = Nr^{n-1}e^{-\zeta r/a_0}$ , where  $N$  is a normalization constant,  $n$  is the principal quantum number, and  $\zeta$  is a variational parameter (the *orbital exponent*). The function  $G_n(r)$  differs from a hydrogenlike radial factor in containing  $r^{n-1}$  in place of  $r^l$  times a polynomial in  $r$ . It has been shown that the set of STOs with  $n, l$ , and  $m$  given by (18.11) to (18.13) and with all possible positive values of  $\zeta$  forms a complete set. Although, in principle, one needs an infinite number of basis functions to express a Hartree–Fock orbital, in practice, each atomic Hartree–Fock orbital can be very accurately approximated using only a few well-chosen STOs.

For example, for the helium ground state, Clementi expressed the Hartree–Fock orbital  $\phi$  of the electrons as a linear combination of five  $1s$  STOs that differ in their values of  $\zeta$ . Thus  $\phi = \sum_{k=1}^5 b_k g_k$ , where the coefficients  $b_k$  are found by solving the Hartree–Fock equation (18.57) and each  $g_k$  function is a  $1s$  STO with the form  $g_k = N_k \exp(-\zeta_k r/a_0)$ . Each  $N_k$  is a normalization constant, and each  $g_k$  function has a fixed value of  $\zeta_k$ . (The  $\zeta_k$  values used were 1.417, 2.377, 4.396, 6.527, and 7.943, and the values found for  $b_k$  were 0.768, 0.223, 0.041,  $-0.010$ , and 0.002, respectively.) The Hartree–Fock helium ground-state wave function is then (18.56) with the function  $\phi$  given by the five-term sum just discussed.

To solve (18.57) for the Hartree–Fock orbitals of an atom or molecule with many electrons requires a huge amount of computation, and it wasn't until the advent of high-speed computers in the 1960s that such calculations became practicable. Hartree–Fock wave functions have been computed for the ground states and certain excited states of the first 54 atoms of the periodic table. Hartree–Fock wave functions play a key role in the quantum chemistry of molecules (Chapter 19).

Although a Hartree–Fock wave function is an improvement on one that uses hydrogenlike orbitals, it is still only an approximation to the true wave function. The Hartree–Fock wave function assigns each electron pair to its own orbital. The forms of these orbitals are computed to take interelectronic repulsions into account in an average way. However, electrons are not actually smeared out into a static distribution of charge but interact with one another instantaneously. An orbital wave function cannot account for these instantaneous interactions, so the true wave function cannot be expressed as an antisymmetrized product of orbitals.

For helium, the use of a hydrogenlike  $1s$  orbital with a variable orbital exponent gives a ground-state energy of  $-77.5$  eV (Sec. 18.6) compared with the true value  $-79.0$  eV. The Hartree–Fock wave function for the helium ground state gives an energy of  $-77.9$  eV, which is still in error by 1.1 eV. The energy error of the Hartree–Fock wave function is called the **correlation energy**, since it results from the fact that the Hartree–Fock wave function neglects the instantaneous correlations in the motions of the electrons. Electrons repel one another and correlate their motions to avoid being close together; this phenomenon is called **electron correlation**.

## Configuration Interaction

A method used to improve a Hartree–Fock wave function is configuration interaction. When a Hartree–Fock ground-state wave function of an atom or molecule is calculated, one also obtains expressions for unoccupied excited-state orbitals. It is possible to show that the set of functions obtained by making all possible assignments of electrons to the available orbitals is a complete set. Hence, the true wave function  $\psi$  of the ground state can be expressed as

$$\psi = \sum_j a_j \psi_{\text{orb},j} \quad (18.60)$$

where the  $\psi_{\text{orb},j}$ 's are approximate orbital wave functions that differ in the assignment of electrons to orbitals. Each  $\psi_{\text{orb},j}$  is a Slater determinant of spin-orbitals. The functions  $\psi_{\text{orb},j}$  are called *configuration functions* (or *configurations*). One uses a variational procedure to find the values of the coefficients  $a_j$  that minimize the variational integral. This type of calculation is called **configuration interaction** (CI).

For the helium ground state, the term with the largest coefficient in the CI wave function will be a Slater determinant with both electrons in orbitals resembling  $1s$  orbitals, but Slater determinants with electrons in  $2s$ -like and higher orbitals will also contribute. A CI wave function for the He ground state has the form  $\psi = a_1\psi(1s^2) + a_2\psi(1s2s) + a_3\psi(1s3s) + a_4\psi(2s^2) + a_5\psi(2p^2) + a_6\psi(2s3s) + a_7\psi(3s^2) + a_8\psi(2p3p) + a_9\psi(3d^2) + \dots$ , where the  $a$ 's are numerical coefficients and  $\psi(1s2s)$  indicates a Slater determinant with one electron in a  $1s$ -like orbital and one in a  $2s$ -like orbital. (This last statement is inaccurate; see Prob. 18.62.)

CI computer calculations are extremely time-consuming, since it often requires a linear combination of thousands or even millions of configuration functions to give an accurate representation of  $\psi$ .

## 18.10 SUMMARY

The potential energy of interaction between two charges separated by distance  $r$  is  $V = Q_1Q_2/4\pi\epsilon_0r$ .

The Schrödinger equation for the H-atom internal motion is separable in spherical coordinates  $r$ ,  $\theta$ , and  $\phi$ . The stationary-state hydrogenlike-atom wave functions and bound-state energies are  $\psi = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi)$  and  $E = -(Z^2/n^2)(e^2/8\pi\epsilon_0a)$ , where  $a \equiv \hbar^2 4\pi\epsilon_0/\mu e^2$  ( $\mu$  is the reduced mass) and the quantum numbers take the values  $n = 1, 2, 3, \dots$ ;  $l = 0, 1, 2, \dots, n-1$ ;  $m = -l, \dots, +l$ . The letters  $s, p, d, f, \dots$  indicate  $l = 0, 1, 2, 3, \dots$ , respectively. The magnitude of the electron's orbital angular momentum with respect to the nucleus is  $|\mathbf{L}| = [l(l+1)]^{1/2}\hbar$ , and  $L_z$  equals  $m\hbar$ . An orbital is a one-electron spatial wave function. The shape of an orbital is defined as a surface of constant  $|\psi|$  that encloses some large fraction of the probability density. Figure 18.6 shows some H-atom orbital shapes.

The average value of any function  $f$  of  $r$  for a hydrogen-atom stationary state is given by  $\langle f(r) \rangle = \int |\psi|^2 f(r) d\tau$ . Use of  $\psi = R\Theta\Phi$ ,  $d\tau = r^2 \sin\theta dr d\theta d\phi$ , and the limits  $0 \leq r \leq \infty$ ,  $0 \leq \theta \leq \pi$ ,  $0 \leq \phi \leq 2\pi$  gives

$$\langle f(r) \rangle = \int_0^\infty f(r) |R(r)|^2 r^2 dr \int_0^\pi |\Theta(\theta)|^2 \sin\theta d\theta \int_0^{2\pi} |\Phi(\phi)|^2 d\phi$$

Electrons and other elementary particles have a built-in angular momentum (spin angular momentum)  $\mathbf{S}$  of magnitude  $[s(s+1)]^{1/2}\hbar$ , where  $s = \frac{1}{2}$  for an electron. The  $z$  component of  $\mathbf{S}$  is  $m_s\hbar$ , where  $m_s = \pm\frac{1}{2}$  for an electron. The symbols  $\alpha$  and  $\beta$  denote spin functions with  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$ , respectively. A product of one-electron spatial and spin functions is called a spin-orbital. The complete wave function of a

system of identical particles with half-integral spin must be antisymmetric with respect to interchange of all coordinates (spatial and spin) of any two particles, meaning that such an interchange multiplies the wave function by  $-1$ . The wave function of a system of identical integral-spin particles must be symmetric.

There are three symmetric two-electron spin functions [Eq. (18.40)] and one antisymmetric one [Eq. (18.41)]. An approximate ground-state wave function for He is  $1s(1)1s(2)$  times (18.41).

In a many-electron atom, the total electronic orbital and spin angular momenta are  $[L(L + 1)]^{1/2}\hbar$  and  $[S(S + 1)]^{1/2}\hbar$ , respectively, where the quantum number  $L$  can be  $0, 1, 2, \dots$  and the quantum number  $S$  can be  $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ . The  $L$  value is indicated using the letter code  $S, P, D, F, \dots$ , and the value of  $2S + 1$  (the spin multiplicity) is written as a left superscript to the  $L$  code letter. Atomic states that correspond to the same electron configuration and have the same  $L$  and  $S$  values belong to the same atomic term. Usually, the lowest-energy term of a given electron configuration is the term with the largest  $S$  value (Hund's rule).

An approximate (antisymmetric) wave function for a many-electron atom can be written as a Slater determinant of spin-orbitals. In such an approximate wave function, no more than one electron can occupy a given spin-orbital (the Pauli exclusion principle). The variation of atomic-orbital energy with atomic number is given in Fig. 18.15. The periodic table, ionization energies, and electron affinities were discussed.

The best possible (that is, lowest-energy) wave function that assigns each electron to a single spin-orbital is called the Hartree–Fock wave function. Hartree–Fock orbitals are expressed as linear combinations of basis functions. The Hartree–Fock wave function is still an approximation to the true wave function. In a configuration-interaction (CI) calculation, the wave function is written as a linear combination of the Hartree–Fock wave function and functions in which some of the electrons occupy excited orbitals. A CI wave function can approach the true wave function if enough configuration functions are included.

## FURTHER READING

*Hanna*, chap. 6; *Karplus and Porter*, chaps. 3, 4; *Levine*, chaps. 10, 11; *Lowe and Peterson*, chaps. 4, 5; *McQuarrie* (1983), chap. 8; *Ratner and Schatz*, chaps. 6–9; *Atkins and Friedman*, chap. 7.

## PROBLEMS

### Section 18.1

**18.1** True or false? (a) Doubling the distance between two charges multiplies the force between them by one-half. (b) Doubling the distance between two charges multiplies the potential energy of their interaction by one-half. (c) One joule is many orders of magnitude larger than one electronvolt.

**18.2** Use the relation  $V = Q_1Q_2/4\pi\epsilon_0r$  to deduce the SI units of  $4\pi\epsilon_0$ .

**18.3** Maxwell's electromagnetic theory of light (Sec. 20.1) shows that the speed of light in vacuum is  $c = (\mu_0\epsilon_0)^{-1/2}$ ,

where  $\epsilon_0$  occurs in the proportionality constant in Coulomb's law and  $\mu_0$  occurs in the proportionality constant in Ampère's law for the magnetic field produced by an electric current.  $\mu_0$  is arbitrarily assigned the value  $\mu_0 \equiv 4\pi \times 10^{-7} \text{ N s}^2/\text{C}^2$  in the SI system. Use  $c = (\mu_0\epsilon_0)^{-1/2}$  to verify Eq. (18.2) for  $1/4\pi\epsilon_0$ .

**18.4** (a) Calculate the electrostatic potential energy of two electrons separated by  $3.0 \text{ \AA}$  in vacuum. Express your answer in joules and in electronvolts. (b) Calculate the electrostatic potential energy in eV of a system of two electrons and a proton in vacuum if the electrons are separated by  $3.0 \text{ \AA}$  and the electron–proton distances are  $4.0$  and  $5.0 \text{ \AA}$ .

## Section 18.2

**18.5** What fraction of the volume of an atom of radius  $10^{-8}$  cm is occupied by its nucleus if the nuclear radius is  $10^{-12}$  cm?

## Section 18.3

**18.6** True or false? (a) The photon emitted in an  $n = 3$  to  $n = 2$  transition in the H atom has a lower frequency than the photon for an  $n = 2$  to  $n = 1$  H-atom transition. (b) The ground-state energy of  $\text{He}^+$  is about 4 times the ground-state energy of H. (c)  $\psi$  is zero at the nucleus for all H-atom stationary states. (d) For the ground state of the H atom,  $|\psi|^2$  is a maximum at the nucleus. (e) The most probable value of the electron–nucleus distance in a ground-state H atom is zero. (f) The smallest allowed value of the atomic quantum number  $n$  is 0. (g) For H-atom stationary states with  $l = 0$ ,  $\psi$  is independent of  $\theta$  and  $\phi$ . (h) For the H-atom ground state, the electron is confined to move on the surface of a sphere centered around the nucleus. (i) For the H-atom ground state, the electron is confined to move within a sphere of fixed radius.

**18.7** Match each of the spherical coordinates  $r$ ,  $\theta$ , and  $\phi$  with each of the following descriptions and give the range of each coordinate. (a) Angle between the positive  $z$  axis and the radius vector. (b) Distance to the origin. (c) Angle between the positive  $x$  axis and the projection of the radius vector in the  $xy$  plane.

**18.8** True or false? For the hydrogen atom, (a) the allowed energy levels are  $E = -(13.60 \text{ eV})/n^2$  and  $E \geq 0$ ; (b) any photon with energy  $E_{\text{photon}} \geq 13.60 \text{ eV}$  can ionize a hydrogen atom in the  $n = 1$  state; (c) Any photon with  $E_{\text{photon}} \geq 0.75(13.60 \text{ eV})$  can cause a hydrogen atom to go from the  $n = 1$  state to the  $n = 2$  state.

**18.9** Give the allowed values of (a)  $l$  for  $n = 5$  and (b)  $m$  if  $l = 5$ .

**18.10** Omitting spin considerations, give the degeneracy of the hydrogenlike energy level with (a)  $n = 1$ ; (b)  $n = 2$ ; (c)  $n = 3$ .

**18.11** Calculate the ionization potential in V of (a)  $\text{He}^+$ ; (b)  $\text{Li}^{2+}$ .

**18.12** Calculate the wavelength of the photon emitted when an electron goes from the  $n = 3$  to  $n = 2$  level of a hydrogen atom.

**18.13** Calculate  $a$  in Eq. (18.14).

**18.14** Positronium is a species consisting of an electron bound to a positron. Calculate its ionization potential. A positron has the same mass as an electron and the same charge as a proton.

**18.15** Show that  $\langle r \rangle = 3a/2Z$  for a ground-state hydrogenlike atom. Use a table of integrals.

**18.16** Use the Taylor-series expansions about  $\phi = 0$  for  $e^{i\phi}$ ,  $\sin \phi$ , and  $\cos \phi$  to verify that  $e^{i\phi} = \cos \phi + i \sin \phi$ .

**18.17** Verify Eq. (18.26) for  $2p_x$  and  $2p_y$ .

**18.18** (a) Let  $z_1 = a_1 + ib_1$  and  $z_2 = a_2 + ib_2$ , where  $i = \sqrt{-1}$  and the  $a$ 's and  $b$ 's are real. If  $z_1 = z_2$ , what must be

true about the  $a$ 's and  $b$ 's? (b) Verify that the requirement that  $\Phi(\phi) = \Phi(\phi + 2\pi)$  leads to the requirement that  $m$  in (18.10) be an integer.

**18.19** Draw a rough graph (not to scale) of the value of  $\psi_{2p_z}$  along the  $z$  axis versus  $z$ . Then do the same for  $|\psi_{2p_z}|^2$ .

**18.20** (a) Find  $r_{2s}$  for H using the 90% probability definition. (b) Find  $r_{2s}$  for H using a 95% probability definition.

**18.21** Verify that the  $1s$  wave function in Table 18.1 is an eigenfunction of the hydrogenlike Hamiltonian operator. (Use the chain rule to find the partial derivatives.)

**18.22** Show that the average potential energy  $\langle V \rangle$  for a ground-state hydrogenlike atom is  $-Z^2 e^2 / 4\pi\epsilon_0 a$ .

**18.23** (a) Complete Example 18.3 in Sec. 18.3 and find  $\langle r \rangle$  for a hydrogen atom in the  $2p_z$  state. (b) Without doing any calculations, give the value of  $\langle r \rangle$  for a  $2p_x$  H atom. (c) Verify your answer to (b) by evaluating the appropriate triple integral.

**18.24** Show that the maximum in the radial distribution function of a ground-state hydrogenlike atom is at  $a/Z$ .

**18.25** For a hydrogen atom in a  $1s$  state, calculate the probability that the electron is between 0 and  $2.00 \text{ \AA}$  from the nucleus.

**18.26** Verify that  $\int_0^{2\pi} |\Phi|^2 d\phi = 1$ , where  $\Phi$  is given by (18.10).

## Section 18.4

**18.27** True or false for the classical-mechanical angular momentum  $\mathbf{L}$ ? (a)  $\mathbf{L}$  of a particle depends on which point is chosen as the origin. (b) For a particle vibrating back and forth on a straight line through the origin,  $\mathbf{L}$  is zero. (c) For a particle revolving around the origin on a circle,  $\mathbf{L}$  is nonzero.

**18.28** Calculate the angles the three angular-momentum vectors make with the  $z$  axis in Fig. 18.10.

**18.29** (a) From the definition of angular momentum in Sec. 18.4, show that for a classical particle of mass  $m$  moving on a circle of radius  $r$ , the magnitude of the angular momentum with respect to the circle's center is  $mvr$ . (b) What is the direction of the  $\mathbf{L}$  vector for this system?

**18.30** Give the magnitude of the ground-state orbital angular momentum of the electron in a hydrogen atom according to (a) quantum mechanics; (b) the Bohr theory.

**18.31** Calculate the magnitude of the orbital angular momentum of a  $3p$  electron in a hydrogenlike atom.

## Section 18.5

**18.32** Calculate in SI units the magnitude of the spin angular momentum of an electron.

**18.33** Calculate the angles between the spin vectors and the  $z$  axis in Fig. 18.11.

**18.34** State what physical property is associated with each of the following quantum numbers in a one-electron atom and give the value of this physical property in terms of the quantum number. (a)  $l$ ; (b)  $m$ ; (c)  $s$ ; (d)  $m_s$ .

**18.35** For a particle with  $s = 3/2$ : (a) sketch the possible orientations of the  $\mathbf{S}$  vector with the  $z$  axis; (b) calculate the smallest possible angle between  $\mathbf{S}$  and the  $z$  axis.

## Section 18.6

**18.36** True or false? (a) The spatial factor in the ground-state wave function of He is antisymmetric. (b) All two-electron spin functions are antisymmetric. (c) The wave function of every system of identical particles must be antisymmetric with respect to exchange of all coordinates of any two particles. (d) Interchange of electrons 1 and 2 in the He-atom Hamiltonian (18.35) does not change this Hamiltonian.

**18.37** State whether each of these functions is symmetric, antisymmetric, or neither: (a)  $f(1)g(2)$ ; (b)  $g(1)g(2)$ ; (c)  $f(1)g(2) - g(1)f(2)$ ; (d)  $r_1^2 - 2r_1r_2 + r_2^2$ ; (e)  $(r_1 - r_2)e^{-br_{12}}$ , where  $r_{12}$  is the distance between particles 1 and 2.

**18.38** If  $g(1, 2)$  is a symmetric function for particles 1 and 2, and  $h(1, 2)$  and  $k(1, 2)$  are each antisymmetric functions, state whether each of the following functions is symmetric, antisymmetric, or neither. (a)  $g(1, 2)h(1, 2)$ ; (b)  $h(1, 2)k(1, 2)$ ; (c)  $h(1, 2) + k(1, 2)$ ; (d)  $g(1, 2) + k(1, 2)$ .

**18.39** A professor does a variational calculation on the ground state of He and finds that the variational integral equals  $-86.7$  eV. Explain why it is certain that the professor made an error.

## Section 18.7

**18.40** Give the term symbol for the term arising from each of the following H-atom electron configurations: (a)  $1s$ ; (b)  $3p$ ; (c)  $3d$ .

**18.41** Give the values of  $L$  and  $S$  for a  $^4F$  term.

**18.42** State what physical property is associated with each of the following quantum numbers in a many-electron atom and give the value of this property in terms of the quantum number: (a)  $L$ ; (b)  $S$ ; (c)  $M_S$ .

**18.43** For a  $^3D$  term, give the value of (a) the total electronic orbital angular momentum; (b) the total electronic spin angular momentum.

**18.44** Give the terms arising from each of the following electron configurations of K: (a)  $1s^22s^22p^63s^23p^63d$ ; (b)  $1s^22s^22p^63s^23p^64p$ .

**18.45** Draw a sketch like Fig. 18.14 that shows the orientations of  $\mathbf{S}_1$ ,  $\mathbf{S}_2$ , and  $\mathbf{S}$  for the spin function  $\alpha(1)\alpha(2)$ . (Hint: Begin by finding the angles between the  $z$  axis and each of  $\mathbf{S}_1$ ,  $\mathbf{S}_2$ , and  $\mathbf{S}$ .)

