

# FRENCH AND TAYLOR

profound effects of these apparently simple features of the properties of electrons.

The two-electron system, such as helium, simple as it is, is too complicated to allow closed analytic solutions for the wave functions. Of course the same is true for all other multielectron atoms. The fundamental reason for this complication is that the electrons repel one another electrically. Roughly speaking, we cannot calculate the state of one electron in the atom until we know the states of all other electrons in the atom, but the states of these other electrons depend on the state of the electron we are considering. Added to this is the fundamental complication that the electrons are indistinguishable! The result of electron interaction and indistinguishability is that there is no natural way to break the multielectron problem down into smaller subproblems without introducing approximations. Even these approximations involve considerable numerical computation. Happily a good deal of intuitive insight can be provided by such approximations, even for atoms with very many electrons. Nevertheless, for atoms with two or more electrons, exact wave functions cannot be found.

Before taking up the problem of the helium atom itself, we consider in more general and basic terms the extension of Schrödinger's equation to two particles.

## 13-2 SCHRÖDINGER'S EQUATION FOR TWO NONINTERACTING PARTICLES

Suppose that two *noninteracting* particles are bound in the same environment, consisting, for example, of an external electric field. Let the masses of the particles be  $m_1$  and  $m_2$ . For the moment we limit attention to a one-dimensional system in which the positions of the particles are  $x_1$  and  $x_2$ . The potential energies of the particles due to their environment can then be written as  $V_1(x_1)$  and  $V_2(x_2)$  respectively. In general, even though the environment is the same for both, the values of  $V_1$  and  $V_2$  need not be the same, even when  $x_1 = x_2$ ; the particles might, for example, be a proton (charge  $+e$ ) and an alpha particle (charge  $+2e$ ). The cases of most interest to us will in fact be those for which the particles are identical, so that  $q_1 = q_2$ ,  $m_1 = m_2$ , and  $V_1(x) = V_2(x)$ , but we do not introduce these conditions just yet.

Classically, the total energy of the system described

above will be given by the following equation:

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V_1(x_1) + V_2(x_2) = E \quad (13-1)$$

We now suppose that the state of the two particles together can be described by a certain function  $\Psi$  that depends on  $x_1$ ,  $x_2$ , and  $t$ . Introducing the operators corresponding to  $p_1$ ,  $p_2$ , and  $E$ , we deduce that  $\Psi$  must obey the following form of the time-dependent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1} \frac{\partial^2 \Psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2 \Psi}{\partial x_2^2} + V_1(x_1)\Psi + V_2(x_2)\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (13-2)$$

Now each kinetic and potential energy operator is a function of one coordinate only, either  $x_1$  or  $x_2$  but not both. Moreover, the term on the right side of Eq. 13-2 involves an operator that is a function of time alone. When this type of condition occurred before, for example with the  $x$ ,  $y$ , and  $z$  coordinates of a particle in a rectangular box (Section 5-4), the  $x$  and  $y$  coordinates for a two-dimensional harmonic oscillator (Section 10-8), or with the  $r$ ,  $\theta$ ,  $\phi$ , coordinates of the electron in the hydrogen atom (Section 12-2), it was possible to separate the variables by substituting a product solution, each factor of which is a function of only one variable. In the present case we look for solutions  $\Psi$  which can be expressed as products of three separate functions of the individual independent variables  $x_1$ ,  $x_2$ , and  $t$ :

$$\Psi(x_1, x_2, t) = \psi_A(x_1) \cdot \psi_B(x_2) \cdot f(t) \quad (13-3)$$

Substituting this into Eq. 13-2, we then obtain the following equation:

$$\begin{aligned} & \left[ -\frac{\hbar^2}{2m_1} \frac{d^2 \psi_A}{dx_1^2} + V_1(x_1)\psi_A \right] \psi_B f \\ & + \left[ -\frac{\hbar^2}{2m_2} \frac{d^2 \psi_B}{dx_2^2} + V_2(x_2)\psi_B \right] \psi_A f = i\hbar \psi_A \psi_B \frac{df}{dt} \end{aligned}$$