**18.46** Consider two angular momenta  $\mathbf{M}_1$  and  $\mathbf{M}_2$  (these can be orbital or spin angular momenta) whose magnitudes are  $[j_1(j_1 + 1)]^{1/2}\hbar$  and  $[j_2(j_2 + 1)]^{1/2}\hbar$ , respectively. Let  $\mathbf{M}_1$  and  $\mathbf{M}_2$  combine with each other to give a total angular momentum  $\mathbf{M}$ , which is the vector sum of  $\mathbf{M}_1$  and  $\mathbf{M}_2$ ;  $\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2$ . The magnitude of  $\mathbf{M}$  can be shown to be  $[J(J + 1)]^{1/2}\hbar$ , where the quantum number  $J$  has the possible values (Levine, sec. 11.4)

$$j_1 + j_2, j_1 + j_2 - 1, j_1 + j_2 - 2, \dots, |j_1 - j_2|$$

For example, when the spins of two electrons with spin quantum numbers  $s_1 = \frac{1}{2}$  and  $s_2 = \frac{1}{2}$  combine to give a total electronic spin, the possible values of the total spin quantum number are  $\frac{1}{2} + \frac{1}{2} = 1$  and  $|\frac{1}{2} - \frac{1}{2}| = 0$ . (a) For terms arising from the electron configuration  $1s^22s^22p^63s^23p3d$ , give the possible values of the total electronic orbital-angular-momentum quantum number  $L$  (electrons in filled subshells contribute zero to the total orbital angular momentum and to the total spin angular momentum and so can be ignored) and give the possible values of the total electronic spin quantum number  $S$ . (b) Pair each possible value of  $L$  with each possible value of  $S$  to give the terms that arise from the  $\dots 3p3d$  electron configuration. (Note: For an electron configuration like  $1s^22s^22p^2$  that has two or more electrons in a partly filled subshell, the Pauli exclusion principle restricts the possible terms, and special techniques must be used to find the terms in this case. See Levine, sec. 11.5.)

**18.47** When spin-orbit interaction splits an atomic term into energy levels, each energy level can be characterized by a total electronic angular momentum  $\mathbf{J}$  that is the vector sum of the total electronic orbital and spin angular momenta:  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ . The magnitude of  $\mathbf{J}$  is  $[J(J + 1)]^{1/2}\hbar$ , where the possible values of the quantum number  $J$  are given by the angular-momentum addition rule in Prob. 18.46 as

$$J = L + S, L + S - 1, L + S - 2, \dots, |L - S|$$

Each level is indicated by writing its  $J$  value as a subscript on the term symbol. For example, the Na electron configuration  $1s^22s^22p^63p$  gives rise to the term  $^2P$  with  $L = 1$  and  $S = \frac{1}{2}$ . With  $L = 1$  and  $S = \frac{1}{2}$ , the possible  $J$  values are  $1 + \frac{1}{2} = \frac{3}{2}$  and  $|1 - \frac{1}{2}| = \frac{1}{2}$ . Therefore, a  $^2P$  term has two energy levels,  $^2P_{3/2}$  and  $^2P_{1/2}$ . Give the levels that arise from each of the following terms: (a)  $^2S$ ; (b)  $^4P$ ; (c)  $^5F$ ; (d)  $^3D$ .

## Section 18.8

**18.48** Write down the Hamiltonian operator for the internal motion in Li.

**18.49** For a system of two electrons in a one-dimensional box, write down the approximate wave functions (interelectronic repulsion ignored) including spin for states that have one electron with  $n = 1$  and one electron with  $n = 2$ . Which of these states has (have) the lowest energy?

**18.50** Write down an approximate wave function for the Be ground state.

**18.51** Which of the first 10 elements in the periodic table have paramagnetic ground states?

**18.52** Calculate the eighteenth ionization potential of Ar.

**18.53** Use the ionization-potential data in Sec. 18.8 to calculate  $Z_{\text{eff}}$  for the  $2s$  electrons in (a) Li; (b) Be.

**18.54** (a) Suppose the electron had spin quantum number  $s = \frac{3}{2}$ . What would be the ground-state configurations of atoms with 3, 9, and 17 electrons? (b) Suppose the electron had  $s = 1$ . What would be the ground-state configurations of atoms with 3, 9, and 17 electrons?



**18.55** For each pair, state which would have the higher first ionization potential (refer to a periodic table): (a) Na, K; (b) K, Ca; (c) Cl, Br; (d) Br, Kr.

**18.56** Use Fig. 18.15 to calculate  $Z_{\text{eff}}$  for the  $1s$ ,  $2s$ , and  $2p$  electrons in Ne.

**18.57** True or false? (a) The  $2s$  orbital energy in K is lower than the  $1s$  orbital energy in H. (b) Interchange of two rows of a determinant multiplies the determinant's value by  $-1$ .

**18.58** Of the elements with  $Z \leq 10$ , which one has the largest number of unpaired electrons in its ground state?

**18.59** Consider the systems (a)  $\text{Na}^+ + 2e^-$ , (b)  $\text{Na} + e^-$ , (c)  $\text{Na}^-$ , where in each system the Na atom or ion and the electron(s) are at infinite separation from one another. Use data in Sec. 18.8 to decide which system has the lowest energy and which has the highest energy.

**18.60** Which species in each of the following pairs has the larger atomic radius: (a) Ca, Sr; (b) F, Ne; (c) Ar, K; (d) C, O; (e)  $\text{Cl}^-$ , Ar?

## General

**18.61** Write out the explicit form for the five-term ground-state helium-atom Hartree–Fock orbital given in Sec. 18.9. The only nonnumerical constants in your expression should be  $a_0$  and  $\pi$ .

**18.62** Let  $D_1$ ,  $D_2$ ,  $D_3$ , and  $D_4$  be two-row Slater determinants that contain the following spin-orbitals:  $1s\alpha$  and  $2s\alpha$  in  $D_1$ ;  $1s\alpha$  and  $2s\beta$  in  $D_2$ ;  $1s\beta$  and  $2s\alpha$  in  $D_3$ ;  $1s\beta$  and  $2s\beta$  in  $D_4$ . Consider the four helium-atom approximate wave functions given in Fig. 18.13 for states of the  $1s2s$  configuration. Show that two of these wave functions are each equal to one of the determinants  $D_1$ ,  $D_2$ ,  $D_3$ ,  $D_4$  but that the other two wave functions must each be expressed as a linear combination of two of these determinants. Thus, an orbital wave function for a state with partly filled orbitals must sometimes be expressed as a linear combination of more than one Slater determinant. [In the CI wave function (18.60), each  $\psi_{\text{orb},j}$  should have the same  $S$  and  $M_S$  spin quantum numbers as the wave function  $\psi$ . Thus, for a CI wave function for the He ground state, the  $\psi_{\text{orb},j}$  that corresponds to the  $1s2s$  configuration must have the spin function (18.41) (Fig. 18.13). As shown in this problem, this  $\psi_{\text{orb},j}$  is a linear combination of two Slater determinants.]

**18.63** Derive the formula for the volume of a sphere by integrating the spherical coordinate volume element (18.27) over the sphere's volume.

**18.64** For each of the following pairs, state which quantity (if any) is larger: (a) the ground-state energy of H or  $\text{He}^+$ ; (b) the ionization energy of K or  $\text{K}^+$ ; (c) the wavelength of the longest-wavelength electronic absorption of ground-state H or  $\text{He}^+$ ; (d) the ionization energy of  $\text{Cl}^-$  or the electron affinity of Cl?

**18.65** Give an example of a quantum-mechanical system for which the spacing between energy levels: (a) increases as  $E$

increases; (b) remains the same as  $E$  increases; (c) decreases as  $E$  increases.

**18.66** For the ground state of the hydrogen atom, find the probability the electron is in a tiny spherical region of radius  $1.0 \times 10^{-3} \text{ \AA}$  if this sphere is centered at a point that is (a) at the origin (nucleus); (b) a distance  $0.50 \text{ \AA}$  from the nucleus; (c) a distance  $5.0 \text{ \AA}$  from the nucleus. Consider the tiny sphere to be infinitesimal.

**18.67** For the ground state of the hydrogen atom, find the probability that the distance between the electron and the proton lies in each of the following ranges (treat each range as infinitesimal): (a)  $0.100$  and  $0.101 \text{ \AA}$ ; (b)  $0.500$  and  $0.501 \text{ \AA}$ ; (c)  $1.000$  and  $1.001 \text{ \AA}$ ; (d)  $5.000$  and  $5.001 \text{ \AA}$ .

**18.68** For each of the following systems, give the expression for  $d\tau$  in the equation  $\int |\psi|^2 d\tau = 1$  and give the limits on each coordinate: (a) one-dimensional harmonic oscillator; (b) particle in a three-dimensional rectangular box with edges  $a$ ,  $b$ , and  $c$ ; (c) the hydrogen atom internal motion using spherical coordinates.

**18.69** Is there a gravitational attraction between the electron and the proton in the H atom? If there is, why is this not taken into account in the Hamiltonian? Do a calculation to support your answer.

**18.70** (a) Show that the maximum value of  $\psi_{2p_z}$  for  $Z = 1$  is  $\psi_{\text{max}} = 1/(2a)^{3/2}\pi^{1/2}e$ . (b) Write a computer program that will vary  $z/a$  from  $0.01$  to  $10$  in steps of  $0.01$  and for each value of  $z/a$  will calculate values of  $y/a$  for which  $|\psi_{2p_z}/\psi_{\text{max}}|$  is equal to a certain constant  $k$ , where the value of  $k$  is input at the start of the program. Note that for some values of  $z/a$ , there are no values of  $y/a$  that satisfy the condition. Be careful that spurious values of  $y/a$  are eliminated. (The output of this program can be used as input to a graphing program to graph contours of the  $2p_z$  orbital.)

**18.71** *Physicist trivia question.* Name the physicist referred to in each of the following descriptions. All names appear in Chapter 18. Two of these physicists have elements named after them. (a) This experimental physicist (rated the 10th greatest physicist of all times in a 1999 poll) was weak in mathematics. Norman Ramsey took a course given by him in the 1930s and found that when this physicist tried to derive in class the formula for Rutherford scattering of alpha particles, “he got completely fouled up in the math, and he finally ended up telling us to go home and work it out for ourselves.” Later, Ramsey came to recognize the great physical insight this physicist had and Ramsey concluded that “an ability to make a formal mathematical derivation was not the criterion of being a good physicist.” (b) He was friends with the Swiss psychoanalyst Carl Jung and contributed a chapter to a book written by Jung. Jung published analyses of many of the dreams of this physicist; the number 4 often occurred in these dreams. (c) He was noted for his sarcastic comments about other physicists’ work. His first wife (a cabaret entertainer) left him after less than a year of marriage and after the divorce married the chemist Paul Goldfinger. This physicist then became deeply depressed and sought psychological treatment. He remarked that “Had she taken a bullfighter, I

would have understood, but a chemist . . .” (d) He was one of the few twentieth-century physicists who did outstanding work in both experiments and theory. In the mid-1930s, he and coworkers bombarded many elements with neutrons and produced radioactive products. He found that uranium irradiated with neutrons gave products whose atomic numbers did not lie in the range 86 to 92 and concluded that he had produced new elements with atomic numbers of 93 and 94, which he called ausenium and hasperium, respectively. He received a Nobel Prize in physics “for his demonstration of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons.” In fact, he had not prepared elements with  $Z > 92$ . One month after he received his Nobel Prize, Hahn and Strassmann published work showing that neutron irradiation of uranium gave barium as one product. Meitner and Frisch used Bohr’s liquid-drop model of the nucleus to interpret the Hahn–Strassmann results as the fission of a uranium nucleus to produce two lighter nuclei. On December 2, 1942, the first human-produced self-sustaining nuclear-fission chain reaction

was achieved on a squash court at the University of Chicago in a uranium pile constructed under the direction of the subject of this question. The success of the experiment was reported in a coded telephone conversation with the words “The Italian navigator has just landed in the New World.”

**18.72** True or false? (a) In this chapter,  $e$  stands for the charge on an electron. (b) The exact helium-atom ground-state wave function is a product of wave functions for each electron. (c) The wave function of every system of fermions must be antisymmetric with respect to interchange of all coordinates of any two particles. (d) The spin quantum number  $s$  of an electron has the possible values  $\pm\frac{1}{2}$ . (e) The shape of a  $2p_z$  orbital is two tangent spheres. (f) All states belonging to the same electron configuration of a given atom must have the same energy. (g) Every solution of the time-independent Schrödinger equation is a possible stationary state. (h) The ground-state wave function of a lithium atom cannot be expressed as a spatial factor times a spin factor. (i) Every linear combination of two solutions of the time-independent Schrödinger equation is a solution of this equation.

# Molecular Electronic Structure

## CHAPTER OUTLINE

- 19.1 Chemical Bonds
- 19.2 The Born–Oppenheimer Approximation
- 19.3 The Hydrogen Molecule Ion
- 19.4 The Simple MO Method for Diatomic Molecules
- 19.5 SCF and Hartree–Fock Wave Functions
- 19.6 The MO Treatment of Polyatomic Molecules
- 19.7 The Valence-Bond Method
- 19.8 Calculation of Molecular Properties
- 19.9 Accurate Calculation of Molecular Electronic Wave Functions and Properties
- 19.10 Density-Functional Theory (DFT)
- 19.11 Semiempirical Methods
- 19.12 Performing Quantum Chemistry Calculations
- 19.13 The Molecular-Mechanics (MM) Method
- 19.14 Future Prospects
- 19.15 Summary

A full and correct treatment of molecules must be based on quantum mechanics. Indeed, the stability of a covalent bond cannot be understood without quantum mechanics. Because of the mathematical difficulties involved in the application of quantum mechanics to molecules, chemists developed a variety of empirical concepts to describe bonding. Section 19.1 discusses some of these concepts. Section 19.2 describes how the molecular Schrödinger equation is separated into Schrödinger equations for electronic motion and for nuclear motion. The one-electron molecule  $\text{H}_2^+$  is discussed in Sec. 19.3 to develop some ideas about electron orbitals in molecules. A major approximation method used in describing molecular electronic structure is the molecular-orbital method, developed in Secs. 19.4 to 19.6. Section 19.8 shows how molecular properties are calculated from electronic wave functions. Section 19.9 discusses some of the remarkable advances in calculation of molecular electronic structure made in recent years. The currently most widely used method for calculating molecular properties, density-functional theory, is presented in Sec. 19.10. Section 19.11 discusses semiempirical methods of calculation, which can treat large molecules. Section 19.12 gives details on how electronic-structure calculations are done. Section 19.13 presents the molecular-mechanics method, a nonquantum-mechanical method that can be applied to very large molecules.

## 19.1 CHEMICAL BONDS

### Bond Radii

The length of a bond in a molecule is the distance between the nuclei of the two atoms forming the bond. Spectroscopic and diffraction methods (Chapters 20 and 23) enable bond lengths to be measured accurately. Bond lengths range from 0.74 Å in  $\text{H}_2$  to 4.65 Å in  $\text{Cs}_2$  and are usually in the range 1–2 Å for bonds between elements in the first, second, and third periods. The length of a given kind of bond is found to be approximately constant from molecule to molecule. For example, the carbon–carbon single-bond length in most nonconjugated molecules lies in the range 1.53 to 1.54 Å. Moreover, one finds that the bond length  $d_{\text{AB}}$  between atoms A and B is *approximately* equal to  $\frac{1}{2}(d_{\text{AA}} + d_{\text{BB}})$ , where  $d_{\text{AA}}$  and  $d_{\text{BB}}$  are the typical A–A and B–B bond lengths. For example, let A and B be Cl and C. The bond length in  $\text{Cl}_2$  is 1.99 Å, and  $\frac{1}{2}(d_{\text{AA}} + d_{\text{BB}}) = \frac{1}{2}(1.99 + 1.54) \text{ Å} = 1.76 \text{ Å}$ , in good agreement with the observed bond length 1.76<sub>6</sub> Å in  $\text{CCl}_4$ .

One can therefore take  $\frac{1}{2}d_{\text{AA}}$  as the **bond radius** (or **covalent radius**)  $r_{\text{A}}$  for atom A and use a table of bond radii to estimate the bond length  $d_{\text{AB}}$  as  $r_{\text{A}} + r_{\text{B}}$ . Double and triple bonds are shorter than the corresponding single bonds, and so different bond

radii are used for single, double, and triple bonds. Some bond radii (due mainly to Pauling) in angstroms (Å) are ( $1 \text{ Å} \equiv 10^{-8} \text{ cm} \equiv 10^{-10} \text{ m}$ ):

	H	C	N	O	F	P	S	Cl	Br	I
Single	0.30	0.77	0.70	0.66	0.64	1.10	1.04	0.99	1.14	1.33
Double		0.67	0.60	0.56		1.00	0.94			
Triple		0.60	0.55							

The bond length 0.74 Å in  $\text{H}_2$  indicates  $r_{\text{A}} = 0.37 \text{ Å}$  for H, but the listed value 0.30 Å works better in predicting bond lengths between H and other elements.

When atoms A and B differ substantially in electronegativity, the observed bond length is often shorter than  $r_{\text{A}} + r_{\text{B}}$ .

The carbon–carbon bond length in benzene is 1.40 Å. This lies between the carbon–carbon single-bond length 1.54 Å and double-bond length 1.34 Å, which indicates that the benzene bonds are intermediate between single and double bonds.

### Bond Angles

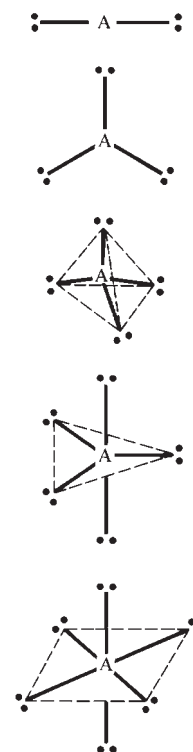
The VSEPR (valence-shell electron-pair repulsion) method estimates bond angles at an atom A by counting the number of valence electron pairs that surround atom A in the molecule's Lewis electron-dot formula. The valence pairs around A are arranged in space to minimize electrostatic repulsions between pairs. The VSEPR arrangements for various numbers of pairs are (Fig. 19.1):

Number of pairs	2	3	4	5	6
Arrangement	linear	trigonal planar	tetrahedral	trigonal bipyramidal	octahedral
Angles	$180^\circ$	$120^\circ$	$109.5^\circ$	$90^\circ, 120^\circ$	$90^\circ$

For five valence electron pairs, lone pairs are placed in the equatorial position(s) (Fig. 19.2). A double bond or a triple bond is counted as one pair for the purposes of the VSEPR method. Lone pairs are more spread out in space than bonding pairs, so the lone pairs push the bonding pairs on an atom together a bit, making the bond angle(s) at that atom a bit less than the values listed in the table just given. For example, the bond angle in  $\text{H}_2\text{O}$  (which has two bonding pairs and two lone pairs on O) is  $104.5^\circ$  instead of  $109.5^\circ$ , and the bond angles in  $\text{ClF}_3$  (Fig. 19.2) are a bit less than  $90^\circ$ . In  $\text{H}_2\text{C}=\text{CH}_2$ , the double bond exerts greater repulsions than the single bonds and so the HCH angle is  $117^\circ$ , somewhat less than the  $120^\circ$  trigonal-planar angle.

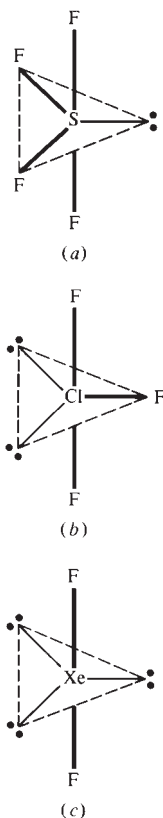
### Dihedral Angles

Except for small molecules, specification of bond lengths and bond angles does not completely specify a molecule's geometry. One must also specify the dihedral angles of rotation about single bonds, which differ for different conformations. For example, Figs. 19.33 and 20.24 show different conformations of butane and glycine. A molecular bond angle is defined by specifying three atoms in a particular order. A dihedral angle is defined by specifying four atoms in a particular order. Figure 19.3 is a Newman projection of the molecule  $\text{BrIFCC(O)H}$ ; one carbon atom is directly behind the other, and the O atom on the rear carbon is directly behind the I atom on the front carbon. The dihedral angle  $D(\text{BrCCO})$  is  $120^\circ$  because a clockwise rotation of  $120^\circ$  about the C—C single bond is needed to make the CBr bond eclipse the CO bond. The usual convention is to take the molecular dihedral angle  $D(\text{ABFG})$  (also called the **torsion angle**) to be in the range  $-180^\circ < D(\text{ABFG}) \leq 180^\circ$ , with a negative angle meaning that a counterclockwise rotation of the front AB bond is needed to make it eclipse the rear FG bond. The  $D(\text{FCCO})$  dihedral angle in Fig. 19.3 is  $-120^\circ$ , since a

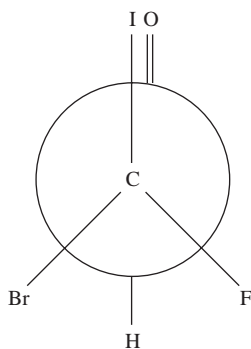


**Figure 19.1**

Arrangements of valence electron pairs around a central atom.

**Figure 19.2**

Some molecules with five valence electron pairs around the central atom.

**Figure 19.3**

Newman projection of one conformation of the CBrICH<sub>3</sub>O molecule. The O and H atoms are bonded to the rear carbon.

counterclockwise rotation of 120° is needed to make the CF bond eclipse the CO bond. The  $D(\text{ICCO})$  angle is 0° and  $D(\text{ICCH}) = 180^\circ$ .

Some empirical rules for predicting dihedral angles in organic compounds without rings are [J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967)]

1. If atoms A and B both have tetrahedral bond angles, the conformation about the A—B bond is usually staggered. For example, in CH<sub>3</sub>CH<sub>3</sub> and CH<sub>3</sub>NH<sub>2</sub>, the bonds are staggered.
2. If atom A has tetrahedral bond angles and atom B has trigonal (120°) bond angles, then (a) one of the non-B atoms bonded to atom A lies in the plane defined by atom B and the atoms bonded to it; (b) in the lowest-energy conformation, one of the single bonds to A eclipses the double bond to B. For example, in CH<sub>3</sub>CHO, one of the methyl CH bonds eclipses the CO double bond.
3. If atoms A and B both have trigonal bond angles, all the atoms bonded to A and to B lie in the same plane. For example, ethene, CH<sub>2</sub>CH<sub>2</sub>, is planar.

### Bond Energies

Section 5.10 explained how experimental  $\Delta H_{298}^\circ$  values for gas-phase atomization processes can be used to give average bond energies (which can be used to estimate  $\Delta H_{298}^\circ$  for gas-phase reactions). Table 19.1 lists some average bond energies. The values listed for H—H, F—F, Cl—Cl, O=O, and N≡N are  $\Delta H_{298}^\circ$  for dissociation of the appropriate gas-phase diatomic molecule. Double and triple bonds are stronger than single bonds. The N—N, O—O, and N—O single bonds are quite weak.

The fact that the bond energy of a carbon–carbon double bond is less than twice the energy of a carbon–carbon single bond makes vinyl addition polymerizations possible. The reaction  $\text{RCH}_2\text{CH}_2 \cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \cdot$  has  $\Delta S^\circ$  negative, since two molecules are replaced by one, and has  $\Delta H^\circ$  negative, since one C=C bond is replaced by two C—C bonds.

Tabulated bond energies are on a per-mole basis. To convert to a per-molecule basis, we divide by the Avogadro constant. One kJ/mol corresponds to  $(1 \text{ kJ/mol})/N_A = 1.66054 \times 10^{-21} \text{ J}$  per molecule. Since  $1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$  [Eq. (18.3)], 1 kJ/mol corresponds to 0.010364 eV per molecule. Thus

$$1 \text{ eV/molecule corresponds to } 96.485 \text{ kJ/mol (23.061 kcal/mol)} \quad (19.1)$$

### Bond Moments

The **electric dipole moment**  $\mu$  of a charge distribution is defined by Eq. (13.82). Molecular dipole moments can be found by microwave spectroscopy (Sec. 20.7) or by dielectric-constant measurements (Sec. 13.14). From (13.82), the SI unit of  $\mu$  is the

**TABLE 19.1**

#### Average Bond Energies in kJ/mol<sup>a</sup>

C—H	C—C	C—O	C—N	C—S	C—F	C—Cl	C—Br	C—I	F—F
415	344	350	292	259	441	328	276	240	158
N—H	O—H	S—H	S—S	N—O	O—O	N—N	N—Cl	H—H	Cl—Cl
391	463	368	266	175	143	159	200	436	243
C=C	C=O	C=N	N=N	O=O	C≡C	C≡N	N≡N		
615	725	615	418	498	812	890	946		

<sup>a</sup>Data from L. Pauling, *General Chemistry*, 3d ed., Freeman, 1970, p. 913.

coulomb-meter (C m). Molecular dipole moments are usually quoted in units of **debyes** (D), where

$$1 \text{ D} \equiv 3.335641 \times 10^{-30} \text{ C m} \quad (19.2)$$

For example  $\mu$  of HCl is  $1.07 \text{ D} = 3.57 \times 10^{-30} \text{ C m}$ .

The dipole moment of a molecule can be roughly estimated by taking the *vector* sum of assigned **bond dipole moments** for the bonds. Some bond moments in debyes are:

H—O	H—N	H—C	C—Cl	C—Br	C—O	C=O	C—N	C≡N
1.5	1.3	0.4	1.5	1.4	0.8	2.5	0.5	3.5

where the first-listed atom is the positive end of the bond moment. The value for H—C is an assumed one, and the other moments involving C depend on the magnitude and sign of this assumed value. The above table uses the traditionally assumed polarity  $\text{H}^+ - \text{C}^-$ .

The H—O and H—N bond moments are calculated from the observed dipole moments of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  without explicitly considering the contributions of the lone pairs to the dipole moment. Their contributions are absorbed into the values calculated for the OH and NH moments. For example, the observed  $\mu$  for  $\text{H}_2\text{O}$  is 1.85 D, and the bond angle is  $104.5^\circ$ ; Fig. 19.4 gives  $2\mu_{\text{OH}} \cos 52.2^\circ = 1.85 \text{ D}$ , and the O—H bond moment is  $\mu_{\text{OH}} = 1.5 \text{ D}$ . The other moments listed are calculated from the experimental dipole moments and geometries of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3)_2\text{CO}$ ,  $(\text{CH}_3)_3\text{N}$ , and  $\text{CH}_3\text{CN}$  using the assumed CH bond moment and the OH and NH moments.

A shortcut in bond-moment calculations is to note that the vector sum of the three CH bond moments of a tetrahedral  $\text{CH}_3$  group equals the moment of one CH bond. This follows from the zero dipole moment of methane ( $\text{HCH}_3$ ).

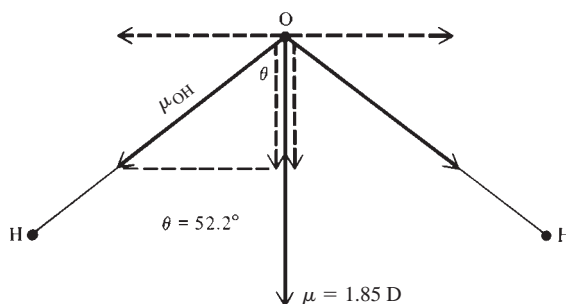
## Electronegativity

The **electronegativity**  $x$  of an element is a measure of the ability of an atom of that element to attract the electrons in a bond. The degree of polarity of an A—B bond is related to the difference in the electronegativities of the atoms forming the bond.

Many electronegativity scales have been proposed [J. Mullay, *Structure and Bonding*, **66**, 1 (1987); L. C. Allen, *Acc. Chem. Res.*, **23**, 175 (1990)]. The best-known is the Pauling scale, based on bond energies. Pauling observed that the A—B average bond energy generally exceeds the mean of the A—A and B—B average bond energies by an amount that increases with increasing polarity of the A—B bond. The Pauling electronegativity scale defines the electronegativity difference between elements A and B as

$$|x_A - x_B| \equiv 0.102(\Delta_{\text{AB}}/\text{kJ mol}^{-1})^{1/2} \quad (19.3)$$

where  $\Delta_{\text{AB}} \equiv E(\text{A—B}) - \frac{1}{2}[E(\text{A—A}) + E(\text{B—B})]$  and where the  $E$ 's are average single-bond energies. The electronegativity of H is arbitrarily set at 2.2.



**Figure 19.4**

Calculation of the OH bond moment in  $\text{H}_2\text{O}$ . The dashed vectors are the bond-moment components along  $\mu$  and perpendicular to  $\mu$ .

**TABLE 19.2****Some Pauling Electronegativities<sup>a</sup>**

H	Li	Be	B	C	N	O	F
2.2	1.0	1.6	2.0	2.5	3.0	3.4	4.0
	Na	Mg	Al	Si	P	S	Cl
	0.9	1.3	1.6	1.9	2.2	2.6	3.2
	K	Ca	Ga	Ge	As	Se	Br
	0.8	1.0	1.8	2.0	2.2	2.6	3.0
	Rb	Sr	In	Sn	Sb	Te	I
	0.8	0.9	1.8	2.0	2.1		2.7

<sup>a</sup>Data from A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

The exothermicity of the combustion of hydrocarbons can be explained in terms of electronegativities. The large electronegativity differences between C and O and between O and H lead to highly polar bonds in the products CO<sub>2</sub> and H<sub>2</sub>O, whereas the C—H, C—C, and O=O bonds in the reactants have low or no polarity. Therefore the total bond energy of the products is substantially greater than that of the reactants and the reaction is very exothermic.

The Allred–Rochow scale [A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264, 269 (1958)] defines the electronegativity  $x_A$  of element A as

$$x_A \equiv 0.359Z_{\text{eff}}/(r_A/\text{\AA})^2 + 0.744 \quad (19.4)$$

where  $r_A$  is the bond radius of A and  $Z_{\text{eff}}$  is the effective nuclear charge [Eq. (18.55)] that would act on an electron added to the valence shell of a neutral A atom. The quantity  $Z_{\text{eff}}e^2/4\pi\epsilon_0r_A^2$  is the average force exerted by atom A on an added electron. The constants 0.359 and 0.744 were chosen to make the scale as consistent as possible with the Pauling scale.

The Allen scale [L. C. Allen, *J. Am. Chem. Soc.*, **111**, 9003 (1989); J. B. Mann et al., *J. Am. Chem. Soc.*, **122**, 2780, 5132 (2000)] takes the electronegativity  $x$  of an atom as proportional to the average ionization energy  $\langle E_{i,\text{val}} \rangle$  of the valence-shell electrons of the ground-state free atom:  $x = 0.169\langle E_{i,\text{val}} \rangle/\text{eV}$ .

The Nagle scale [J. K. Nagle, *J. Am. Chem. Soc.*, **112**, 4741 (1990)] defines the electronegativity  $x$  in terms of the polarizability  $\alpha$  (Sec. 13.14) of the atom:  $x = 1.66[n(4\pi\epsilon_0 \text{\AA}^3/\alpha)]^{1/3} + 0.37$ , where  $n$  is the number of valence electrons of the atom and  $1 \text{\AA} = 10^{-10} \text{ m}$ . Nagle assumed  $n = 2$  (the valence  $s$  electrons) for each transition element.

Some electronegativities on the Pauling scale are given in Table 19.2. Electronegativities tend to decrease going down a group in the periodic table (because of the increasing distance of the valence electrons from the nucleus) and to increase going across a period (mainly because of the increasing  $Z_{\text{eff}}$  resulting from the lesser screening by electrons added to the same shell). Although electronegativity is an imprecise concept, electronegativities on various scales generally agree well. Defects of the Pauling scale are discussed in L. R. Murphy et al., *J. Phys. Chem. A*, **104**, 5867 (2000).

**19.2****THE BORN–OPPENHEIMER APPROXIMATION**

All molecular properties are, in principle, calculable by solving the Schrödinger equation for the molecule. Because of the great mathematical difficulties involved in solving the molecular Schrödinger equation, one must make approximations. Until about

1960, the level of approximations was such that the calculations gave only qualitative and not quantitative information. Since then, the use of computers has made molecular wave-function calculations accurate enough to give reliable quantitative information in many cases.

The Hamiltonian operator for a molecule is

$$\hat{H} = \hat{K}_N + \hat{K}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} \quad (19.5)$$

where  $\hat{K}_N$  and  $\hat{K}_e$  are the kinetic-energy operators for the nuclei and the electrons, respectively,  $\hat{V}_{NN}$  is the potential energy of repulsions between the nuclei,  $\hat{V}_{Ne}$  is the potential energy of attractions between the electrons and the nuclei, and  $\hat{V}_{ee}$  is the potential energy of repulsions between the electrons.

### The Born–Oppenheimer Approximation

The molecular Schrödinger equation  $\hat{H}\psi = E\psi$  is extremely complicated, and it would be almost hopeless to attempt an exact solution, even for small molecules. Fortunately, the fact that nuclei are much heavier than electrons allows the use of a very accurate approximation that greatly simplifies things. In 1927, Max Born and J. Robert Oppenheimer showed that it is an excellent approximation to treat the electronic and nuclear motions separately. The mathematics of the Born–Oppenheimer approximation is complicated, and so we shall give only a qualitative physical discussion.

Because of their much greater masses, the nuclei move far more slowly than the electrons, and the electrons carry out many “cycles” of motion in the time it takes the nuclei to move a short distance. The electrons see the heavy, slow-moving nuclei as almost stationary point charges, whereas the nuclei see the fast-moving electrons as essentially a three-dimensional distribution of charge.

One therefore assumes a fixed configuration of the nuclei, and for this configuration one solves an electronic Schrödinger equation to find the molecular electronic energy and wave function. This process is repeated for many different fixed nuclear configurations to give the electronic energy as a function of the positions of the nuclei. The nuclear configuration that corresponds to the minimum value of the electronic energy is the equilibrium geometry of the molecule. Having found how the electronic energy varies as a function of the nuclear configuration, one then uses this electronic energy function as the potential-energy function in a Schrödinger equation for the nuclear motion, thereby obtaining the molecular vibrational and rotational energy levels for a given electronic state.

The electronic Schrödinger equation is formulated for a fixed set of locations for the nuclei. Therefore, the nuclear kinetic-energy operator  $\hat{K}_N$  in (19.5) is omitted from the Hamiltonian, and the **electronic Hamiltonian**  $\hat{H}_e$  and **electronic Schrödinger equation** are

$$\hat{H}_e = \hat{K}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN} \quad (19.6)$$

$$\hat{H}_e\psi_e = E_e\psi_e \quad (19.7)$$

$E_e$  is the **electronic energy**, including the energy  $V_{NN}$  of nuclear repulsion. Note that  $V_{NN}$  in (19.6) is a constant, since the nuclei are held fixed. The electronic wave function  $\psi_e$  is a function of the  $3n$  spatial and  $n$  spin coordinates (Sec. 18.5) of the  $n$  electrons of the molecule. The electronic energy  $E_e$  contains potential and kinetic energy of the electrons and potential energy of the nuclei.

Consider a diatomic (two-atom) molecule with nuclei A and B with atomic numbers  $Z_A$  and  $Z_B$ . The spatial configuration of the nuclei is specified by the distance  $R$  between the two nuclei. The potential-energy operator  $\hat{V}_{Ne}$  depends on  $R$  as a parameter, as does the internuclear repulsion  $\hat{V}_{NN}$ , which equals  $Z_A Z_B e^2 / 4\pi\epsilon_0 R$  [Eq. (18.1)]. (A **parameter** is a quantity that is constant for one set of circumstances but may vary



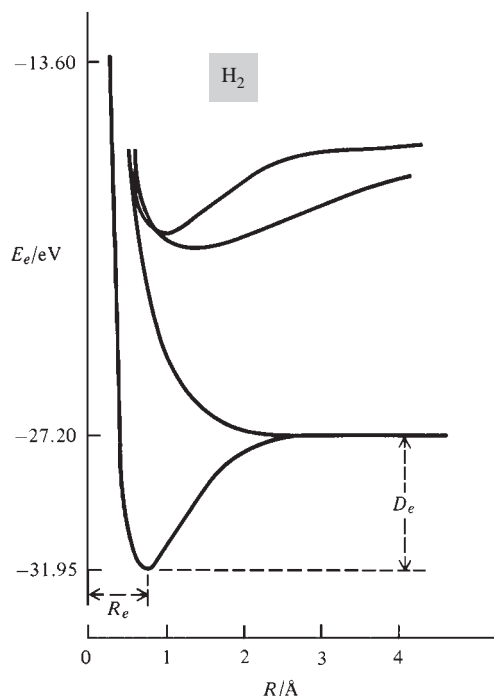
for other circumstances.) Hence, at each value of  $R$ , we get a different electronic wave function and energy. These quantities depend on  $R$  as a parameter and vary continuously as  $R$  varies. We therefore have  $\psi_e = \psi_e(q_1, \dots, q_n; R)$  and  $E_e = E_e(R)$ , where  $q_n$  stands for the spatial coordinates and spin coordinate of electron  $n$ . For a polyatomic molecule,  $\psi_e$  and  $E_e$  will depend parametrically on the locations of all the nuclei:

$$\psi_e = \psi_e(q_1, \dots, q_n; Q_1, \dots, Q_N), \quad E_e = E_e(Q_1, \dots, Q_N) \quad (19.8)$$

where the  $Q$ 's are the coordinates of the  $N$  nuclei.

Of course, a molecule has many different possible electronic states. For each such state, there is a different electronic wave function and energy, which vary as the nuclear configuration varies. Figure 19.5 shows  $E_e(R)$  curves for the ground electronic state and some excited states of  $\text{H}_2$ . Since  $E_e(R)$  is the potential-energy function for motion of the nuclei, a state with a minimum in the  $E_e(R)$  curve is a bound state, with the atoms bonded to each other. For an electronic state with no minimum,  $E_e(R)$  increases continually as  $R$  decreases. This means that the atoms repel each other as they come together, and this is not a bound state. The colliding atoms simply bounce off each other. The two lowest electronic states in Fig. 19.5 each dissociate to two ground-state ( $1s$ ) hydrogen atoms. [Note from (18.18) that  $-27.2$  eV is the energy of two  $1s$  hydrogen atoms.] The ground electronic state of  $\text{H}_2$  dissociates to (and arises from)  $1s$  H atoms with opposite electronic spins, whereas the repulsive first excited electronic state arises from  $1s$  H atoms with parallel electron spins.

The internuclear distance  $R_e$  at the minimum in the  $E_e$  curve for a bound electronic state is the **equilibrium bond length** for that state. (Because of molecular zero-point vibrations,  $R_e$  is not quite the same as the observed bond length.) As  $R$  goes to zero,  $E_e$  goes to infinity, because of the internuclear repulsion  $V_{NN}$ . As  $R$  goes to infinity,  $E_e$  goes to the sum of the energies of the separated atoms into which the molecule decomposes. The difference  $E_e(\infty) - E_e(R_e)$  is the **equilibrium dissociation energy**  $D_e$  of the molecule (Fig. 19.5). Some  $D_e$  and  $R_e$  values (found by spectroscopy) for the ground electronic states of diatomic molecules are given in Table 19.3. Note the high  $D_e$  values of CO and  $\text{N}_2$ , which have triple bonds.



**Figure 19.5**

Potential-energy curves for the lowest few electronic states of  $\text{H}_2$ .  $R_e$  and  $D_e$  of the ground electronic state are shown.

TABLE 19.3

Diatomic-Molecule Ground-State  $D_e$  and  $R_e$  Values

	H <sub>2</sub> <sup>+</sup>	H <sub>2</sub>	He <sub>2</sub> <sup>+</sup>	Li <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>
$D_e/\text{eV}$	2.8	4.75	2.5	1.1	6.3	9.9	5.2	1.7
$R_e/\text{\AA}$	1.06	0.74	1.1	2.7	1.24	1.10	1.21	1.41
	CH	CO	NaCl	OH	HCl	CaO	NaH	NaK
$D_e/\text{eV}$	3.6	11.2	4.3	4.6	4.6	4.8	2.0	0.6
$R_e/\text{\AA}$	1.12	1.13	2.36	0.97	1.27	1.82	1.89	3.59

We now resume consideration of the Born–Oppenheimer approximation. Having solved the electronic Schrödinger equation (19.7) to obtain the electronic energy  $E_e(Q_1, \dots, Q_N)$  as a function of the nuclear coordinates, we use this as the potential-energy function in the Schrödinger equation for nuclear motion:

$$(\hat{K}_N + E_e)\psi_N \equiv \hat{H}_N\psi_N = E\psi_N \quad (19.9)$$

The Hamiltonian  $\hat{H}_N$  for nuclear motion equals the nuclear kinetic-energy operator  $\hat{K}_N$  plus the electronic energy function  $E_e$ , so  $E$  in (19.9) includes both electronic and nuclear energies and is the total energy of the molecule. The nuclear wave function  $\psi_N$  is a function of the  $3N$  spatial and  $N$  spin coordinates of the  $N$  nuclei.

$E_e$  is the potential energy for nuclear vibration. As the relatively sluggish nuclei vibrate, the rapidly moving electrons almost instantaneously adjust their wave function  $\psi_e$  and energy  $E_e$  to follow the nuclear motion. The electrons act somewhat like springs connecting the nuclei. As the internuclear distances change, the energy stored in the “springs” (that is, in the electronic motions) changes.

The nuclear kinetic-energy operator  $\hat{K}_N$  involves vibrational, rotational, and translational kinetic energies. (Rotational and translational motions do not change the electronic energy  $E_e$ .) We shall deal with nuclear vibrations and rotations in Chapter 20. The remainder of this chapter deals with the electronic wave function and energy.

The Born–Oppenheimer treatment shows that the complete molecular wave function  $\psi$  is to a very good approximation equal to the product of electronic and nuclear wave functions:  $\psi = \psi_e\psi_N$ .

In addition to making the Born–Oppenheimer approximation, one usually neglects relativistic effects in treating molecules. This is a very good approximation for molecules composed of light atoms, but it is not good for molecules containing heavy atoms. Inner-shell electrons in atoms of high atomic number move at very high speeds and are significantly affected by the relativistic increase of mass with speed. The valence electrons can undergo relativistic effects due to interactions with the inner-shell electrons and to the portion of the valence-electrons’ probability density that deeply penetrates the inner-shell electrons. Relativistic effects have substantial influence on bond lengths and binding energies of molecules containing atoms of high atomic number (for example, Au). See P. Pyykkö, *Chem. Rev.*, **88**, 563 (1988).

### Ionic and Covalent Bonding

A bound electronic state of a diatomic molecule has a minimum in its curve of electronic energy  $E_e$  versus internuclear distance  $R$  (Fig. 19.5). Why is  $E_e$  lower in the molecule than in the separated atoms?

An ionic molecule like NaCl is held together by the Coulombic attraction between the ions. Solid NaCl consists of an array of alternating  $\text{Na}^+$  and  $\text{Cl}^-$  ions, and one

cannot pick out individual NaCl molecules. However, gas-phase NaCl consists of individual ionic NaCl molecules. (In aqueous solution, hydration of the ions makes the separated hydrated ions more stable than  $\text{Na}^+\text{Cl}^-$  molecules.) Ionic molecules dissociate to neutral atoms in the gas phase. Consider, for example, NaCl. The ionization energy of Na is 5.14 eV, whereas the electron affinity of Cl is only 3.61 eV. Hence, isolated Na and Cl atoms are more stable than isolated  $\text{Na}^+$  and  $\text{Cl}^-$  ions. Thus as the internuclear distance  $R$  increases, the bonding in NaCl shifts from ionic to covalent at very large  $R$  values.