We can then see that this factorization permits solutions in which  $\psi_A$  and  $\psi_B$  represent solutions of time-independent Schrödinger equations for the particles individually. (This is not surprising since the particles are assumed to be nonin-

teracting.) We can, in fact, put

$$-\frac{\hbar^2}{2m_1} \frac{d^2\psi_A}{dx_1^2} + V_1(x_1)\psi_A = E_A\psi_A$$

and

$$-\frac{\hbar^2}{2m_2} \frac{d^2\psi_B}{dx_2^2} + V_2(x_2)\psi_B = E_B\psi_B$$

Substituting these in the previous equation, we arrive at the following simple differential equation for the time-dependent factor  $f$ :

$$(E_A + E_B)f = i\hbar \frac{df}{dt}$$

leading to the solution

$$f(t) = e^{-i(E_A + E_B)t/\hbar}$$

This means that the Schrödinger wave function  $\Psi$  can be written in the form

$$\Psi(x_1, x_2, t) = \psi_A(x_1) \cdot \psi_B(x_2) e^{-iEt/\hbar} \quad (13-4)$$

where  $E = E_A + E_B$ . Thus we have an overall solution that is a product of single-particle space functions, but whose time dependence is defined by the total energy of the two particles.

The interpretation of  $\Psi$  as a probability amplitude involves the specification of the positions of *both* particles. The probability that particle number 1 is within a small range of positions  $dx_1$  at  $x_1$  and that particle number 2 is within a small range of positions  $dx_2$  at  $x_2$  is given by

$$dP = |\Psi|^2 dx_1 dx_2 = |\psi_A(x_1)|^2 dx_1 \cdot |\psi_B(x_2)|^2 dx_2$$

Note that this expression conforms to the rule for the joint occurrence of two independent events, that is, the probability of occurrence of both of two independent events is the product of the individual probabilities.

### 13-3 THE CONSEQUENCES OF IDENTITY

We now add the condition that the two particles are identical and therefore truly indistinguishable. It then follows that although the symbols  $x_1$  and  $x_2$  continue to denote the positions (in general different) of the two particles, we can no longer interpret them as meaning that particle number 1 is at  $x_1$  and particle number 2 is at  $x_2$ ; it could just as well be the other way around. And what this means is that the combined states hitherto described by  $\psi_A(x_1) \cdot \psi_B(x_2)$  and  $\psi_A(x_2) \cdot \psi_B(x_1)$  must be physically indistinguishable. However, the product functions as they stand are not consistent with this indistinguishability. We illustrate this with a specific example.<sup>1</sup>

Suppose that our two particles are confined to the one-dimensional box with infinite walls, and that  $\psi_A$  and  $\psi_B$  represent the first and second energy states in this potential. Then we shall have (see Chapter 3),

$$\psi_A(x_1)\psi_B(x_2) \sim \sin\left(\frac{\pi x_1}{L}\right) \cdot \sin\left(\frac{2\pi x_2}{L}\right)$$

and

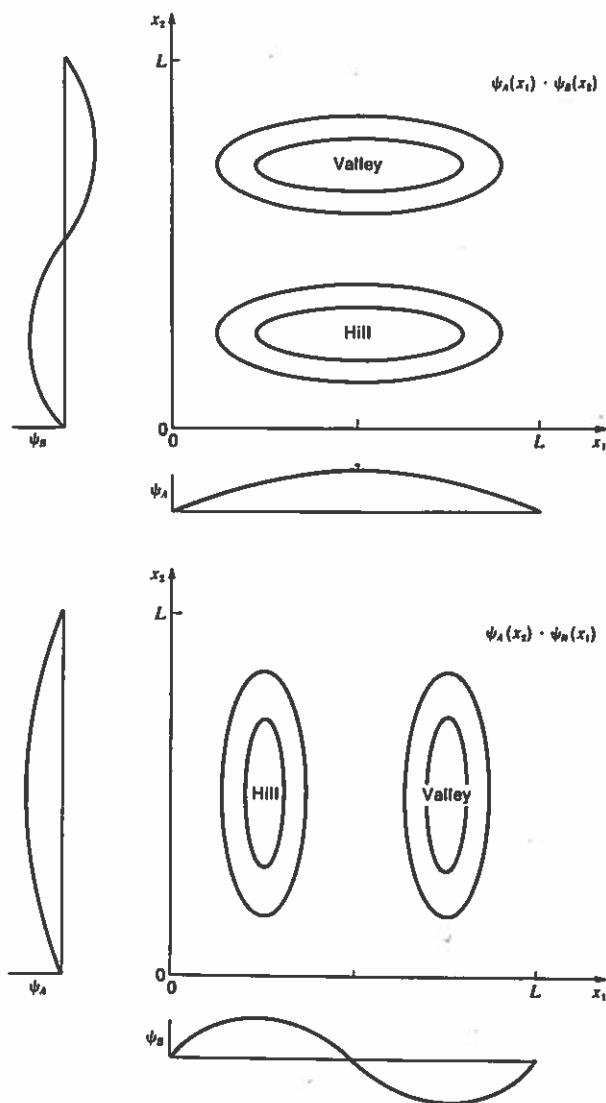
$$\psi_A(x_2)\psi_B(x_1) \sim \sin\left(\frac{\pi x_2}{L}\right) \cdot \sin\left(\frac{2\pi x_1}{L}\right)$$

If we pick arbitrary values of  $x_1$  and  $x_2$ , the values of these two products are different; for example, if  $x_1 = L/2$  and  $x_2 = L/4$  the first product of sines is unity and the second is zero. We can give a vivid picture of the overall situation by constructing a sort of contour map, as shown in Figure 13-1, in which the individual coordinates  $x_1$  and  $x_2$  are displayed on two perpendicular axes and the values of  $\psi_A \cdot \psi_B$  are plotted as positive or negative magnitudes with respect to the plane of the paper. The contours are lines of constant  $\psi_A \cdot \psi_B$ . Each of the two possible products then gives a hill and a valley in this representation of  $\psi_A \cdot \psi_B$ , but the two diagrams imply different probability densities, in general, for an arbitrary choice of the pair of coordinates  $(x_1, x_2)$ . This cannot be tolerated if the particles are indistinguishable. Any acceptable wave function  $\psi(x_1, x_2)$  for the system must have  $|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$ .

The kind of contradiction shown in the above example can be removed if we construct a wave function that is either the

<sup>1</sup>Our treatment from here on in this section owes a large debt to a discussion of the same problem in C. W. Sherwin, *Introduction to Quantum Mechanics*, Holt-Dryden, New York, 1959.

Fig. 13-1 Product wave functions for two noninteracting particles in an infinite square well. One of the particles is in the lowest-energy state, the other is in the second energy state. The product functions do not yield probability densities that are indistinguishable with respect to exchange of the two particles and therefore cannot be valid wave functions. (After Chalmers W. Sherwin, *Introduction to Quantum Mechanics*, Holt-Dryden, New York, 1959.)



sum or the difference of the product functions with  $x_1$  and  $x_2$  interchanged. Each of these combinations gives a probability distribution that is unaffected by an interchange of the two particles. Allowing for correct normalization, these combinations are as follows:

*Symmetric:*

$$\psi_s(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1) \cdot \psi_B(x_2) + \psi_A(x_2) \cdot \psi_B(x_1)] \quad (13-5a)$$

*Antisymmetric:*

$$\psi_a(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1) \cdot \psi_B(x_2) - \psi_A(x_2) \cdot \psi_B(x_1)] \quad (13-5b)$$

The labels *symmetric* and *antisymmetric* arise from the fact that an interchange of the coordinates  $x_1$  and  $x_2$  leaves the first combination unchanged, but leads to a reversal of sign in the second combination. The values of the probability density  $|\psi|^2$  are thus invariant with respect to the interchange in both cases.