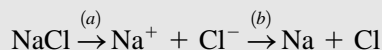
### EXAMPLE 19.1 $D_e$ and $\mu$ of NaCl

Use the model of an NaCl molecule as consisting of nonoverlapping spherical  $\text{Na}^+$  and  $\text{Cl}^-$  ions separated by the experimentally observed distance  $R_e = 2.36 \text{ \AA}$  (Table 19.3) to estimate the equilibrium dissociation energy  $D_e$  and the dipole moment of NaCl.

Equation (18.1) gives the potential energy of interaction between two charges as  $V = Q_1 Q_2 / 4\pi\epsilon_0 r$ . Therefore the energy needed to take the  $\text{Na}^+$  and  $\text{Cl}^-$  ions from a  $2.36\text{-\AA}$  separation to an infinite separation (where  $V = 0$ ) is  $e^2/4\pi\epsilon_0 R_e$ . The use of (18.4) for  $e$  and of (18.3) gives

$$\begin{aligned} \frac{e^2}{4\pi\epsilon_0 R_e} &= \frac{(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)(2.36 \times 10^{-10} \text{ m})} \\ &= 9.77 \times 10^{-19} \text{ J} = 6.10 \text{ eV} \end{aligned}$$

However, this is not the estimate of  $D_e$ , since (as already noted) NaCl dissociates to neutral atoms. Breaking the dissociation into two hypothetical steps, we have



where the two ions (and the two atoms) are at infinite separation from each other. We estimated the energy change for step (a) as 6.10 eV. Addition of an electron to  $\text{Na}^+$  lowers the energy by the Na ionization energy 5.14 eV, and removal of an electron from  $\text{Cl}^-$  raises the energy by the Cl electron affinity 3.61 eV. Hence, the nonoverlapping-spherical-ion model gives the energy needed to dissociate NaCl into Na + Cl as

$$6.10 \text{ eV} - 5.14 \text{ eV} + 3.61 \text{ eV} = 4.57 \text{ eV}$$

which is only 7 percent away from the experimental value  $D_e = 4.25 \text{ eV}$ . The error results from neglect of the repulsion between the slightly overlapping electron probability densities of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions, which makes the molecule less stable than calculated.

The dipole moment of a charge distribution is given by Eq. (13.82) as  $\mu = \sum_i Q_i \mathbf{r}_i$ . The charge on  $\text{Na}^+$  equals the proton charge  $e$ . Taking the coordinate origin at the center of the  $\text{Cl}^-$  ion, we estimate  $\mu$  as

$$\mu = eR_e = (1.602 \times 10^{-19} \text{ C})(2.36 \times 10^{-10} \text{ m}) = 3.78 \times 10^{-29} \text{ C m} = 11.3 \text{ D}$$

where (19.2) was used. This value is not far from the experimental value 9.0 D. The error can be attributed to polarization of one ion by the other.

#### Exercise

The LiF molecule has  $R_e = 1.56 \text{ \AA}$ . Estimate  $D_e$  and  $\mu$  of LiF. Use data in Chapter 18. (Answers: 7.2 eV and 7.5 D.)

The ionic bonding in NaCl can be contrasted with the nonpolar covalent bonding in  $\text{H}_2$  and other homonuclear diatomic molecules. Here, the bonding electrons are shared equally. For a diatomic molecule formed from different nonmetals (for example, HCl, BrCl) or from different metals (for example, NaK), the bonding is polar covalent, the more electronegative atom having a greater share of the electrons and a partial negative charge. Bonds between metals with relatively high electronegativities and nonmetals are sometimes polar covalent, rather than ionic, as noted in Sec. 10.5.

The physical reason for the stability of a covalent bond is not a fully settled question. A somewhat oversimplified statement is that the stability is due to the decrease in the average potential energy of the electrons forming the bond. This decrease results from the greater electron–nuclear attractions in the molecule compared with those in the separated atoms. The electrons in the bond can feel the simultaneous attractions of two nuclei. This decrease in electronic potential energy outweighs the increases in interelectronic repulsions and internuclear repulsions that occur as the atoms come together.

### 19.3 THE HYDROGEN MOLECULE ION

The simplest molecule is  $\text{H}_2^+$ , which consists of two protons and one electron.

Adopting the Born–Oppenheimer approximation, we hold the nuclei at a fixed distance  $R$  and deal with the electronic Schrödinger equation  $\hat{H}_e\psi_e = E_e\psi_e$  [Eq. (19.7)]. The electronic Hamiltonian including nuclear repulsion for  $\text{H}_2^+$  is given by Eqs. (19.6), (18.1), and (17.58) as

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \quad (19.10)$$

where  $r_A$  and  $r_B$  are the distances from the electron to nuclei A and B and  $R$  is the internuclear distance (Fig. 19.6). The first term on the right side of (19.10) is the operator for the kinetic energy of the electron. The second and third terms are the potential energies of attraction between the electron and the nuclei. The last term is the repulsion between the nuclei. Since  $\text{H}_2^+$  has only one electron, there is no interelectronic repulsion. Figure 19.7 is a three-dimensional plot of values of  $-e^2/4\pi\epsilon_0 r_A - e^2/4\pi\epsilon_0 r_B$  in a plane containing the nuclei.

The electronic Schrödinger equation  $\hat{H}_e\psi_e = E_e\psi_e$  can be solved exactly for  $\text{H}_2^+$ , but the solutions are complicated. For our purposes, an approximate treatment will suffice. The lowest electronic state of  $\text{H}_2^+$  will dissociate to a ground-state ( $1s$ ) H atom and a proton as  $R$  goes to infinity. Suppose the electron in  $\text{H}_2^+$  is close to nucleus A and rather far from nucleus B. The  $\text{H}_2^+$  electronic wave function should then resemble a ground-state H-atom wave function for atom A; that is,  $\psi_e$  will be approximately given by the function (Table 18.1 in Sec. 18.3)

$$1s_A \equiv (1/a_0)^{3/2} \pi^{-1/2} e^{-r_A/a_0} \quad (19.11)$$

where the Bohr radius  $a_0$  is used since the nuclei are fixed. Similarly, when the electron is close to nucleus B,  $\psi_e$  can be roughly approximated by

$$1s_B \equiv (1/a_0)^{3/2} \pi^{-1/2} e^{-r_B/a_0}$$

This suggests as an approximate wave function for the  $\text{H}_2^+$  ground electronic state:

$$\phi = c_A 1s_A + c_B 1s_B = a_0^{-3/2} \pi^{-1/2} (c_A e^{-r_A/a_0} + c_B e^{-r_B/a_0}) \quad (19.12)$$

which is a linear combination of the  $1s_A$  and  $1s_B$  atomic orbitals. When the electron is very close to nucleus A, then  $r_A$  is much less than  $r_B$  and  $e^{-r_A/a_0}$  is much greater than  $e^{-r_B/a_0}$ . Hence, the  $1s_A$  term in (19.12) dominates, and the wave function resembles that

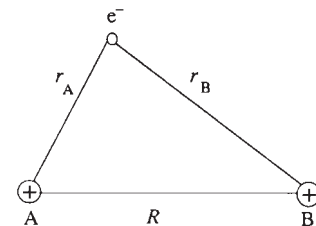


Figure 19.6

Interparticle distances in the  $\text{H}_2^+$  molecule.

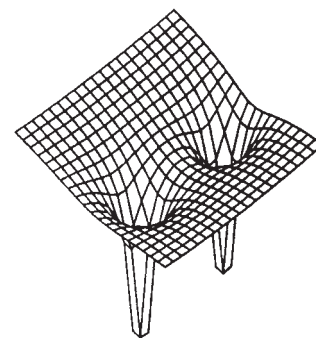


Figure 19.7

Three-dimensional plot of the potential energy of attraction between the electron and the nuclei of  $\text{H}_2^+$  in a plane containing the nuclei.

of an H atom at nucleus A, as it should. Similarly for the electron close to nucleus B. One multiplies the spatial function of (19.12) by a spin function (either  $\alpha$  or  $\beta$ ) to get the complete approximate wave function.

The function (19.12) can be regarded as a variation function and the constants  $c_A$  and  $c_B$  chosen to minimize the variational integral  $W = \int \phi^* \hat{H} \phi d\tau / \int \phi^* \phi d\tau$ . The function (19.12) is a linear combination of two functions, and, as noted in Sec. 17.15, the conditions  $\partial W / \partial c_A = 0 = \partial W / \partial c_B$  will be satisfied by two sets of values of  $c_A$  and  $c_B$ . These sets will yield approximate wave functions and energies for the lowest two electronic states of  $H_2^+$ . We need not go through the details of evaluating  $W$  and setting  $\partial W / \partial c_A = 0 = \partial W / \partial c_B$ , since the fact that the nuclei are identical requires that the electron probability density be the same on each side of the molecule. Restricting ourselves to a real variation function, the electron probability density is  $\phi^2 = c_A^2(1s_A)^2 + c_B^2(1s_B)^2 + 2c_Ac_B1s_A1s_B$ . To have  $\phi^2$  be the same at corresponding points on each side of the molecule, we must have either  $c_B = c_A$  or  $c_B = -c_A$ . For  $c_B = c_A$ , we have

$$\phi = c_A(1s_A + 1s_B), \quad \phi^2 = c_A^2(1s_A^2 + 1s_B^2 + 2 \cdot 1s_A1s_B) \quad (19.13)$$

For  $c_B = -c_A$ ,

$$\phi' = c'_A(1s_A - 1s_B), \quad \phi'^2 = c'^2_A(1s_A^2 + 1s_B^2 - 2 \cdot 1s_A1s_B) \quad (19.14)$$

The constants  $c_A$  and  $c'_A$  are found by requiring that  $\phi$  and  $\phi'$  be normalized.

The normalization condition for the function in (19.13) is

$$1 = \int \phi^2 d\tau = c_A^2 \left( \int 1s_A^2 d\tau + \int 1s_B^2 d\tau + 2 \int 1s_A1s_B d\tau \right)$$

The H-atom wave functions are normalized, so  $\int 1s_A^2 d\tau = \int 1s_B^2 d\tau = 1$ . Defining the **overlap integral**  $S$  as

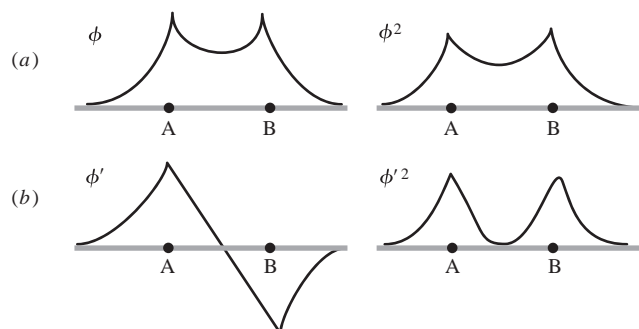
$$S \equiv \int 1s_A1s_B d\tau$$

we get  $1 = c_A^2(2 + 2S)$  and  $c_A = (2 + 2S)^{-1/2}$ . Similarly, one finds  $c'_A = (2 - 2S)^{-1/2}$ . Hence the normalized approximate wave functions for the lowest two  $H_2^+$  electronic states are

$$\phi = (2 + 2S)^{-1/2}(1s_A + 1s_B), \quad \phi' = (2 - 2S)^{-1/2}(1s_A - 1s_B) \quad (19.15)$$

For completeness, each spatial function should be multiplied by a one-electron spin function, either  $\alpha$  or  $\beta$ .

The value of the overlap integral  $\int 1s_A1s_B d\tau$  depends on how much the functions  $1s_A$  and  $1s_B$  overlap each other. Only regions of space where both  $1s_A$  and  $1s_B$  are of significant magnitude will contribute substantially to  $S$ . The main contribution to  $S$  therefore comes from the region between the nuclei. The value of  $S$  clearly depends on the internuclear distance  $R$ . For  $R = 0$ , we have  $1s_A = 1s_B$  and  $S = 1$ . For  $R = \infty$ , the  $1s_A$  and  $1s_B$  atomic orbitals don't overlap, and  $S = 0$ . For  $R$  between 0 and  $\infty$ ,  $S$  is between 0 and 1 and is easily evaluated from the expressions for  $1s_A$  and  $1s_B$ .



**Figure 19.8**

Graphs of (a) ground state and (b) first excited state  $H_2^+$  approximate wave functions for points on the internuclear axis. (Not drawn to scale.)

The probability density  $\phi^2$  in (19.13) can be written as  $c_A^2(1s_A^2 + 1s_B^2)$  plus  $2c_A^2 1s_A 1s_B$ . The  $1s_A^2 + 1s_B^2$  part of  $\phi^2$  is proportional to the probability density due to two separate noninteracting  $1s$  H atoms. The term  $2c_A^2 1s_A 1s_B$  is large only in regions where both  $1s_A$  and  $1s_B$  are reasonably large. This term therefore increases the electron probability density in the region between the nuclei. This buildup of probability density between the nuclei (at the expense of regions outside the internuclear region) causes the electron to feel the attractions of both nuclei at once, thereby lowering its average potential energy and providing a stable covalent bond. The bonding is due to the overlap of the atomic orbitals  $1s_A$  and  $1s_B$ .

Figure 19.8a graphs  $\phi$  and  $\phi^2$  of (19.13) for points along the line joining the nuclei. The probability-density buildup between the nuclei is evident.

For the function  $\phi'$  of (19.14), the term  $-2c_A'^2 1s_A 1s_B$  decreases the electron probability density between the nuclei. At any point on a plane midway between the nuclei and perpendicular to the internuclear axis we have  $r_A = r_B$  and  $1s_A = 1s_B$ . Hence  $\phi' = 0 = \phi'^2$  on this plane, which is a *nodal plane* for the function  $\phi'$ . Figure 19.8b shows  $\phi'$  and  $\phi'^2$  for points along the internuclear axis.

The functions  $\phi$  and  $\phi'$  depend on the internuclear distance  $R$ , since  $r_A$  and  $r_B$  in  $1s_A$  and  $1s_B$  depend on  $R$  (see Fig. 19.6). The variational integral  $W$  is therefore a function of  $R$ . When  $W$  is evaluated for  $\phi$  and  $\phi'$ , one finds that  $\phi$  gives an electronic energy curve  $W(R) \approx E_e(R)$  with a minimum; see the lower curve in Fig. 19.9. In contrast, the  $W(R)$ -versus- $R$  curve for the  $H_2^+$  function  $\phi'$  in (19.15) has no minimum (Fig. 19.9), indicating an unbound electronic state. These facts are understandable from the preceding electron-probability-density discussion.

The true values of  $R_e$  and  $D_e$  for  $H_2^+$  are  $1.06 \text{ \AA}$  and  $2.8 \text{ eV}$ . The function (19.13) gives  $R_e = 1.32 \text{ \AA}$  and  $D_e = 1.8 \text{ eV}$ , which is rather poor. Substantial improvement can be obtained if a variational parameter  $\zeta$  is included in the exponentials, so that  $1s_A$  and  $1s_B$  become proportional to  $e^{-\zeta r_A/a_0}$  and  $e^{-\zeta r_B/a_0}$ . One then finds  $R_e = 1.07 \text{ \AA}$  and  $D_e = 2.35 \text{ eV}$  (Fig. 19.10). The parameter  $\zeta$  depends on  $R$  and is found to equal  $1.24$  at  $R_e$ .

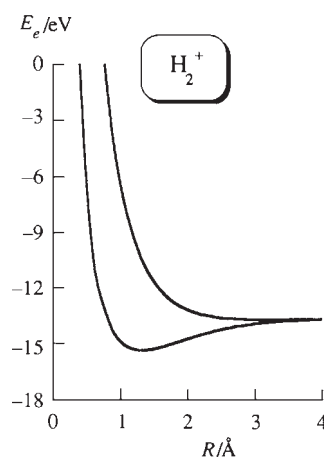
An orbital is a one-electron spatial wave function.  $H_2^+$  has but one electron, and the approximate wave functions  $\phi$  and  $\phi'$  in (19.13) and (19.14) are approximations to the orbitals of the two lowest electronic states of  $H_2^+$ . An orbital for an atom is called an **atomic orbital** (AO). An orbital for a molecule is a **molecular orbital** (MO). Just as the wave function of a many-electron atom can be approximated by use of AOs, the wave function of a many-electron molecule can be approximated by use of MOs. Each MO can hold two electrons of opposite spin.

The situation is more complicated for molecules than for atoms, in that the number of nuclei varies from molecule to molecule. Whereas hydrogenlike orbitals with effective nuclear charges are useful for all many-electron atoms, the  $H_2^+$ -like orbitals with effective nuclear charges are directly applicable only to molecules with two identical nuclei, that is, **homonuclear** diatomic molecules. We shall later see, however, that since a molecule is held together by bonds and since (with some exceptions) each bond is between two atoms, we can construct an approximate molecular wave function using bond orbitals (and lone-pair and inner-shell orbitals), where the bond orbitals resemble diatomic-molecule MOs.

Let us consider further excited electronic states of  $H_2^+$ . We expect such states to dissociate to a proton and a  $2s$  or  $2p$  or  $3s$  or  $\dots$  H atom. Therefore, analogous to the functions (19.13) and (19.14), we write as approximate wave functions (molecular orbitals) for excited  $H_2^+$  states

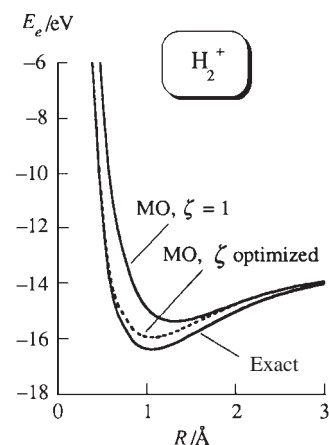
$$N(2s_A + 2s_B), \quad N(2s_A - 2s_B), \quad N(2p_{xA} + 2p_{xB}), \quad N(2p_{xA} - 2p_{xB}), \quad \text{etc.} \quad (19.16)$$

where the normalization constant  $N$  differs for different states. Actually, because of the degeneracy of the  $2s$  and  $2p$  states in the H atom, we should expect extensive mixing together of  $2s$  and  $2p$  AOs in the  $H_2^+$  MOs. Since we are mainly interested in  $H_2^+$  MOs



**Figure 19.9**

Electronic energy (including internuclear repulsion) versus  $R$  for the ground state and first excited state of  $H_2^+$  as calculated from the approximate wave functions  $N(1s_A + 1s_B)$  and  $N'(1s_A - 1s_B)$  [Eq. (19.15)].

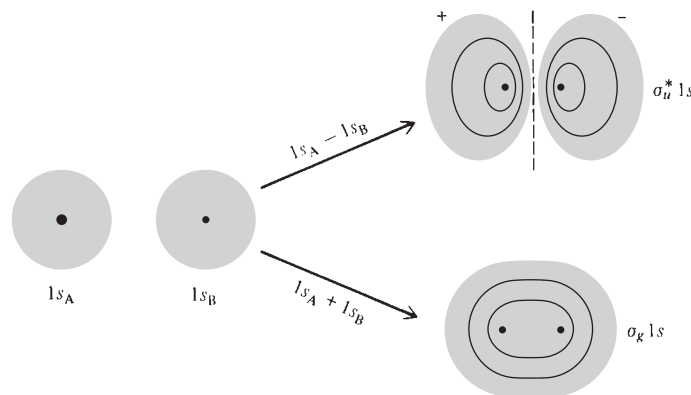


**Figure 19.10**

Electronic energy including internuclear repulsion for the  $H_2^+$  ground electronic state. The curves are calculated from the exact wave function, from the LCAO MO function with optimized orbital exponent  $\zeta$ , and from the LCAO MO function with  $\zeta = 1$  (as in the lower curve in Fig. 19.9).

**Figure 19.11**

Formation of homonuclear diatomic MOs from  $1s$  AOs. The dashed line indicates a nodal plane.



for use in many-electron molecules, and since the  $2s$  and  $2p$  levels are not degenerate in many-electron atoms, we shall ignore such mixing for now. A wave function like  $2s_A + 2s_B$  expresses the fact that there is a 50-50 probability as to which nucleus the electron will go with when the molecule dissociates ( $R \rightarrow \infty$ ).

The MOs in (19.15) and (19.16) are linear combinations of atomic orbitals and so are called LCAO MOs. There is no necessity for MOs to be expressed as linear combinations of AOs, but this approximate form is a very convenient one. Let us see what these MOs look like.

Since the functions  $1s_A$  and  $1s_B$  are both positive in the internuclear region, the function  $1s_A + 1s_B$  shows a buildup of probability density between the nuclei, whereas the linear combination  $1s_A - 1s_B$  has a nodal plane between the nuclei. Figure 19.11 shows contours of constant probability density for the two MOs (19.13) and (19.14) formed from  $1s$  AOs. The three-dimensional shape of these orbitals is obtained by rotating the contours about the line joining the nuclei. See also Fig. 19.12.

A word about terminology. The component of electronic orbital angular momentum along the internuclear ( $z$ ) axis of  $\text{H}_2^+$  can be shown to have the possible values  $L_z = m\hbar$ , where  $m = 0, \pm 1, \pm 2, \dots$  (Unlike the H atom, there is no  $l$  quantum number in  $\text{H}_2^+$ , since the magnitude of the total electronic orbital angular momentum is not fixed in  $\text{H}_2^+$ . This is because there is spherical symmetry in H but only axial symmetry in  $\text{H}_2^+$ .) The following code letters are used to indicate the  $|m|$  value:

$ m $	0	1	2	3	$\dots$
Letter	$\sigma$	$\pi$	$\delta$	$\phi$	$\dots$

(19.17)

These are the Greek equivalents of  $s, p, d, f$ .

The AOs  $1s_A$  and  $1s_B$  have zero electronic orbital angular momentum along the molecular axis, and so the two MOs formed from these AOs have  $m = 0$  and from (19.17) are  $\sigma$  (sigma) MOs. We call these the  $\sigma_g 1s$  MO and the  $\sigma_u^* 1s$  MO. The  $1s$  indicates that they originate from separated-atom  $1s$  AOs. The star indicates the **anti-bonding** character of the  $1s_A - 1s_B$  MO, associated with the nodal plane and the charge depletion between the nuclei.

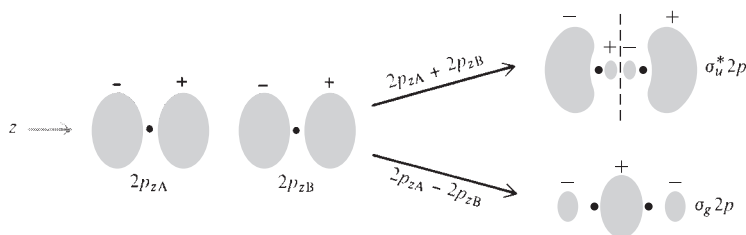
The  $g$  subscript (from the German *gerade*, “even”) means that the orbital has the same value at two points that are on diagonally opposite sides of the center of the molecule and equidistant from the center. The  $u$  subscript (*ungerade*, “odd”) means that the values of the orbital differ by a factor  $-1$  at two such points. [The point diagonally opposite  $(x, y, z)$  is at  $(-x, -y, -z)$ . An **even function** of  $x, y$ , and  $z$  is one for which  $f(-x, -y, -z) = f(x, y, z)$ . An **odd function** is one that satisfies  $f(-x, -y, -z) = -f(x, y, z)$ .]

The linear combinations  $2s_A + 2s_B$  and  $2s_A - 2s_B$  give the  $\sigma_g 2s$  and  $\sigma_u^* 2s$  MOs, whose shapes resemble those of the  $\sigma_g 1s$  and  $\sigma_u^* 1s$  MOs.

**Figure 19.12**

Electron probability density in a plane containing the nuclei for the ground and first excited states of  $\text{H}_2^+$ .



**Figure 19.13**

Formation of homonuclear diatomic MOs from  $2p_z$  AOs.

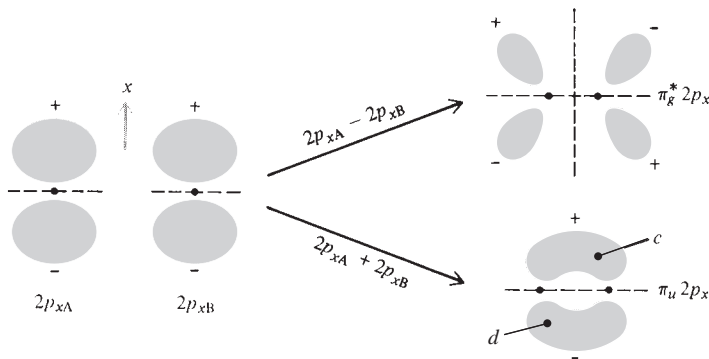
Let the molecular axis be the  $z$  axis. Because of the opposite signs of the right lobe of  $2p_{zA}$  and the left lobe of  $2p_{zB}$  (Fig. 19.13), the linear combination  $2p_{zA} + 2p_{zB}$  has a nodal plane midway between the nuclei, as indicated by the dashed line. The charge depletion between the nuclei makes this an antibonding MO. The linear combination  $2p_{zA} - 2p_{zB}$  gives charge buildup between the nuclei and is a bonding MO. The  $2p_z$  AO has atomic quantum number  $m = 0$  (Sec. 18.3) and so has  $L_z = 0$ . The MOs formed from  $2p_z$  AOs are therefore  $\sigma$  MOs, the  $\sigma_g 2p$  and  $\sigma_u^* 2p$  MOs. Their three-dimensional shapes are obtained by rotating the contours in Fig. 19.13 about the internuclear ( $z$ ) axis.

Formation of homonuclear diatomic MOs from the  $2p_x$  AOs is shown in Fig. 19.14. The  $p_x$  AO is a linear combination of  $m = 1$  and  $m = -1$  AOs [see Eq. (18.25)] and has  $|m| = 1$ . Therefore the MOs made from the  $2p_x$  AOs have  $|m| = 1$  and are  $\pi$  MOs [Eq. (19.17)]. The linear combination  $N(2p_{xA} + 2p_{xB})$  has charge buildup in the internuclear regions above and below the  $z$  axis and is therefore bonding. This MO has opposite signs at the diagonally opposite points  $c$  and  $d$  in Fig. 19.14 and so is a  $u$  MO, the  $\pi_u 2p_x$  MO. The linear combination  $N(2p_{xA} - 2p_{xB})$  gives the antibonding  $\pi_g^* 2p_x$  MO.

The  $\sigma$  MOs in Figs. 19.11 and 19.13 are symmetric about the internuclear axis; the orbital shapes are figures of rotation about the  $z$  axis. In contrast, the  $\pi_u 2p_x$  and  $\pi_g^* 2p_x$  MOs consist of blobs of probability density above and below the  $yz$  plane, which is a nodal plane for these MOs.

The linear combinations  $2p_{yA} + 2p_{yB}$  and  $2p_{yA} - 2p_{yB}$  give the  $\pi_u 2p_y$  and  $\pi_g^* 2p_y$  MOs. These MOs have the same shapes as the  $\pi_u 2p_x$  and  $\pi_g^* 2p_x$  MOs but are rotated by  $90^\circ$  about the internuclear axis compared with the  $\pi 2p_x$  MOs. Since they have the same shapes, the  $\pi_u 2p_x$  and  $\pi_u 2p_y$  MOs have the same energy. Likewise, the  $\pi_g^* 2p_x$  and  $\pi_g^* 2p_y$  MOs have the same energy (see Fig. 19.15).

The  $\sigma$  MOs have no nodal planes containing the internuclear axis. (Some  $\sigma$  MOs have a nodal plane or planes perpendicular to the internuclear axis.) Each  $\pi$  MO has one nodal plane containing the internuclear axis. This is true provided one uses the real  $2p$  AOs to form the MOs, as we have done. It turns out that  $\delta$  MOs have two nodal planes containing the internuclear axis (see Fig. 19.29c). We shall later use the number of nodal planes to classify bond orbitals in polyatomic molecules.

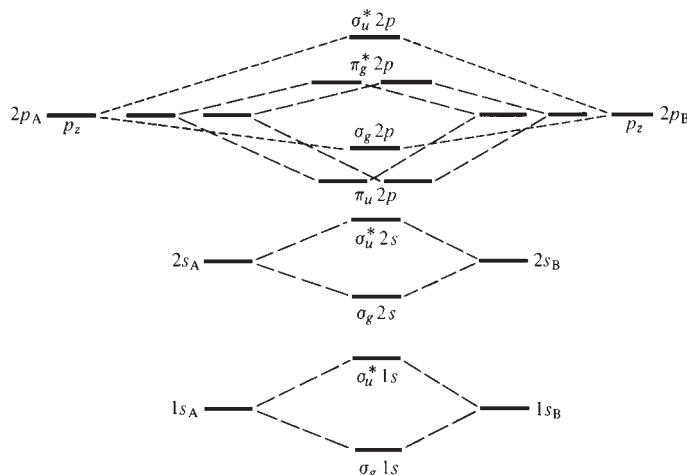
**Figure 19.14**

Formation of homonuclear diatomic MOs from  $2p_x$  AOs.



**Figure 19.15**

Lowest-lying homonuclear diatomic MOs. The dashed lines show which AOs contribute to each MO.



## 19.4 THE SIMPLE MO METHOD FOR DIATOMIC MOLECULES

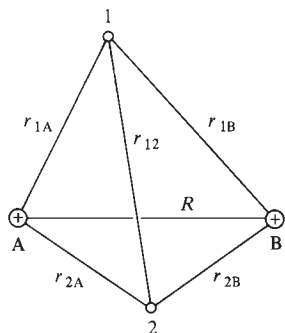
### MOs for Homonuclear Diatomic Molecules

Just as we constructed approximate wave functions for many-electron atoms by feeding electrons two at a time into hydrogenlike AOs, we shall construct approximate wave functions for many-electron homonuclear diatomic molecules by feeding electrons two at a time into  $H_2^+$ -like MOs. Figure 19.15 shows the lowest-lying  $H_2^+$ -like MOs (Sec. 19.3). Similar to AO energies (Fig. 18.15), the energies of these MOs vary from molecule to molecule. They also vary with varying internuclear distance in the same molecule. The energy order shown in the figure is the order in which the MOs are filled in going through the periodic table, as shown by spectroscopic observations. The AOs at the sides are connected by dashed lines to the MOs to which they contribute. Note that each pair of AOs leads to the formation of two MOs, a bonding MO with energy lower than that of the AOs and an antibonding MO with energy higher than that of the AOs.

### The Hydrogen Molecule

$H_2$  consists of two protons (A and B) and two electrons (1 and 2); see Fig. 19.16. The electronic Hamiltonian (including nuclear repulsion) is [Eqs. (19.6), (18.1), and (17.58)]

$$\begin{aligned} \hat{H}_e = & -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 \\ & - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \end{aligned} \quad (19.18)$$

**Figure 19.16**

Interparticle distances in the  $H_2$  molecule.

where  $r_{1A}$  is the distance between electron 1 and nucleus A,  $r_{12}$  is the distance between the electrons, and  $R$  is the distance between the nuclei. The first two terms are the kinetic-energy operators for electrons 1 and 2, the next four terms are the potential energy of attractions between the electrons and the nuclei,  $e^2/4\pi\epsilon_0 r_{12}$  is the potential energy of repulsion between the electrons, and  $e^2/4\pi\epsilon_0 R$  is the potential energy of internuclear repulsion.  $R$  is held fixed.

Because of the interelectronic repulsion term  $e^2/4\pi\epsilon_0 r_{12}$ , the electronic Schrödinger equation  $\hat{H}_e \psi_e = E_e \psi_e$  cannot be solved exactly for  $H_2$ . If this term is ignored, we get

an approximate electronic Hamiltonian that is the sum of two  $\text{H}_2^+$ -like electronic Hamiltonians, one for electron 1 and one for electron 2. [This isn't quite true, because the internuclear repulsion  $e^2/4\pi\epsilon_0 R$  is the same in (19.10) and (19.18). However,  $e^2/4\pi\epsilon_0 R$  is a constant and therefore only shifts the energy by  $e^2/4\pi\epsilon_0 R$  but does not affect the wave functions; see Prob. 19.33.] The approximate electronic wave function for  $\text{H}_2$  is then the product of two  $\text{H}_2^+$ -like electronic wave functions, one for each electron [Eq. (17.68)]. This is exactly analogous to approximating the He wave function by the product of two H-like wave functions in Sec. 18.6.

The function  $(2 + 2S)^{-1/2}(1s_A + 1s_B)$  in Eq. (19.15) is an approximate wave function for the  $\text{H}_2^+$  ground electronic state, and so the MO approximation to the  $\text{H}_2$  ground-electronic-state spatial wave function is

$$\sigma_g 1s(1) \cdot \sigma_g 1s(2) = N[1s_A(1) + 1s_B(1)] \cdot [1s_A(2) + 1s_B(2)] \quad (19.19)$$

where the normalization constant  $N$  is  $(2 + 2S)^{-1}$ . The numbers in parentheses refer to the electrons. For example,  $1s_A(2)$  is proportional to  $e^{-r_{2A}/a_0}$ . The MO wave function (19.19) is analogous to the He ground-state AO wave function  $1s(1)1s(2)$  in Eq. (18.38); the MO  $\sigma_g 1s$  replaces the AO  $1s$ .

To take care of spin and to satisfy the requirement that the complete electronic wave function be antisymmetric (Sec. 18.6), the symmetric two-electron spatial wave function (19.19) must be multiplied by the antisymmetric spin function (18.41). The approximate MO ground-state wave function for  $\text{H}_2$  is then

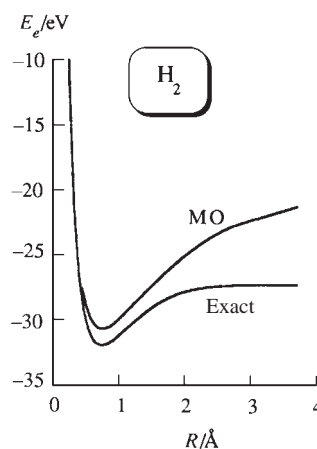
$$\sigma_g 1s(1)\sigma_g 1s(2)2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g 1s(1)\alpha(1) & \sigma_g 1s(1)\beta(1) \\ \sigma_g 1s(2)\alpha(2) & \sigma_g 1s(2)\beta(2) \end{vmatrix} \quad (19.20)$$

where we introduced the Slater determinant (Sec. 18.8). Just as the ground-state electron configuration of He is  $1s^2$ , the ground-state electron configuration of  $\text{H}_2$  is  $(\sigma_g 1s)^2$ ; compare (19.20) with (18.43).

We have put each electron in  $\text{H}_2$  into an MO. This allows for interelectronic repulsion only in an average way, so the treatment is an approximate one. We are using the crudest possible version of the MO approximation.

Using the approximate wave function (19.20), one evaluates the variational integral  $W$  to get  $W$  as a function of  $R$ . Since evaluation of molecular quantum-mechanical integrals is complicated, we shall just quote the results. With inclusion of a variable orbital exponent, the function (19.20) and (19.19) gives a  $W(R)$  curve (Fig. 19.17) with a minimum at  $R = 0.73 \text{ \AA}$ , which is close to the observed value  $R_e = 0.74 \text{ \AA}$  in  $\text{H}_2$ . The calculated  $D_e$  is 3.49 eV, which is far from the experimental value 4.75 eV. This is the main failing of the MO method; molecular dissociation energies are not accurately calculated.

We approximated the  $\sigma_g 1s$  MO in the  $\text{H}_2$  ground-state approximate wave function (19.19) by the linear combination  $N(1s_A + 1s_B)$ . To improve the MO wave function, we can look for the best possible form for the  $\sigma_g 1s$  MO, still writing the spatial wave function as the product of an orbital for each electron. The best possible MO wave function is the Hartree–Fock wave function (Secs. 18.9 and 19.5). Finding the Hartree–Fock wave function for  $\text{H}_2$  is not too difficult. The  $\text{H}_2$  Hartree–Fock wave function predicts  $R_e = 0.73 \text{ \AA}$  and  $D_e = 3.64 \text{ eV}$ ;  $D_e$  is still substantially in error. As noted in Sec. 18.9, the Hartree–Fock wave function is not the true wave function, because of neglect of electron correlation.



**Figure 19.17**

Ground-state electronic energy including internuclear repulsion for  $\text{H}_2$  as calculated from the LCAO-MO wave function (19.19) with an optimized orbital exponent compared with the exact ground-state electronic energy curve. Note the incorrect behavior of the MO function as  $R \rightarrow \infty$ .

In the 1960s, Kolos and Wolniewicz used very complicated variational functions that go beyond the Hartree–Fock approximation. With the inclusion of relativistic corrections and corrections for deviations from the Born–Oppenheimer approximation, they calculated  $D_0/hc = 36117.9 \text{ cm}^{-1}$  for  $\text{H}_2$ . ( $D_0$  differs from  $D_e$  by the zero-point vibrational energy; see Chapter 20.) At the time the calculation was completed, the experimental  $D_0/hc$  was  $36114 \pm 1 \text{ cm}^{-1}$ , and the  $4 \text{ cm}^{-1}$  discrepancy was a source of embarrassment to the theoreticians. Finally, reinvestigations of the spectrum of  $\text{H}_2$  showed that the experimental result was in error and gave the new experimental value  $36118.1 \pm 0.2 \text{ cm}^{-1}$ , in excellent agreement with the value calculated from quantum mechanics.

What about excited electronic states for  $\text{H}_2$ ? The lowest-lying excited  $\text{H}_2$  MO is the  $\sigma_u^*1s$  MO. Just as the lowest excited electron configuration of He is  $1s2s$ , the lowest excited electron configuration of  $\text{H}_2$  is  $(\sigma_g1s)(\sigma_u^*1s)$ , with one electron in each of the MOs  $\sigma_g1s$  and  $\sigma_u^*1s$ . Like the He  $1s2s$  configuration, the  $(\sigma_g1s)(\sigma_u^*1s)$   $\text{H}_2$  configuration gives rise to two terms, a singlet with total spin quantum number  $S = 0$  and a triplet with total spin quantum number  $S = 1$ . In accord with Hund's rule, the triplet lies lower and is therefore the lowest excited electronic level of  $\text{H}_2$ . In analogy with (18.46), the triplet has the MO wave functions

$$2^{-1/2}[\sigma_g1s(1)\sigma_u^*1s(2) - \sigma_g1s(2)\sigma_u^*1s(1)] \times \text{spin function} \quad (19.21)$$

where the spin function is one of the three symmetric spin functions (18.40). With one electron in a bonding orbital and one in an antibonding orbital, we expect no net bonding. This is borne out by experiment and by accurate theoretical calculations, which show the  $E_e(R)$  curve to have no minimum (Fig. 19.5).

The  $\text{H}_2$  levels (19.20) and (19.21) both dissociate into two H atoms in  $1s$  states. The bonding level (19.20) has the electrons paired with opposite spins and a net spin of zero. The repulsive level (19.21) has the electrons unpaired with approximately parallel spins. Whether two approaching  $1s$  H atoms attract or repel each other depends on whether their spins are antiparallel or parallel.

### Other Homonuclear Diatomic Molecules

The simple MO treatment of  $\text{He}_2$  places the four electrons into the two lowest available MOs to give the ground-state configuration  $(\sigma_g1s)^2(\sigma_u^*1s)^2$ . The MO wave function is a Slater determinant with four rows and four columns. With two bonding and two antibonding electrons, we expect no net bonding and no stability for the ground electronic state. This is in agreement with experiment. When two ground-state He atoms approach each other, the electronic energy curve  $E_e(R)$  resembles the second lowest curve of Fig. 19.5. Since  $E_e(R)$  is the potential energy for nuclear motion, two  $1s^2$  He atoms strongly repel each other. Actually, in addition to the strong, relatively short-range repulsion, there is a very weak attraction at relatively large values of  $R$  that produces a very slight minimum in the He–He potential-energy curve. This attraction is responsible for the liquefaction of He at very low temperature and produces an extremely weakly bound ground-state  $\text{He}_2$  molecule ( $D_0 = 10^{-7} \text{ eV}$ ) that has been detected at  $T = 10^{-3} \text{ K}$  (see Sec. 21.10). At ordinary temperatures, the  $\text{He}_2$  concentration is negligible.

Similar to the repulsion between two  $1s^2$  He atoms is the observed repulsion whenever two closed-shell atoms or molecules approach each other closely. This repulsion is important in chemical kinetics, since it is related to the activation energy of chemical reactions (see Sec. 22.2). Part of this repulsion is due to the Coulombic repulsion between electrons, but a major part of the repulsion is a consequence of the antisymmetry requirement (Sec. 18.6), as we now show. Let  $\psi(q_1, q_2, q_3, \dots)$  be

**Section 19.4**  
The Simple MO Method  
for Diatomic Molecules

the wave function for a system of electrons, where  $q_1$  stands for the four coordinates (three spatial and one spin) of electron 1. Since  $\psi$  is antisymmetric, interchange of the coordinates of electrons 1 and 2 multiplies  $\psi$  by  $-1$ . Therefore,  $\psi(q_2, q_1, q_3, \dots) = -\psi(q_1, q_2, q_3, \dots)$ . Now suppose that electrons 1 and 2 have the same spin coordinate (both  $\alpha$  or both  $\beta$ ) and the same spatial coordinates. Then  $q_1 = q_2$ , and  $\psi(q_1, q_1, q_3, \dots) = -\psi(q_1, q_1, q_3, \dots)$ . Hence,  $2\psi(q_1, q_1, q_3, \dots) = 0$ , and  $\psi(q_1, q_1, q_3, \dots) = 0$ .

The vanishing of  $\psi(q_1, q_1, q_3, \dots)$  shows that there is zero probability for two electrons to have the same spatial and spin coordinates. Two electrons that have the same spin (both with  $m_s = \frac{1}{2}$  or both with  $m_s = -\frac{1}{2}$ ) have zero probability of being at the same point in space. Moreover, because  $\psi$  is a continuous function, the probability that two electrons with the same spin will approach each other closely must be very small. Electrons with the same spin tend to avoid each other and act as if they repelled each other over and above the Coulombic repulsion. This apparent extra repulsion of electrons with like spins is called the **Pauli repulsion**. The Pauli repulsion is not a real physical force. It is an apparent force that is a consequence of the antisymmetry requirement of the wave function.

When two  $1s^2$  He atoms approach, the antisymmetry requirement causes an apparent Pauli repulsion between the spin- $\alpha$  electron on one atom and the spin- $\alpha$  electron on the other atom; likewise for the spin- $\beta$  electrons. As the He atoms approach each other, there is a depletion of electron probability density in the region between the nuclei (and a corresponding buildup of probability density in regions outside the nuclei) and the atoms repel each other.