The resulting contour maps of the probability amplitudes of the symmetric and antisymmetric functions are somewhat as shown in the two diagrams of Figure 13-2. We note some

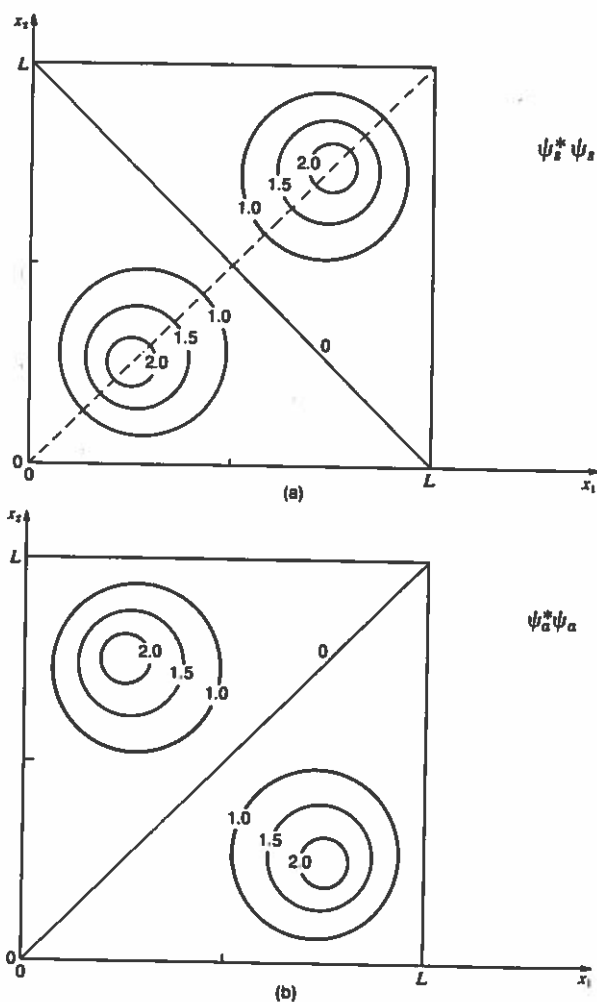


Fig. 13-2 (a) The joint probability distribution for two identical particles in a symmetric combination of the two lowest states in an infinite square well. (b) The joint probability distribution for the antisymmetric combination of the same two states.

very striking features. In the symmetric state the maximum probability occurs for two points at which  $x_1 = x_2 = L/4$  or  $3L/4$ , and quite generally the probability is large only if the difference between  $x_1$  and  $x_2$  is small (particles close together). In the antisymmetric state, on the other hand, the probability is zero everywhere along the diagonal that corresponds to  $x_1 = x_2$ , and the peaks of the probability distribution occur for situations in which  $x_1$  and  $x_2$  are widely different (particles far apart). Thus if the particles are described by a symmetric function of the space coordinates they tend to huddle together, whereas if they are described by an antisymmetric function they act as if they were repelling one another.

It is important to recognize that the properties of "huddling together" or "avoiding one another" that characterize symmetric and antisymmetric states respectively arise *without our invoking specific forces of attraction or repulsion between the particles themselves*. These properties arise naturally out of the indistinguishability of the particles and the symmetry of the wave functions that describe them. What we see here is a uniquely quantum-mechanical effect, having no counterpart in the description of nature according to classical physics.

Naturally one asks the question: Which choice do two identical particles in fact make—do they congregate or do they avoid one another? The answer depends in a basic way on what type of particles one is considering. However, the question, as posed above, does not have an unequivocal answer; its scope is too limited. What is involved is a symmetry property that applies to a *complete* interchange of the roles of the two particles, not just exchange of their spatial coordinates. In particular, if the particles have an intrinsic spin, the overall exchange symmetry involves the combined spin state. We shall now examine this problem primarily as it applies to two electrons or other particles with spin  $\frac{1}{2}$ .

## 13-4 SPIN STATES FOR TWO PARTICLES

We saw in Chapter 11 (Section 11-4) how the property that we call electron spin is expressed in two possible configurations—"spin up" or "spin down"—of an electron with respect to a given axis of quantization. Let us label these spin states  $\alpha$  and  $\beta$ , respectively, and then consider the spin states available to two electrons together. We shall label the elec-

trons as number 1 and number 2, so that, for example, the combination  $\alpha(1) \cdot \beta(2)$  describes a situation in which number 1 has spin up and number 2 has spin down. The possible combinations of the individual spin states are then the following:

$$\alpha(1) \cdot \alpha(2) \quad \alpha(1) \cdot \beta(2) \quad \alpha(2) \cdot \beta(1) \quad \beta(1) \cdot \beta(2)$$

The first and the last are automatically symmetric with respect to an interchange of the two electrons, but the second and third, like the products  $\psi_A \psi_B$  of the space functions, are neither symmetric nor antisymmetric. However, from these second and third products we can, just as with the space functions, construct two other spin functions that have definite symmetry properties:

*Symmetric:*

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

*Antisymmetric:*

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

We then observe that we have a total of four combined spin states with definite exchange symmetry, three of them being symmetric and one antisymmetric:

<i>Symmetric</i>	<i>Antisymmetric</i>
$\alpha(1)\alpha(2)$	
$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$	$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
$\beta(1)\beta(2)$	

Looking at the *symmetric* spin states, we notice that one of them describes both spins up, one describes both spins down, and one is a superposition of up-and-down spins. The values of the  $z$  component of the *combined* spin defined by these functions correspond to resultant  $z$  components of spin equal to  $+1$ ,  $0$ , and  $-1$ . In contrast, the single *antisymmetric* spin function with its equal superposition of up and down spins corresponds to a spin  $z$  component of zero only. These respec-



tive values of  $z$  angular momentum are those we would associate, by analogy with the properties of orbital angular momentum, with combined spin quantum numbers  $S = 1$  for the symmetric states, and  $S = 0$  for the antisymmetric. Thus for two electrons, or for a pair of any particles of half-integer spin, there are two basic kinds of spin states: a group of three symmetric states (a *triplet*) belonging to  $S = 1$ , and one antisymmetric state (a *singlet*) belonging to  $S = 0$ . We shall denote the complete set of spin functions of these two different kinds of states by  $\chi_s$  and  $\chi_a$ , respectively.

If we had considered two spinless particles, for example two alpha particles, there would of course be no spin states and the above complications would never arise. On the other hand, for two particles of intrinsic spin greater than  $\frac{1}{2}$ , we should have a classification into symmetric and antisymmetric states much as we have found for electrons, with singlets, triplets, and this time also with *multiplets*. For example, for two particles of intrinsic spin one (e.g., deuterons), their combination can have  $S = 0$  (one state),  $S = 1$  (three states), and  $S = 2$  (five states).

The total wave function for two identical particles is then the product of a spatial function  $\psi$  and one of the possible spin functions  $\chi$ . It is the *overall* symmetry of this *total* wave function that we shall now consider.

## 13-5 EXCHANGE SYMMETRY AND THE PAULI PRINCIPLE

### *Overall Symmetry of the Wave Function*

Given the existence of symmetric and antisymmetric space functions ( $\psi_s, \psi_a$ ) and symmetric and antisymmetric spin functions ( $\chi_s, \chi_a$ ), it is possible to construct symmetric and antisymmetric total wave functions as follows:

*Symmetric:*

$$\psi_s \chi_s \quad \text{or} \quad \psi_a \chi_a$$

*Antisymmetric:*

$$\psi_s \chi_a \quad \text{or} \quad \psi_a \chi_s$$

All of these wave functions satisfy the property of indistin-

**TABLE 13-1 Some Fermions and Bosons**  
(Intrinsic Spin Given in Parenthesis)

<i>Fermions</i>	<i>Bosons</i>
<i>Antisymmetric with respect to complete exchange</i>	<i>Symmetric with respect to complete exchange</i>
electron ( $\frac{1}{2}$ )	pi meson (0)
proton ( $\frac{1}{2}$ )	alpha particle (0)
neutron ( $\frac{1}{2}$ )	He <sup>4</sup> atom (0)
He <sup>3</sup> atom ( $\frac{1}{2}$ )	deuteron (1)

guishability between the two particles involved. Therefore, in distinguishability alone gives us no basis for deciding which of these functions is valid for any species of particle. However these different functions predict different *properties* of the two particle systems, in particular the quantized energies of the combined system. For two electrons, the only states found in nature are those for which the total wave function is *antisymmetric*. This fact was first recognized (in 1926) by Heisenberg,<sup>2</sup> and led to a detailed understanding of the energy-level system of the helium atom (which we shall discuss in Section 13-8). The condition of antisymmetry eliminates half of the combined states that would otherwise be possible for two electrons.