The ground-state electron configurations of  $\text{Li}_2$ ,  $\text{Be}_2$ , etc., are formed by filling in the homonuclear diatomic MOs in Fig. 19.15 (see Prob. 19.30). For example,  $\text{O}_2$  has 16 electrons, and Fig. 19.15 gives the ground-state configuration

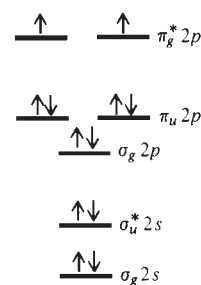
$$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^2$$

Actually, spectroscopic evidence shows that in  $\text{O}_2$  the  $\sigma_g 2p$  MO lies slightly lower than the  $\pi_u 2p$  MOs, so  $\sigma_g 2p$  precedes  $\pi_u 2p$  in the electron configuration. Figure 19.18 shows the distribution of the valence electrons in MOs in the  $\text{O}_2$  ground state. In accord with Hund's rule of maximum multiplicity for the ground state, the two antibonding  $\pi$  electrons are placed in separate orbitals to allow a triplet ground state. This agrees with the observed paramagnetism of ground-state  $\text{O}_2$ . In  $\text{O}_2$ , there are four more bonding electrons than antibonding electrons, and so the MO theory predicts a double bond (composed of one  $\sigma$  bond and one  $\pi$  bond) for  $\text{O}_2$ . Note the higher  $D_e$  for  $\text{O}_2$  compared with the single-bonded species  $\text{F}_2$  and  $\text{Li}_2$  (Table 19.3). The double bond makes  $R_e$  of  $\text{O}_2$  less than  $R_e$  of  $\text{Li}_2$ .  $R_e$  of  $\text{O}_2$  is greater than  $R_e$  of  $\text{H}_2$  because of the presence of the inner-shell  $1s$  electrons on the O atoms.

In  $\text{O}_2$ , the high nuclear charge draws the  $1s$  orbitals on each atom in close to the nuclei, and there is virtually no overlap between these AOs. Therefore, the  $\sigma_g 1s$  and  $\sigma_u^* 1s$  MO energies in  $\text{O}_2$  are each nearly the same as the  $1s$  AO energy in an O atom. Inner-shell electrons play no real part in chemical bonding, other than to screen the valence electrons from the nuclei.

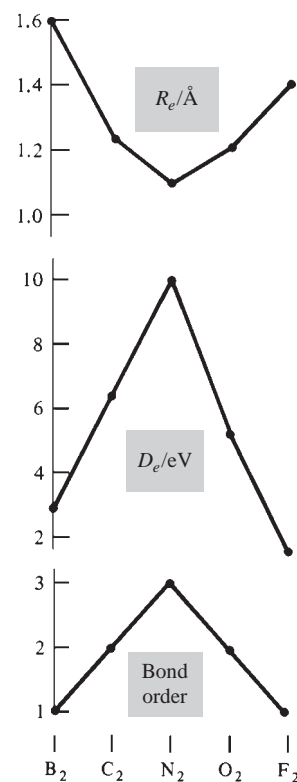
Figure 19.19 plots  $R_e$ ,  $D_e$ , and the MO *bond order* (defined as half the difference between the number of bonding and antibonding electrons) for some second-row homonuclear diatomic molecules. The higher the bond order, the greater is  $D_e$  and the smaller is  $R_e$ .

Instead of the separated-atoms notation for homonuclear diatomic MOs, quantum chemists prefer a notation in which the lowest  $\sigma_g$  MO is called  $1\sigma_g$ , the next lowest  $\sigma_g$  MO is called  $2\sigma_g$ , etc. In this notation, the MOs in Fig. 19.15 are called (in order of increasing energy)  $1\sigma_g$ ,  $1\sigma_u$ ,  $2\sigma_g$ ,  $2\sigma_u$ ,  $1\pi_u$ ,  $3\sigma_g$ ,  $1\pi_g$ ,  $3\sigma_u$ .



**Figure 19.18**

Occupied valence MOs in the  $\text{O}_2$  ground electronic state. (Not to scale.)



**Figure 19.19**

Correlation between bond orders and bond lengths and dissociation energies for some homonuclear diatomic molecules.

## Heteronuclear Diatomic Molecules

The MO method feeds the electrons of a heteronuclear diatomic molecule into molecular orbitals. In the crudest approximation, each bonding MO is taken as a linear combination of two AOs, one from each atom. In constructing MOs, one uses the principle that *only AOs of reasonably similar energies contribute substantially to a given MO*.

As an example, consider HF. Figure 18.15 shows that the energy of a  $2p$  AO in  ${}_9\text{F}$  is reasonably close to the  $1s$  AO energy in H, but the  $2s$  AO in F is substantially lower in energy than the  $1s$  H AO. (The logarithmic scale makes the fluorine  $2s$  level appear closer to the  $2p$  level than it actually is.) The  $2p$  AO in F lies somewhat lower than the  $1s$  AO in H because the five  $2p$  electrons in F screen one another rather poorly, giving a large  $Z_{\text{eff}}$  for the  $2p$  electrons [Eq. (18.55)]; this large  $Z_{\text{eff}}$  makes F more electronegative than H [Eq. (19.4)].

Let the HF molecular axis be the  $z$  axis, and let  $\text{F}2p_z$  and  $\text{H}1s$  denote a  $2p$  AO on F and a  $1s$  AO on H. The  $\text{F}2p_z$  AO has quantum number  $m = 0$  and has no nodal plane containing the internuclear axis. The overlap of this AO with the  $\text{H}1s$  AO, which also has  $m = 0$  and no nodal plane containing the  $z$  axis, therefore gives rise to a  $\sigma$  MO (Fig. 19.20). We therefore form the linear combination  $c_1\text{H}1s + c_2\text{F}2p_z$ . Minimization of the variational integral will lead to two sets of values for  $c_1$  and  $c_2$ , one set giving a bonding MO and the other an antibonding MO:

$$\sigma = c_1\text{H}1s + c_2\text{F}2p_z \quad \text{and} \quad \sigma^* = c_1'\text{H}1s - c_2'\text{F}2p_z \quad (19.22)$$

The  $\sigma$  MO in (19.22) has  $c_1$  and  $c_2$  both positive and is bonding because of the charge buildup between the nuclei. The antibonding  $\sigma^*$  MO in (19.22) has opposite signs for the coefficients of the AOs and so has charge depletion between the nuclei. This MO is unoccupied in the HF ground state. The  $g, u$  designation does not apply to heteronuclear diatomics.

In contrast to the  $\text{F}2p_z$  AO, the  $\text{F}2p_x$  and  $\text{F}2p_y$  AOs have  $|m| = 1$  and have one nodal plane containing the internuclear ( $z$ ) axis. These AOs will therefore be used to form  $\pi$  MOs in HF. Since H has no valence-shell AOs with  $|m| = 1$ , the  $\pi$  MOs in HF will consist entirely of F AOs, and these MOs are  $\pi_x = \text{F}2p_x$  and  $\pi_y = \text{F}2p_y$ .

The  $1s$  and  $2s$  AOs in F are too low in energy to take a substantial part in the bonding and therefore form nonbonding  $\sigma$  MOs in HF. Don't confuse a nonbonding MO with an antibonding MO. A nonbonding MO shows neither charge depletion nor charge buildup between the nuclei.

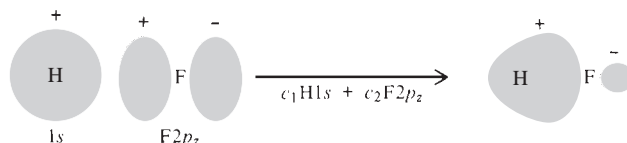
In the standard notation for heteronuclear diatomic molecules, the lowest  $\sigma$  MO is called the  $1\sigma$  MO, the next lowest  $\sigma$  MO is the  $2\sigma$  MO, etc. The lowest  $\pi$  energy level is called the  $1\pi$  level, etc. In our crude approximation, the occupied MOs in hydrogen fluoride are

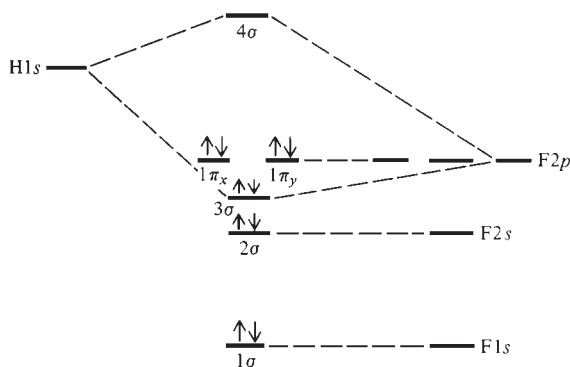
$$\begin{aligned} 1\sigma &= \text{F}1s, & 2\sigma &= \text{F}2s, & 3\sigma &= c_1\text{H}1s + c_2\text{F}2p_z \\ 1\pi_x &= \text{F}2p_x, & 1\pi_y &= \text{F}2p_y \end{aligned} \quad (19.23)$$

where  $1\pi_x$  and  $1\pi_y$  have the same energy. Since F is more electronegative than H, we expect  $|c_2| > |c_1|$  in the  $3\sigma$  MO; the electrons of the bond are more likely to be found close to F than to H.

**Figure 19.20**

Formation of the bonding MO in HF.



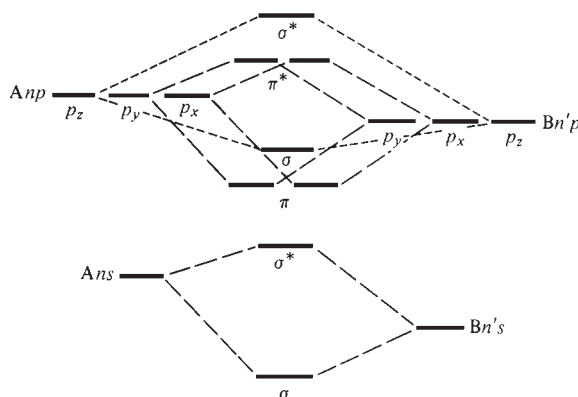
**Figure 19.21**

MO energies in HF. (Not to scale.)

Figure 19.21 shows the energy-level scheme for HF in the simple approximation (19.23). The  $1\pi$  MOs are lone-pair AOs on F and have nearly the same energy as F  $2p$  AOs. The  $2\sigma$  MO is also a lone-pair orbital.

An H atom is special, since it has no  $p$  valence orbitals. Consider a polar-covalent heteronuclear diatomic molecule AB, where both A and B are from the second or a higher period and hence have  $s$  and  $p$  valence levels. Let B be somewhat more electronegative than A. We draw Fig. 19.22 similar to Figs. 19.15 and 19.21 to show the formation of valence MOs from the  $ns$  and  $np$  valence AOs of A and the  $n's$  and  $n'p$  valence AOs of B;  $n$  and  $n'$  are the principal quantum numbers of the valence electrons and equal the periods of A and B in the periodic table. [It is assumed that B and A don't differ greatly in electronegativity. If B were much more electronegative than A (as, for example, in BF), then the valence  $p$  level of B might lie close to the valence  $s$  level of A, and the  $p_z$  AO of B would combine mainly with the  $s$  valence AO of A.] The MO shapes are similar to those in Figs. 19.11 to 19.14 for homonuclear diatomics, except that in each bonding MO the probability density is greater around the more electronegative element B than around A, and each bonding MO contour is therefore larger around B than A. In each antibonding MO, the probability density is larger around A, since more of the atom-B AO has been “used up” in forming the corresponding bonding MO.

To get the valence MO configuration of molecules like CN, NO, CO, or ClF, we feed the valence electrons into the MOs of Fig. 19.22. For example, CO has 10 valence electrons and has the configuration  $(\sigma_s)^2(\sigma_s^*)^2(\pi)^4(\sigma_p)^2$ . With six more bonding than antibonding electrons, the molecule has a triple bond (composed of one  $\sigma$  and two  $\pi$  bonds), in accord with the dot structure  $\text{:C}\equiv\text{O:}$ . The lowest two MOs in CO are the  $1\sigma$  and  $2\sigma$  MOs, formed from linear combinations of C  $1s$  and O  $1s$  AOs, and the complete MO configuration of CO in the standard notation is  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$ .

**Figure 19.22**

MOs formed from valence  $s$  and  $p$  AOs of atoms A and B with rather similar electronegativities.

## 19.5 SCF AND HARTREE–FOCK WAVE FUNCTIONS

The best possible wave function with electrons assigned to orbitals is the Hartree–Fock wave function. Starting in the 1960s, the use of electronic computers allowed Hartree–Fock wave functions for many molecules to be calculated. The Hartree–Fock orbitals  $\phi_i$  of a molecule must be found by solving the Hartree–Fock equations (18.57):  $\hat{F}\phi_i = \varepsilon_i\phi_i$ . The terms in the Fock operator  $\hat{F}$  for an atom were discussed after (18.57).  $\hat{F}$  for a molecule is the same as  $\hat{F}$  for an atom except that the electron–nucleus attraction  $-Ze^2/4\pi\epsilon_0r_1$  in an atom (term  $b$ ) is replaced by  $-\sum_{\alpha} Z_{\alpha}e^2/4\pi\epsilon_0r_{1\alpha}$ , which gives the potential energy of the attractions between electron 1 and all the nuclei;  $r_{1\alpha}$  is the distance between electron 1 and nucleus  $\alpha$ .

As is done for atoms, each Hartree–Fock MO is expressed as a linear combination of a set of functions called basis functions. If enough basis functions are included, one can get MOs that differ negligibly from the true Hartree–Fock MOs. Any functions can be used as basis functions, so long as they form a complete set (as defined in Sec. 18.9). Since molecules are made of bonded atoms, it is most convenient to use atomic orbitals as the basis functions. Each MO is then written as a linear combination of the basis-set AOs, and the coefficients of the AOs are found by solving the Hartree–Fock equations.

To have an accurate representation of an MO requires that the MO be expressed as a linear combination of a complete set of functions. This means that all the AOs of a given atom, whether occupied or unoccupied in the free atom, contribute to the MOs. To simplify the calculation, one frequently solves the Hartree–Fock equations using in the basis set only those AOs from each atom whose principal quantum number does not exceed the principal quantum number of the atom's valence electrons. Such a basis set limited to inner-shell and valence-shell AOs is called a **minimal basis set**. Use of a minimal basis set gives only an approximation to the Hartree–Fock MOs. Any wave function found by solving the Hartree–Fock equations is called a **self-consistent-field (SCF) wave function**. Only if the basis set is very large is an SCF wave function accurately equal to the Hartree–Fock wave function.

*Which AOs contribute to a given MO is determined by the symmetry properties of the MO.* For example, we saw at the end of Sec. 19.3 that MOs of a diatomic molecule can be classified as  $\sigma$ ,  $\pi$ ,  $\delta$ , . . . according to whether they have 0, 1, 2, . . . nodal planes containing the internuclear axis. Only AOs that have 0 such nodal planes contribute to a  $\sigma$  MO; only AOs that have 1 such nodal plane contribute to a  $\pi$  MO; etc. In Sec. 19.4, we took each diatomic MO as a linear combination of only two AOs. This is the crudest approximation and does not give an accurate representation of MOs. In actuality, all  $\sigma$  AOs of the two atoms contribute to each  $\sigma$  MO; similarly for  $\pi$  MOs. (By a  $\sigma$  AO is meant one with no nodal plane containing the internuclear axis.)

Consider, for example, a minimal-basis-set calculation of HF. The valence electron in H has  $n = 1$ , so we use only the  $1s$  AO. The valence electrons in F have  $n = 2$ , so we use the  $1s$ ,  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$  AOs of F. This gives a total of six basis functions. The  $1s$ ,  $F1s$ ,  $F2s$ , and  $F2p_z$  AOs each have 0 nodal planes containing the internuclear ( $z$ ) axis, so each  $\sigma$  MO of the HF molecule is a linear combination of these four AOs. Solution of the Hartree–Fock equations using this minimal basis set gives the occupied  $\sigma$  MOs as [B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960)]

$$\begin{aligned} 1\sigma &= 1.000(F1s) + 0.012(F2s) + 0.002(F2p_z) - 0.003(H1s) \\ 2\sigma &= -0.018(F1s) + 0.914(F2s) + 0.090(F2p_z) + 0.154(H1s) \\ 3\sigma &= -0.023(F1s) - 0.411(F2s) + 0.711(F2p_z) + 0.516(H1s) \end{aligned} \quad (19.24)$$

The  $1\sigma$  MO has a significant contribution only from the  $F1s$  AO. The  $2\sigma$  MO has a significant contribution only from the  $F2s$  AO. This is in accord with the simple arguments that led to the very approximate MOs in (19.23). The  $3\sigma$  MO has its largest

contributions from  $H1s$  and  $F2p_z$  but [unlike the crude approximation of (19.23)] also has a significant contribution from the  $F2s$  AO. The mixing together of two or more AOs on the same atom is called **hybridization**. [Each AO in (19.24) and in other equations in this section and the next is actually an approximate AO whose form is given by a single Slater-type orbital (Sec. 18.9).]

The  $F2p_x$  and  $F2p_y$  AOs each have one nodal plane containing the internuclear axis, and these AOs form the occupied  $\pi$  MOs of HF:

$$1\pi_x = F2p_x, \quad 1\pi_y = F2p_y \quad (19.25)$$

The  $1\pi$  level is doubly degenerate, so any two linear combinations of the orbitals in (19.25) could be used. (Recall the theorem about degenerate levels in Sec. 18.3.)

For the molecule  $F_2$ , a minimal-basis-set SCF calculation (Ransil, op. cit.) gives the MO we previously called the  $\sigma_g 2p$  MO as  $-0.005(1s_A + 1s_B) - 0.179(2s_A + 2s_B) + 0.648(2p_{zA} - 2p_{zB})$ . This can be compared with the simple expression  $N(2p_{zA} - 2p_{zB})$  used earlier. When a larger basis set is used, this  $F_2$  MO is found to have small contributions also from  $3s$ ,  $3d\sigma$ , and  $4f\sigma$  AOs, where  $3d\sigma$  and  $4f\sigma$  signify AOs with no nodal planes containing the molecular axis.

To reach the true molecular wave function, one must go beyond the Hartree–Fock approximation. Methods that do this are discussed in Secs. 19.9 and 19.10.

## 19.6 THE MO TREATMENT OF POLYATOMIC MOLECULES

As with diatomic molecules, one expresses the MOs of a polyatomic molecule as linear combinations of basis functions. Most commonly, AOs of the atoms forming the molecule are used as the basis functions. To find the coefficients in the linear combinations, one solves the Hartree–Fock equations (18.57). Which AOs contribute to a given MO is determined by the symmetry of the molecule.

### The $BeH_2$ Molecule

We shall apply the MO method to  $BeH_2$ . Since the valence shell of Be has  $n = 2$ , a minimal-basis-set calculation uses the  $Be1s$ ,  $Be2s$ ,  $Be2p_x$ ,  $Be2p_y$ ,  $Be2p_z$  AOs and the  $H_A1s$  and  $H_B1s$  AOs, where  $H_A$  and  $H_B$  are the two H atoms. The molecule has six electrons, and these will fill the lowest three MOs in the ground state.

Accurate theoretical calculations show that the equilibrium geometry is linear and symmetric ( $HBeH$ ), and we shall assume this structure. Each MO of this linear molecule can be classified as  $\sigma$ ,  $\pi$ ,  $\delta$ , . . . according to whether it has 0, 1, 2, . . . nodal planes containing the internuclear axis. Further, since the molecule has a center of symmetry at the Be nucleus, we can classify each MO as  $g$  or  $u$  (as we did with homonuclear diatomics), according to whether it has the same or opposite signs on diagonally opposite sides of the Be atom.

The  $Be1s$  AO has a much lower energy than all the other AOs in the basis set (Fig. 18.15), so the lowest MO will be nearly identical to the  $Be1s$  AO. The function  $Be1s$  has no nodal planes containing the internuclear axis and is a  $\sigma$  function; it also has  $g$  symmetry. We therefore write

$$1\sigma_g = Be1s \quad (19.26)$$

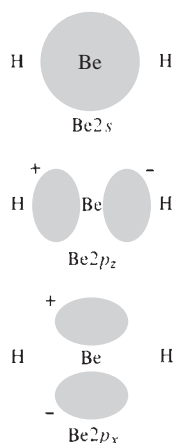
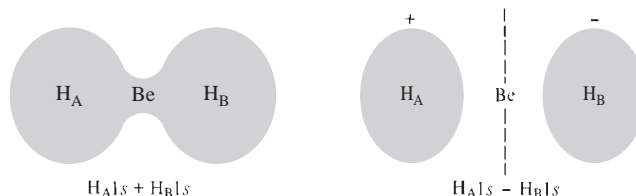
where the 1 indicates that this is the lowest  $\sigma_g$  MO.

The  $2s$  and  $2p$  valence AOs of Be and the  $1s$  valence AOs of  $H_A$  and  $H_B$  have similar energies and will be combined to form the remaining occupied MOs. In forming these MOs one must take the symmetry of the molecule into account. An MO without either  $g$  or  $u$  symmetry could not be a solution of the  $BeH_2$  Hartree–Fock equations. The proof of this requires group theory and is omitted.



**Figure 19.23**

Linear combinations of H-atom 1s AOs in  $\text{BeH}_2$  that have suitable symmetry.

**Figure 19.24**

Be AOs in  $\text{BeH}_2$ .