Not all wave functions for identical particles are antisymmetric, but the study of observed states shows that, for a given kind of particle, states of only one overall symmetry exist: the states of a given species are characteristically all symmetric or all antisymmetric. For all particles of half-integral spin, the total wave function, as for electrons, is always antisymmetric with respect to (complete) interchange, whereas with all particles of integral spin the total wave function is always symmetric. Table 13-1 lists a selection of particles of each main type. In this classification, particles of half-integral spin (such as electrons) are called *fermions* after Enrico Fermi; particles with the other kind of symmetry are called *bosons* after the Indian physicist S. N. Bose.

### *Overall Symmetry and the Exclusion Principle*

As far as atomic structure is concerned, the most important

<sup>2</sup>W. Heisenberg, Z. Phys. 39, 499 (1926).

tant manifestation of these characteristic symmetry properties of identical particles is summarized in the *Pauli exclusion principle*. One can see the basis of this in a property of the antisymmetric space function  $\psi_a$  of Eq. 13-5b:

$$\psi_a(1, 2) = \frac{1}{\sqrt{2}} [\psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1)]$$

If in this expression we choose the states  $A$  and  $B$  to be the *same* single-particle state, then the total wave function vanishes identically. This is another way of saying that no such total state exists. If we now extend the meaning of the symbols  $\psi_A$  and  $\psi_B$  to refer not just to the spatial factors but to the complete space-and-spin state functions of individual particles, then  $\psi_a$  vanishes whenever the states  $A$  and  $B$  are taken to be the same in all respects (now including spin orientation). The *Pauli exclusion principle* spells this out by saying that *no two electrons in the same atom can have all quantum numbers the same*. This result was in fact discovered by W. Pauli in 1924<sup>3</sup> before an understanding of it in terms of the symmetry of wave functions had been developed. Pauli simply inferred, from the detailed structure of atomic energy levels as revealed by spectroscopy, that electrons must have a two-valued quantum number (later to be associated with spin) in addition to the three quantum numbers ( $n, l, m_l$ ) previously known. He inferred, further, that if the three spatial quantum numbers for two electrons in an atom were the same, the fourth (spin) quantum number must be different, which we now describe by saying that their spins are *antiparallel*. Naturally, the same restriction, couched in somewhat different terms, applies if one writes the total wave function as the product of a total space function and a total spin function (see the exercises).

### Exchange Energy

At the end of Section 13-3 we posed a question about the space properties of identical particles bound in a common potential: do they huddle together (symmetric space function) or

<sup>3</sup>W. Pauli, Z. Phys. 31, 373 and 765 (1924). For an interesting account of the historical development of the ideas of the exclusion principle and spin, see the articles by R. Kronig and B. L. van der Waerden in *Theoretical Physics in the Twentieth Century* (a memorial volume to Wolfgang Pauli) ed. M. Fierz and V. F. Weisskopf, Interscience Publications, New York, 1960.

do they avoid one another (antisymmetric space function)? We are now able to answer this question in terms of the kind of particles involved. Any two electrons in a single system, for example, must have an *overall* antisymmetric wave function. There are four ways this can occur:  $\psi_s\chi_a$  with a symmetric space function  $\psi_s$  for which there is only one antisymmetric spin state  $\chi_a$  (a *singlet state*); or  $\psi_a\chi_s$  with an antisymmetric space function  $\psi_a$  for which there are three symmetric spin states (a *triplet state*). Two electrons in the singlet state will tend to huddle together because of their symmetric space function. In contrast two electrons in a triplet state will tend to avoid one another because of their antisymmetric space function. In developing the model that led to this result, we assumed that there was no electron-electron Coulomb interaction; any "huddling" or "avoidance" of electrons in this model is solely a quantum effect. Of course, in a more complete theory, the Coulomb repulsion between electrons must be taken into account. When we include the Coulomb energy in the model of the helium atom (Section 13-8), it will lead to a slightly higher energy for the system in the singlet state (in which electrons huddle) than for the triplet state (in which electrons avoid one another). This difference of energy in the two cases is called the *exchange energy* because it arises from the symmetry properties of electron wave functions under an assumed exchange of space and spin coordinates.

### 13-6 WHEN DOES SYMMETRY OR ANTISYMMETRY MATTER?

In principle the symmetry or antisymmetry of the wave function for two or more identical particles must be involved for every physical system. In practice, however, it will often be unnecessary (as well as impracticable) to apply the symmetry condition explicitly. Consider, for example, two separate hydrogen atoms, both in their ground state. Then, strictly speaking, we ought to construct for this system a total wave function that is antisymmetric with respect to exchange of the two electrons (and of the two protons also). However, it is intuitively more or less obvious that if the atoms are widely separated (by more than a few angstroms), they act as entirely independent systems. The fact that each electron is in the same quantum state with respect to its own proton is in no sense a violation of the Pauli exclusion principle. On the other hand, if the two

atoms are brought so close that they begin to interact (the ultimate result perhaps being the formation of a hydrogen molecule) then the construction of an antisymmetrized wave function is essential to a correct description of the complete system.

There is a simple criterion for whether or not the symmetry must be considered. If the individual-particle wave functions *overlap* significantly, in the sense that there are regions in which both have appreciable magnitude, then the symmetry or antisymmetry is important. If the amount of overlap is negligible, then one can use a simple product wave function that is neither symmetric nor antisymmetric. The formal basis of this criterion can be made apparent if one writes the total space wave function for a system of two particles:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1)\psi_B(x_2) \pm \psi_B(x_1)\psi_A(x_2)]$$

Forming from this the probability density, we have

$$\begin{aligned} |\psi(x_1, x_2)|^2 = & \frac{1}{2} |\psi_A(x_1)\psi_B(x_2)|^2 + \frac{1}{2} |\psi_B(x_1)\psi_A(x_2)|^2 \\ & \pm \frac{1}{2} \{ \psi_A^*(x_1)\psi_B(x_1)\psi_B^*(x_2)\psi_A(x_2) \\ & + \psi_B^*(x_1)\psi_A(x_1)\psi_A^*(x_2)\psi_B(x_2) \} \end{aligned}$$

The term within braces embodies the essential consequence of identity, that each particle must be associated with both of the component wave functions. However, if  $\psi_A$  is negligible at values of  $x$  where  $\psi_B$  is large, and vice versa, the products in this term— $\psi_A^*(x_1)\psi_B(x_1)$ , for example—are negligible because the *same* value of  $x$  is involved in both factors in the product. In this case, only the first two terms in the above equation are significant. Then we are left with a probability function  $|\psi|^2$  given by a sum of squared magnitudes, both of which assign each particle separately to a particular state. In this case the value of the probability density, for given values of  $x_1$  and  $x_2$ , is indifferent to whether the total wave function is symmetric, antisymmetric, or merely a product function with no particular symmetry.

At the end of Chapter 12, we called alkali metals “hydrogen-like.” In a neutral alkali atom the nuclear charge  $+Ze$  is shielded from the outer “valence” electron by  $Z-1$  electrons in completed shells. This outer electron then acts

somewhat like an electron in a hydrogen state. This will be discussed somewhat more rigorously in Section 13-9 below. The important point here is that talking about "the valence electron" as if it had an identity separate from the other electrons in the atom is justified only to the extent that the probability overlap between the valence state and other electron states is small. We saw at the end of Chapter 12 that the electrostatic energy associated with this overlap—and thus presumably the overlap itself—is smaller for larger values of orbital angular momentum for the valence state. Electron indistinguishability and wave function symmetry are less important considerations for these higher- $l$  states.

We can see, then, that although the Pauli exclusion principle is a direct expression of the requirement of antisymmetry for a state of two or more electrons, it acquires physical importance only to the degree that the electrons in question have overlapping wave functions, whether or not they are bound in the same atom.