For a  $\text{BeH}_2$  MO to have  $g$  or  $u$  symmetry (that is, for the square of the MO to have the same value at corresponding diagonally opposite points on each side of the central Be atom) the squares of the coefficients of the  $\text{H}_\text{A}1s$  and  $\text{H}_\text{B}1s$  AOs must be equal in each  $\text{BeH}_2$  MO. Just as the  $1s_\text{A}$  and  $1s_\text{B}$  AOs in a homonuclear diatomic molecule's MOs occur as the linear combinations  $1s_\text{A} + 1s_\text{B}$  and  $1s_\text{A} - 1s_\text{B}$ , the  $\text{H}_\text{A}1s$  and  $\text{H}_\text{B}1s$  AOs in  $\text{BeH}_2$  can occur only as the linear combinations  $\text{H}_\text{A}1s + \text{H}_\text{B}1s$  and  $\text{H}_\text{A}1s - \text{H}_\text{B}1s$  in the  $\text{BeH}_2$  MOs that satisfy the Hartree–Fock equations. Both these linear combinations have no nodal plane containing the internuclear axis. Hence these linear combinations will contribute to  $\sigma$  MOs. The linear combination  $\text{H}_\text{A}1s + \text{H}_\text{B}1s$  has equal values at points diagonally opposite the center of the molecule (Fig. 19.23) and so has  $\sigma_g$  symmetry. The linear combination  $\text{H}_\text{A}1s - \text{H}_\text{B}1s$  has opposite signs at points diagonally opposite the molecular center and thus has  $\sigma_u$  symmetry.

What about the Be AOs? The  $\text{Be}2s$  AO has  $\sigma_g$  symmetry. Calling the internuclear axis the  $z$  axis, we see from Fig. 19.24 that the  $\text{Be}2p_z$  AO has  $\sigma_u$  symmetry. The  $\text{Be}2p_x$  and  $\text{Be}2p_y$  AOs each have  $\pi_u$  symmetry.

The basis-set functions and their symmetries are thus

$\text{Be}1s$	$\text{Be}2s$	$\text{Be}2p_z$	$\text{Be}2p_x$	$\text{Be}2p_y$	$\text{H}_\text{A}1s + \text{H}_\text{B}1s$	$\text{H}_\text{A}1s - \text{H}_\text{B}1s$
$\sigma_g$	$\sigma_g$	$\sigma_u$	$\pi_u$	$\pi_u$	$\sigma_g$	$\sigma_u$

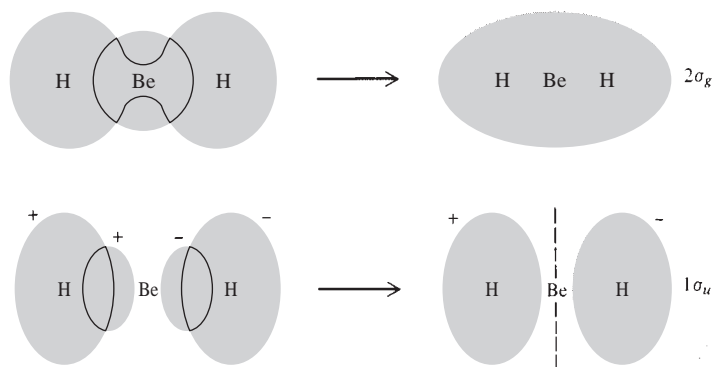
Combining functions that have  $\sigma_g$  symmetry and comparable energies, we form a  $\sigma_g$  MO as follows:

$$2\sigma_g = c_1\text{Be}2s + c_2(\text{H}_\text{A}1s + \text{H}_\text{B}1s) \quad (19.27)$$

The 2 in  $2\sigma_g$  indicates that this is the second lowest  $\sigma_g$  MO, the lowest being (19.26). The very-low-energy  $\text{Be}1s$  AO will make a very slight contribution to  $2\sigma_g$ , which we shall neglect. With  $c_1$  and  $c_2$  both positive, this MO has probability-density buildup between Be and  $\text{H}_\text{A}$  and between Be and  $\text{H}_\text{B}$  and is therefore bonding (Fig. 19.25).

Similarly, we form a bonding  $\sigma_u$  MO as (Fig. 19.25)

$$1\sigma_u = c_3\text{Be}2p_z + c_4(\text{H}_\text{A}1s - \text{H}_\text{B}1s) \quad (19.28)$$

**Figure 19.25**

Formation of bonding MOs in  $\text{BeH}_2$ .

with  $c_3$  and  $c_4$  both positive. This bonding MO has its energy below the energies of the  $\text{Be}2p_z$  and  $\text{H}1s$  AOs from which it is formed.

The coefficients  $c_1, c_2, c_3, c_4$  are found by solving the Hartree–Fock equations.

The  $\text{Be}2p_x$  and  $\text{Be}2p_y$  AOs form two  $\pi_u$  MOs:

$$1\pi_{u,x} = \text{Be}2p_x, \quad 1\pi_{u,y} = \text{Be}2p_y \quad (19.29)$$

These two MOs have the same energy and constitute the doubly degenerate  $1\pi_u$  energy level. The nonbonding  $\pi$  MOs of (19.29) have nearly the same energy as the  $\text{Be}2p_x$  and  $\text{Be}2p_y$  AOs and so lie above the bonding  $2\sigma_g$  and  $1\sigma_u$  MOs. The  $\pi$  MOs are therefore unoccupied in the ground state of this six-electron molecule.

A minimal-basis-set SCF calculation on  $\text{BeH}_2$  [R. G. A. R. MacLagan and G. W. Schnuelle, *J. Chem. Phys.*, **55**, 5431 (1971)] gave the occupied MOs as

$$\begin{aligned} 1\sigma_g &= 1.00(\text{Be}1s) + 0.016(\text{Be}2s) - 0.002(\text{H}_A1s + \text{H}_B1s) \\ 2\sigma_g &= -0.09(\text{Be}1s) + 0.40(\text{Be}2s) + 0.45(\text{H}_A1s + \text{H}_B1s) \\ 1\sigma_u &= 0.44(\text{Be}2p_z) + 0.44(\text{H}_A1s - \text{H}_B1s) \end{aligned} \quad (19.30)$$

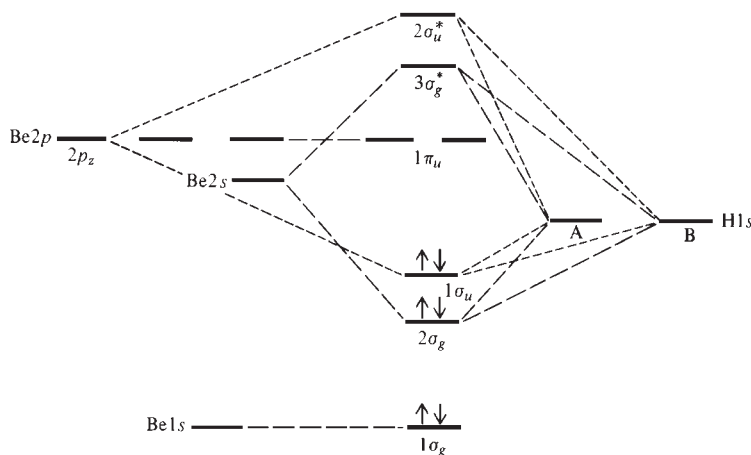
The  $1\sigma_g$  MO is essentially a  $\text{Be}1s$  AO, as anticipated in (19.26). The  $2\sigma_g$  and  $1\sigma_u$  MOs have essentially the forms of (19.27) and (19.28).

There are also two antibonding MOs  $3\sigma_g^*$  and  $2\sigma_u^*$  formed from the same AOs as the two bonding MOs (19.27) and (19.28):

$$3\sigma_g^* = c'_1\text{Be}2s - c'_2(\text{H}_A1s + \text{H}_B1s), \quad 2\sigma_u^* = c'_3\text{Be}2p_z - c'_4(\text{H}_A1s - \text{H}_B1s) \quad (19.31)$$

Figure 19.26 sketches the AO and MO energies for  $\text{BeH}_2$ . Of course, this molecule has many higher unoccupied MOs that are not shown in the figure. These MOs are formed from higher AOs of Be and the H's. The  $\text{BeH}_2$  ground-state configuration is  $(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2$ . There are four bonding electrons and hence two bonds. The  $1\sigma_g$  electrons are nonbonding inner-shell electrons.

Note that a bonding MO has a lower energy than the AOs from which it is formed, an antibonding MO has a higher energy than the AOs from which it is formed, and a nonbonding MO has approximately the same energy as the AO or AOs from which it is formed.



**Figure 19.26**

Energy-level scheme for  $\text{BeH}_2$  MOs. (Not to scale.)

## Localized MOs

The  $\text{BeH}_2$  bonding MOs  $2\sigma_g$  and  $1\sigma_u$  in Fig. 19.25 are each delocalized over the entire molecule. The two electrons in the  $2\sigma_g$  MO move over the entire molecule, as do the two in the  $1\sigma_u$  MO. This is puzzling to a chemist, who likes to think in terms of individual bonds:  $\text{H—Be—H}$  or  $\text{H:Be:H}$ . The existence of bond energies, bond moments, and bond vibrational frequencies (Sec. 20.9) that are roughly the same for a given kind of bond in different molecules shows that there is much validity in the picture of individual bonds. How can we reconcile the existence of individual bonds with the delocalized MOs found by solving the Hartree–Fock equations?

Actually, we *can* use the MO method to arrive at a picture in accord with chemical experience, as we now show. The MO ground-state wave function for  $\text{BeH}_2$  is a  $6 \times 6$  Slater determinant (Sec. 18.8). The first two rows of this Slater determinant are

$$\begin{array}{cccccc} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) & 2\sigma_g(1)\alpha(1) & 2\sigma_g(1)\beta(1) & 1\sigma_u(1)\alpha(1) & 1\sigma_u(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) & 2\sigma_g(2)\alpha(2) & 2\sigma_g(2)\beta(2) & 1\sigma_u(2)\alpha(2) & 1\sigma_u(2)\beta(2) \end{array}$$

The third row involves electron 3, etc. Each column has the same spin-orbital. Now it is a well-known theorem (*Sokolnikoff and Redheffer*, app. A) that addition of a constant times one column of a determinant to another column leaves the determinant unchanged in value. For example, if we add three times column 1 of the determinant in (18.44) to column 2, we get

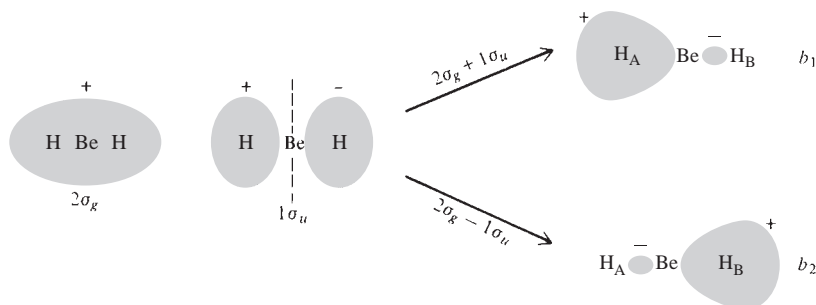
$$\begin{vmatrix} a & b + 3a \\ c & d + 3c \end{vmatrix} = a(d + 3c) - c(b + 3a) = ad - bc = \begin{vmatrix} a & b \\ c & d \end{vmatrix}$$

Thus, if we like, we can add a multiple of one column of the Slater-determinant MO wave function to another column without changing the wave function. This addition will “mix” together different MOs, since each column is a different spin-orbital. We can therefore take linear combinations of MOs to form new MOs without changing the overall wave function. Of course, the new MOs should each be normalized and, for computational convenience, should also be orthogonal to one another.

The  $\text{BeH}_2$  MOs  $1\sigma_g$ ,  $2\sigma_g$ , and  $1\sigma_u$  satisfy the Hartree–Fock equations (18.57) and have the symmetry of the molecule. Because they have the molecular symmetry, they are delocalized over the whole molecule. (More accurately, the  $2\sigma_g$  and  $1\sigma_u$  MOs are delocalized, but the inner-shell  $1\sigma_g$  is localized on the central Be atom.) These delocalized MOs satisfying the Hartree–Fock equations and having the symmetry of the molecule are called the **canonical MOs**. The canonical MOs are unique (except for the possibility of taking linear combinations of degenerate MOs).

As just shown, we can take linear combinations of the canonical MOs to form a new set of MOs that will give the same overall wave function. The new MOs will not individually be solutions of the Hartree–Fock equations  $\hat{F}\phi_i = \varepsilon_i\phi_i$ , but the wave function formed from these MOs will have the same energy and the same total probability density as the wave function formed from the canonical MOs.

Of the many possible sets of MOs that can be formed, we want to find a set that will have each MO classifiable as one of the following: a **bonding** (*b*) orbital localized between two atoms and having charge buildup between the atoms, an **inner-shell** (*i*) orbital, or a **lone-pair** (*l*) orbital. We call such a set of MOs **localized MOs**. Each localized MO will not have the symmetry of the molecule, but the localized MOs will correspond closely to a chemist’s picture of bonding. Since localized MOs are not eigenfunctions of the Hartree–Fock operator  $\hat{F}$ , in a certain sense each such MO does not correspond to a definite orbital energy. However, one can calculate an average energy of a localized MO by averaging over the orbital energies of the canonical MOs that form the localized MO.

**Figure 19.27**

Formation of localized bonding MOs in  $\text{BeH}_2$  from linear combinations of delocalized (canonical) MOs.

Consider  $\text{BeH}_2$ . The  $1\sigma_g$  canonical MO is an inner-shell (*i*) AO on Be and can therefore be taken as one of the localized MOs:  $i(\text{Be}) = 1\sigma_g = \text{Be}1s$ . The  $2\sigma_g$  and  $1\sigma_u$  canonical MOs are delocalized. Figure 19.25 shows that the  $1\sigma_u$  MO has opposite signs in the two halves of the molecule, whereas  $2\sigma_g$  is essentially positive throughout the molecule. Hence, by taking linear combinations that are the sum and difference of these two canonical MOs, we get MOs that are each largely localized between only two atoms (Fig. 19.27). Thus, we take the localized bonding MOs  $b_1$  and  $b_2$  as

$$b_1 = 2^{-1/2}(2\sigma_g + 1\sigma_u), \quad b_2 = 2^{-1/2}(2\sigma_g - 1\sigma_u) \quad (19.32)$$

where the  $2^{-1/2}$  is a normalization constant. The  $b_1$  localized MO corresponds to a bond between Be and  $\text{H}_A$ . The  $b_2$  MO gives the  $\text{Be}-\text{H}_B$  bond.

Using these localized MOs, we write the  $\text{BeH}_2$  MO wave function as a  $6 \times 6$  Slater determinant whose first row is

$$i(1)\alpha(1) \quad i(1)\beta(1) \quad b_1(1)\alpha(1) \quad b_1(1)\beta(1) \quad b_2(1)\alpha(1) \quad b_2(1)\beta(1)$$

This localized-MO wave function is equal to the wave function that uses delocalized (canonical) MOs.

Equation (19.32) expresses the localized bonding MOs  $b_1$  and  $b_2$  in terms of the canonical MOs. Substitution of (19.27) and (19.28) into (19.32) gives

$$\begin{aligned} b_1 &= 2^{-1/2}[c_1\text{Be}2s + c_3\text{Be}2p_z + (c_2 + c_4)\text{H}_A1s + (c_2 - c_4)\text{H}_B1s] \\ b_2 &= 2^{-1/2}[c_1\text{Be}2s - c_3\text{Be}2p_z + (c_2 - c_4)\text{H}_A1s + (c_2 + c_4)\text{H}_B1s] \end{aligned} \quad (19.33)$$

As a rough approximation, we see from (19.27), (19.28), and (19.30) that  $c_2 \approx c_4$  and  $c_1 \approx c_3$ . These approximations give

$$\begin{aligned} b_1 &\approx 2^{-1/2}[c_1(\text{Be}2s + \text{Be}2p_z) + 2c_2\text{H}_A1s] \\ b_2 &\approx 2^{-1/2}[c_1(\text{Be}2s - \text{Be}2p_z) + 2c_2\text{H}_B1s] \end{aligned} \quad (19.34)$$

The approximate MOs (19.34) are each fully localized between Be and one H atom, but the more accurate expressions (19.33) show that the  $\text{Be}-\text{H}_A$  bonding MO  $b_1$  has a small contribution from the  $\text{H}_B1s$  AO and so is not fully localized between the two atoms forming the bond.

Note that [unlike the canonical MOs (19.27) and (19.28)] the  $b_1$  and  $b_2$  localized MOs each have the  $\text{Be}2s$  and  $\text{Be}2p_z$  AOs mixed together, or *hybridized*. **Hybridization** is the mixing of different AOs of the same atom. The precise degree of hybridization depends on the values of  $c_1$  and  $c_3$  in (19.33). In the approximation of

(19.34), the MOs  $b_1$  and  $b_2$  would each contain equal amounts of the  $\text{Be}2s$  and  $\text{Be}2p_z$  AOs. The two normalized linear combinations

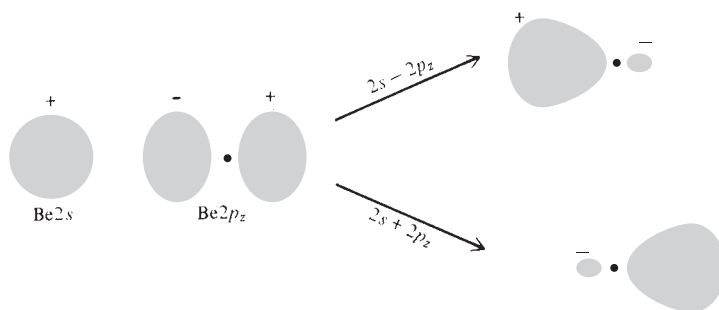
$$2^{-1/2}(2s + 2p_z) \quad \text{and} \quad 2^{-1/2}(2s - 2p_z) \quad (19.35)$$

are called ***sp* hybrid AOs**. Comparison of (19.30) with (19.27) and (19.28) gives  $c_1 = 0.40$  and  $c_3 = 0.44$ , so  $c_1$  and  $c_3$  are not precisely equal, but are nearly equal. Thus, the Be AOs in the  $\text{BeH}_2$  bonding MOs are not precisely *sp* hybrids but are nearly *sp* hybrids.

Note from Eq. (19.33) and Fig. 19.27 that the localized bonding MOs  $b_1$  and  $b_2$  in  $\text{BeH}_2$  are **equivalent** to each other. By this we mean that  $b_1$  and  $b_2$  have the same shapes and are interchanged by a rotation that interchanges the two equivalent chemical bonds in  $\text{BeH}_2$ . If we rotate  $b_1$  and  $b_2$   $180^\circ$  about an axis through Be and perpendicular to the molecular axis (thereby interchanging  $\text{H}_\text{A}1s$  and  $\text{H}_\text{B}1s$  and changing  $\text{Be}2p_z$  to  $-\text{Be}2p_z$ ), then  $b_1$  is changed to  $b_2$ , and vice versa. Because of the symmetry of the molecule, we expect  $b_1$  and  $b_2$  to be equivalent orbitals. It is possible to show that the linear combinations in (19.32) are the only linear combinations of the  $2\sigma_g$  and  $1\sigma_u$  canonical MOs that meet the requirements of being normalized, equivalent, and orthogonal.

We arrived at the approximately *sp* hybrid Be AOs in the localized  $\text{BeH}_2$  bonding MOs by first finding the delocalized canonical MOs and then transforming to localized MOs. A simpler (and more approximate) approach is often preferred by chemists for qualitative discussions of bonding. In this procedure, one omits consideration of the canonical MOs. Instead, one forms the required hybrid AOs on the free Be atom and then uses these hybrids to form localized bonding MOs with the  $\text{H}1s$  AOs. For  $\text{BeH}_2$  with its  $180^\circ$  bond angle, we need two equivalent hybrid AOs on Be that point in opposite directions. The valence AOs of Be are  $2s$  and  $2p$ . Figure 19.28 shows that the linear combinations (19.35) give two equivalent hybridized AOs oriented  $180^\circ$  apart. It is possible to show that the *sp* hybrids (19.35) are the only linear combinations that give AOs at  $180^\circ$  that are equivalent, normalized, and orthogonal in the free atom. We then overlap each of these *sp* hybrid AOs with an  $\text{H}1s$  AO to form the two bonds. This gives the approximate localized bonding MOs of Eq. (19.34).

Although the *sp* hybrids (19.35) are the only linear combinations of  $2s$  and  $2p_z$  that give equivalent orbitals in the free Be atom, we must expect that in the  $\text{BeH}_2$  molecule the interaction between the Be hybrids and the H atoms will alter the nature of these hybrids somewhat. What is really wanted is equivalent, normalized, orthogonal MOs in the  $\text{BeH}_2$  molecule and not equivalent, normalized, orthogonal AOs in the Be atom. The equivalent MOs in  $\text{BeH}_2$  are (19.33), and as noted above, these contain not precisely *sp* hybrids but only approximately *sp* hybrids. Another approximation involved in the use of *sp* Be hybrids to form the MOs (19.34) is neglect of the small contribution of the  $\text{H}_\text{B}1s$  AO to the bonding MO between Be and  $\text{H}_\text{A}$ . This is the term  $(c_2 - c_4)\text{H}_\text{B}1s = 0.01(\text{H}_\text{B}1s)$  in (19.33).



**Figure 19.28**

Formation of *sp* hybrid AOs in the Be atom.

## Energy-Localized MOs

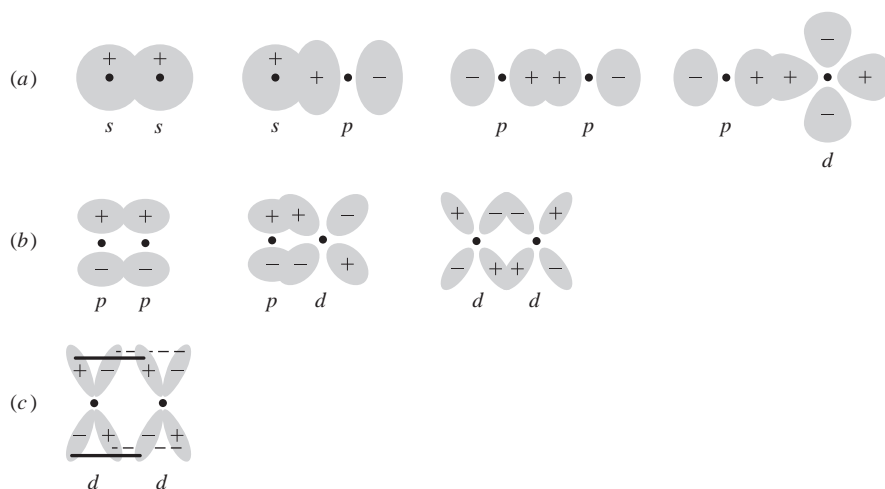
For  $\text{BeH}_2$ , the symmetry of the molecule enables one to determine what linear combination of canonical MOs to use to get localized bonding MOs. For less symmetric molecules, one cannot use symmetry, since the localized MOs need not be equivalent to one another. Several methods have been suggested for finding localized MOs from the canonical MOs. A widely accepted approach is that of Edmiston and Ruedenberg, who defined the **energy-localized MOs** as those orthogonal MOs that minimize the total of the Coulombic repulsions between the various pairs of localized MOs considered as charge distributions in space. This gives localized MOs that are separated as far as possible from one another.

In most cases, the energy-localized MOs agree with what one would expect from the Lewis dot formula. For example, for  $\text{H}_2\text{O}$ , the energy-localized MOs turn out to be one inner-shell MO, two bonding MOs, and two lone-pair MOs, in agreement with the dot formula  $\text{H}:\ddot{\text{O}}:\text{H}$ . The inner-shell MO is nearly identical to the  $\text{O}1s$  AO. One bonding energy-localized MO is largely localized in the  $\text{O}-\text{H}_\text{A}$  region, and the other is largely localized in the  $\text{O}-\text{H}_\text{B}$  region. The angle between the bonding localized MOs is  $103^\circ$ , which is nearly the same as the  $104.5^\circ$  experimental bond angle in water. The angle between the lone-pair localized orbitals is  $114^\circ$ . Each bonding localized MO is mainly a linear combination of  $2s$  and  $2p$  oxygen AOs and a  $1s$  hydrogen AO. Each lone-pair MO is mainly a hybrid of  $2s$  and  $2p$  AOs on oxygen.

## Sigma, Pi, and Delta Bonds

In most cases, each localized bonding MO of a molecule contains substantial contributions from AOs of only two atoms, the atoms forming the bond. In analogy with the classification used for diatomic molecules, each localized bonding MO of a polyatomic molecule is classified as  $\sigma$ ,  $\pi$ ,  $\delta$ , . . . according to whether the MO has 0, 1, 2, . . . nodal planes containing the axis between the two bonded atoms. The  $\text{BeH}_2$  MOs  $b_1$  and  $b_2$  in Fig. 19.27 are clearly  $\sigma$  MOs. One finds that a single bond between two atoms nearly always corresponds to a  $\sigma$  localized MO. Nearly always, a double bond between two atoms is composed of one  $\sigma$  localized MO and one  $\pi$  localized MO. Nearly always, a triple bond is composed of one  $\sigma$ -bond orbital and two  $\pi$ -bond orbitals. A quadruple bond is composed of one  $\sigma$  bond, two  $\pi$  bonds, and one  $\delta$  bond.

A  $\sigma$  bond is formed by overlap of two AOs that have no nodal planes containing the bond axis. Figure 19.29a shows some kinds of AO overlap that produce  $\sigma$  localized bond MOs. Figure 19.29b shows some overlaps that lead to  $\pi$  bonds. Figure 19.29c shows formation of a  $\delta$  bond.



**Figure 19.29**

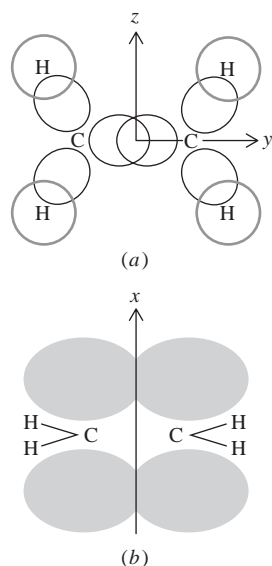
Overlap of AOs to form (a)  $\sigma$  bonds; (b)  $\pi$  bonds; (c) a  $\delta$  bond. The lobes in (c) are in front of and behind the paper.

Chemists have known about  $\sigma$  and  $\pi$  bonds since the 1930s. In 1964, Cotton pointed out that the  $\text{Re}_2\text{Cl}_8^{2-}$  ion has a quadruple bond between the two Re atoms, as shown by an abnormally short Re–Re bond distance. This bond is composed of one  $\sigma$  bond, two  $\pi$  bonds, and one  $\delta$  bond, the  $\delta$  bond being formed by overlap of two  $d_{x^2-y^2}$  AOs, one on each Re atom. Several other transition-metal species have quadruple bonds. [F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975); F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Wiley, 1982.]

### Methane, Ethylene, and Acetylene

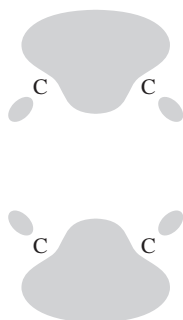
For  $\text{CH}_4$ , the canonical occupied MOs are found to consist of an MO that is a nearly pure  $\text{C}1s$  AO and four delocalized bonding MOs that each extend over much of the molecule. When the canonical MOs are transformed to energy-localized MOs, the localized MOs are found to consist of an inner-shell MO that is essentially a pure  $\text{C}1s$  AO and four localized bonding MOs, each bonding MO pointing toward one of the H atoms of the tetrahedral molecule. The localized bonding MO between C and atom  $\text{H}_A$  is [R. M. Pitzer, *J. Chem. Phys.*, **46**, 4871 (1967)]

$$0.02(\text{C}1s) + 0.292(\text{C}2s) + 0.277(\text{C}2p_x + \text{C}2p_y + \text{C}2p_z) \\ + 0.57(\text{H}_A1s) - 0.07(\text{H}_B1s + \text{H}_C1s + \text{H}_D1s)$$



**Figure 19.30**

Bonding in ethylene: (a)  $\sigma$  bonds; (b)  $\pi$  bond.



**Figure 19.31**

Equivalent “banana” bonds in ethylene. The view is the same as shown in Fig. 19.30b.

The carbon  $2s$  and  $2p$  AOs make nearly equal contributions, and the hybridization on carbon is approximately  $sp^3$ . It would be exactly  $sp^3$  if the coefficient of  $\text{C}2s$  equaled that of the  $\text{C}2p$  AOs. Atom  $\text{H}_A$  is in the positive octant of space, and the combination  $\text{C}2p_x + \text{C}2p_y + \text{C}2p_z$  (which is proportional to  $x + y + z$ ) has its maximum probability density along the line running through C and  $\text{H}_A$  and on both sides of the C nucleus. Addition of  $\text{C}2s$  to  $\text{C}2p_x + \text{C}2p_y + \text{C}2p_z$  cancels most of the probability density on the side of C that is away from  $\text{H}_A$  and reinforces the probability density in the region between C and  $\text{H}_A$ . (This is the same thing that occurs in Fig. 19.28 for the  $\text{BeH}_2$   $sp$  hybrids.) Overlap of the C hybrid AO with the  $\text{H}_A1s$  AO then forms the bond. Each bonding localized MO has no nodal planes containing the axis between the bonded atoms and is a  $\sigma$  MO.

Consider ethylene ( $\text{H}_2\text{C}=\text{CH}_2$ ). The molecule is planar, with the bond angles at each carbon close to  $120^\circ$ . A minimal basis set consists of four  $\text{H}1s$  AOs and two each of  $\text{C}1s$ ,  $\text{C}2s$ ,  $\text{C}2p_x$ ,  $\text{C}2p_y$ , and  $\text{C}2p_z$ . Let the molecular plane be the  $yz$  plane. One way to form localized MOs for  $\text{C}_2\text{H}_4$  is to use linear combinations of the  $\text{C}2s$ ,  $\text{C}2p_y$ , and  $\text{C}2p_z$  AOs at each carbon to form three  $sp^2$  hybrid AOs at each carbon. These hybrids make  $120^\circ$  angles with one another. Overlap of two of the three  $sp^2$  hybrids at each carbon with  $\text{H}1s$  AOs forms the C—H single bonds, and these are  $\sigma$  bonds. Overlap of the third  $sp^2$  hybrid of one carbon with the third  $sp^2$  hybrid of the second carbon gives a  $\sigma$  bonding MO between the two carbons (Fig. 19.30a). Overlap of the  $2p_x$  AOs of each carbon gives a localized  $\pi$  bonding MO between the carbons (Fig. 19.30b). This  $\pi$  MO has a nodal plane coinciding with the molecular plane and containing the C—C axis.

Ethylene has 16 electrons. Four of them fill the two localized inner-shell MOs, each of which is a  $1s$  AO on one of the carbons; eight electrons fill the four C—H bond MOs; two fill the C—C  $\sigma$ -bond MO, and two fill the C—C  $\pi$ -bond MO. (Unlike that in diatomic molecules, the ethylene  $\pi$ -bond MO is nondegenerate.) In this picture, the carbon–carbon double bond consists of one  $\sigma$  bond and one  $\pi$  bond.

The above description of localized MOs for  $\text{C}_2\text{H}_4$  is the traditional one. However, calculation of the energy-localized MOs in ethylene shows that two bent, equivalent “banana” bonds (Fig. 19.31) between the two carbons are more localized than the traditional  $\sigma$ - $\pi$  description [U. Kaldor, *J. Chem. Phys.*, **46**, 1981 (1967)].



The traditional description of  $\text{HC}\equiv\text{CH}$  uses two  $sp$  hybrids on each carbon to overlap the  $1s$  AOs and to form a  $\sigma$  bond between the carbons. The linear combinations  $C_A 2p_x + C_B 2p_x$  and  $C_A 2p_y + C_B 2p_y$  (where the  $z$  axis is the molecular axis) give two  $\pi$  bonds between  $C_A$  and  $C_B$ . In this picture, the triple bond consists of one  $\sigma$  bond and two  $\pi$  bonds. Again, actual calculation shows the energy-localized MOs to consist of three equivalent bent banana bonds.

## Benzene

The carbons in benzene ( $\text{C}_6\text{H}_6$ ) form a regular hexagon with  $120^\circ$  bond angles. We can use three  $sp^2$  hybrid AOs at each carbon to form localized  $\sigma$  bonds with one hydrogen and with two adjacent carbons. This leaves a  $2p_z$  AO at each carbon (where the  $z$  axis is perpendicular to the molecular plane). For benzene, two equivalent Lewis dot formulas can be written; the carbon-carbon single bonds and double bonds are interchanged in the two formulas. Moreover,  $\Delta_f H^\circ$  for benzene (Prob. 19.40) and the chemical behavior of benzene differ from what is expected of a species with localized double bonds. Hence, it would not be suitable to form three localized  $\pi$  MOs by pairwise interactions of the six  $2p_z$  AOs. Instead, all six  $2p_z$  AOs must be considered to interact with one another, and one uses delocalized (canonical) MOs to form the  $\pi$  bonds. The six  $2p_z$  AOs give six delocalized  $\pi$  MOs, three bonding and three antibonding. These six MOs are linear combinations of the six  $2p_z$  AOs; their forms are fully determined by the symmetry of benzene. (See Prob. 19.41 and *Levine*, sec. 17.2.)

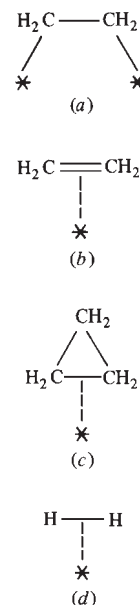
Three of the four valence electrons of each carbon go into the three bonding MOs formed from the  $sp^2$  hybrids, leaving one electron at each carbon to go into the  $\pi$  MOs. These remaining six electrons fill the three bonding  $\pi$  MOs. Each  $\pi$  MO has a nodal plane that coincides with the molecular plane (since each  $2p_z$  AO has such a plane). This nodal plane is analogous to the nodal plane of a localized  $\pi$  bond joining two doubly bonded atoms (for example, as in ethylene), and so these benzene MOs are called  $\pi$  MOs.

A similar situation holds for other planar conjugated organic compounds. (A **conjugated** molecule has a framework consisting of alternating carbon-carbon single and double bonds.) One can form in-plane localized  $\sigma$ -bond MOs using  $sp^2$  hybrids on each carbon, but one uses delocalized (canonical) MOs for the  $\pi$  MOs.

## Three-Center Bonds

$\text{B}_2\text{H}_6$  has 12 valence electrons, which is not enough to allow one to write a Lewis dot structure with two electrons shared between each pair of bonded atoms. Calculation of the energy-localized MOs of  $\text{B}_2\text{H}_6$  shows that two of the localized MOs each extend over two B atoms and one H atom to give two three-center bonds. [E. Switkes et al., *J. Chem. Phys.*, **51**, 2085 (1969).] The H atoms of the three-center bonds lie above and below the plane of the remaining six atoms and midway between the borons. Three-center bonds also occur in higher boron hydrides.

Multicenter bonding occurs in chemisorption. For example, experimental evidence shows that an ethylene molecule can bond to a metal's surface by forming two  $\sigma$  bonds with metal atoms (the stars in Fig. 19.32a) or by forming a  $\pi$  complex (Fig. 19.32b) in which electron probability density of the carbon-carbon  $\pi$  bond bonds the molecule to a metal atom as well as bonding the carbons to each other (*Bamford and Tipper*, vol. 20, pp. 22–23). Such a  $\pi$  complex is stabilized by donation of electron density from the  $\text{C}_2\text{H}_4$   $\pi$  electrons into vacant metal-atom orbitals and by donation of electron density from filled metal-atom orbitals into the vacant antibonding  $\pi$  MO in  $\text{C}_2\text{H}_4$  (back bonding).  $\pi$  complexes occur in such organometallic compounds as dibenzenechromium,  $\text{C}_6\text{H}_6\text{CrC}_6\text{H}_6$ , ferrocene,  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_5$ , and the complex ion  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ ; see *DeKock and Gray*, sec. 6-4.



**Figure 19.32**

Species chemisorbed on the surface of a solid.



Cyclopropane can be weakly chemisorbed by forming a complex in which the electron probability density of a carbon–carbon bond bonds the molecule to a surface metal atom (*Bamford and Tipper*, vol. 20, p. 102), as shown in Fig. 19.32c. H<sub>2</sub> can be nondissociatively weakly chemisorbed to form the complex in Fig. 19.32d. In [Cr(CO)<sub>5</sub>(H<sub>2</sub>)] and a few other coordination compounds, H<sub>2</sub> forms a three-center bond with the central metal atom; see G. Wilkinson (ed.), *Comprehensive Coordination Chemistry*, vol. 2, Pergamon, 1987, pp. 690–691.

### Ligand-Field Theory

The application of MO theory to transition-metal complexes gives what is called *ligand-field theory*. See *DeKock and Gray*, sec. 6-7.

### Canonical versus Localized MOs

For accurate quantitative calculations of molecular properties, one solves the Hartree–Fock equations (18.57) and obtains the canonical (delocalized) MOs. Since each canonical MO corresponds to a definite orbital energy, these MOs are also useful in discussing transitions to excited electronic states and ionization.

For qualitative discussion of bonding in the ground electronic state of a molecule, it is usually simplest to describe things in terms of localized bonding MOs (constructed from suitably hybridized AOs of pairs of bonded atoms), lone-pair MOs, and inner-shell MOs. One can usually get a reasonably good idea of the localized MOs without going through the difficult computations involved in first finding the canonical MOs and then using the Edmiston–Ruedenberg criterion to transform the canonical MOs to localized MOs. Localized MOs are approximately transferable from molecule to molecule; for example, the C–H localized MOs in CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are very similar to each other. Canonical MOs are not transferable.

## 19.7 THE VALENCE-BOND METHOD

So far our discussion of molecular electronic structure has been based on the MO approximation. Historically, the first quantum-mechanical treatment of molecular bonding was the 1927 Heitler–London treatment of H<sub>2</sub>. Their approach was extended by Slater and by Pauling to give the **valence-bond (VB) method**.

Heitler and London started with the idea that a ground-state H<sub>2</sub> molecule is formed from two 1s H atoms. If all interactions between the H atoms were ignored, the wave function for the system of two atoms would be the product of the separate wave functions of each atom. Hence, the first approximation to the H<sub>2</sub> spatial wave function is  $1s_A(1)1s_B(2)$ , where  $1s_A(1) = \pi^{-1/2}a_0^{-3/2}e^{-r_{1A}/a_0}$ . This product wave function is unsatisfactory, since it distinguishes between the identical electrons, saying that electron 1 is on nucleus A and electron 2 is on nucleus B. To take care of electron indistinguishability, we must write the approximation to the ground-state H<sub>2</sub> spatial wave function as the linear combination  $N'[1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)]$ . This function is symmetric with respect to electron interchange and therefore requires the antisymmetric two-electron spin function (18.41). The ground-state H<sub>2</sub> Heitler–London VB wave function is then

$$N'[1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)] \cdot 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (19.36)$$

Introducing a variable orbital exponent and using (19.36) in the variational integral, one finds a predicted  $D_e$  of 3.78 eV compared with the experimental value 4.75 eV and the Hartree–Fock value 3.64 eV.

The Heitler–London function (19.36) is a linear combination of two determinants:

$$N \begin{vmatrix} 1s_A(1)\alpha(1) & 1s_B(1)\beta(1) \\ 1s_A(2)\alpha(2) & 1s_B(2)\beta(2) \end{vmatrix} - N \begin{vmatrix} 1s_A(1)\beta(1) & 1s_B(1)\alpha(1) \\ 1s_A(2)\beta(2) & 1s_B(2)\alpha(2) \end{vmatrix} \quad (19.37)$$

The two determinants differ by giving different spins to the AOs  $1s_A$  and  $1s_B$  involved in the bonding.

When multiplied out, the MO spatial function (19.19) for  $H_2$  equals

$$N[1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)]$$

Because of the terms  $1s_A(1)1s_A(2)$  and  $1s_B(1)1s_B(2)$ , the MO function gives a 50% probability that an  $H_2$  molecule will dissociate into  $H^- + H^+$ , and a 50% probability for dissociation into  $H + H$ . In actuality, a ground-state  $H_2$  molecule always dissociates to two neutral H atoms. This incorrect dissociation prediction is related to the poor dissociation energies predicted by the MO method. In contrast, the VB function (19.36) correctly predicts dissociation into  $H + H$ .

If, instead of the symmetric spatial function in (19.36), one uses the antisymmetric spatial function  $N[1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)]$  multiplied by one of the three symmetric spin functions in (18.40), one gets the VB functions for the first excited electronic level (a triplet level) of  $H_2$ . The minus sign produces charge depletion between the nuclei, and the atoms repel each other as they come together.

To apply the VB method to polyatomic molecules, one writes down all possible ways of pairing up the unpaired electrons of the atoms forming the molecule. Each way of pairing gives one of the **resonance structures** of the molecule. For each resonance structure, one writes down a function (called a *bond eigenfunction*) resembling (19.37), and the molecular wave function is taken as a linear combination of the bond eigenfunctions. The coefficients in the linear combination are found by minimizing the variational integral. Besides covalent pairing structures, one also includes ionic structures. For example, for  $H_2$ , the only covalent pairing structure is  $H-H$ , but one also has the ionic resonance structures  $H^+ H^-$  and  $H^- H^+$ . These ionic structures correspond to the bond eigenfunctions  $1s_A(1)1s_A(2)$  and  $1s_B(1)1s_B(2)$ . By symmetry, the two ionic structures contribute equally, so with inclusion of ionic structures, the VB spatial wave function for  $H_2$  becomes

$$c_1[1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] + c_2[1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)]$$

One says there is *ionic-covalent resonance*. One expects  $c_2 \ll c_1$  for this nonpolar molecule.

In many cases, one uses hybrid atomic orbitals to form the bond eigenfunctions. For example, for the tetrahedral molecule  $CH_4$ , one combines four  $sp^3$  hybrid AOs on carbon with the  $1s$  AOs of the hydrogens.

For polyatomic molecules, the VB wave function is cumbersome. For example,  $CH_4$  has four bonds, and the bond eigenfunction corresponding to the single most important resonance structure (the one with each  $H1s$  AO paired with one of the carbon  $sp^3$  hybrids) turns out to be a linear combination of  $2^4 = 16$  determinants. Inclusion of other resonance structures further complicates the wave function.

The calculations of the VB method turn out to be more difficult than those of the MO method. The various MO approaches have overshadowed the VB method when it comes to actual computation of molecular wave functions and properties. However, the language of VB theory provides organic chemists with a simple qualitative tool for rationalizing many observed trends.