## 13-7 MEASURABILITY OF THE SYMMETRY CHARACTER

### *The Periodic Table*

For electrons, the facts of atomic structure supply the main evidence that only antisymmetric states occur. It is only on this basis that we can understand the building up (German: *Aufbau*) of the total electron configuration of a many-electron atom. Only  $2(2l + 1)$  electrons can be accommodated with different values of  $m_l$  and  $m_s$  in a shell associated with particular values of  $n$  and  $l$ —one electron for each of the states discussed in Chapter 12 (Section 12-6). We shall, however, defer our detailed discussion of this until later in the chapter (Section 13-9).

### *Electron Gas in a Metal*

For a confined system of very many identical particles, the properties of the system can be profoundly influenced according to whether the overall wave function is symmetric or antisymmetric. If the basic character of the particles is such that the wave function is symmetric, this means that an unlimited number of particles can be accommodated in the lowest possible energy level. If, on the other hand, the particles are

such that the overall wave function is antisymmetric, the number of particles in each energy level is strictly limited (to a total of  $2s + 1$ , where  $s$  is the spin quantum number). In highly condensed systems (many particles per unit volume) this has the consequence that fermions "fill up" the lower energy states so that some are driven to occupy eigenstates of high energy, whereas bosons can congregate in states of low energy (see the exercises).

The behavior of the "gas" of conduction electrons in a metal is in accord with the proposition that electrons are fermions obeying the Pauli principle. In a metal at room temperature, electrons are forced to occupy states up to energies corresponding to tens of thousands of degrees Kelvin. One consequence of this is that, if the temperature of the metal is raised through, say, 100 K, the energy distribution of the electrons is scarcely affected. This means that the electron gas does not give rise to any significant contribution to the specific heat of a metal, even though there is of the order of one conduction electron for every atom in the metal (hence about a mole of free electrons in each gram-atom of metal). The absence of any such contribution is inexplicable by classical physics, but can be viewed as further evidence that many-electron wave functions are antisymmetric.

### *Superfluidity*

Limitations imposed by exchange symmetry apply not only to electrons in a single atom but also to whole atoms that are part of a larger system. For example, a system of identical *spinless* atoms (which are therefore bosons) has total wave functions that are symmetric with respect to space exchange alone. The outstanding example of this is helium ( $\text{He}^4$ ) in bulk. The exchange symmetry encourages all of the atoms to be in the same overall quantum state, including both the internal state and the translational state of the atom. One consequence of this is the *superfluidity* of liquid helium, which at temperatures near absolute zero encounters no resistance to its flow through microscopic holes.

A system containing identical photons, too, exhibits this overall symmetric property in its total wave functions. The unique energy spectrum of radiation within an enclosure at a given temperature (*black-body radiation*) is a result of this symmetry.

## Scattering

Perhaps the nearest to a direct measurement of the symmetry character occurs in the analysis of elastic collisions between pairs of identical particles. Suppose that two such particles approach one another and mutually scatter. In the center-of-mass frame the results of the elastic collision are that the velocity of each particle is changed in direction without being changed in magnitude. However, if the particles are identical, a collision involving a change of direction by  $\theta$  is indistinguishable from one involving a change of  $\pi - \theta$  (Figure 13-3). Classically, the deflections through  $\theta$  and  $\pi - \theta$  would represent physically separate events, and the observed intensity at  $\theta$  would be the sum of these independent contributions. If  $p(\theta)$  and  $p(\pi - \theta)$  are the probabilities of these processes, then the total probability of a particle emerging from the collision in the direction  $\theta$  with respect, say, to the particles incident from the left would be given by

$$P_{\text{classical}}(\theta) = p(\theta) + p(\pi - \theta)$$

Quantum-mechanically, however, the scattering probability is the square of the modulus of a net probability *amplitude* which is a coherent superposition of the amplitudes belonging to  $\theta$  and  $\pi - \theta$  separately. This is yet another example of superposing amplitudes for alternative ways to the same outcome, as with double-slit and polarized-photon interference experiments. Thus we have

$$P_{\text{quantum}}(\theta) = |f(\theta) \pm f(\pi - \theta)|^2 \quad (13-6)$$

where the  $+$  sign corresponds to a symmetric space wave function for the two particles, and the  $-$  sign to an antisymmetric

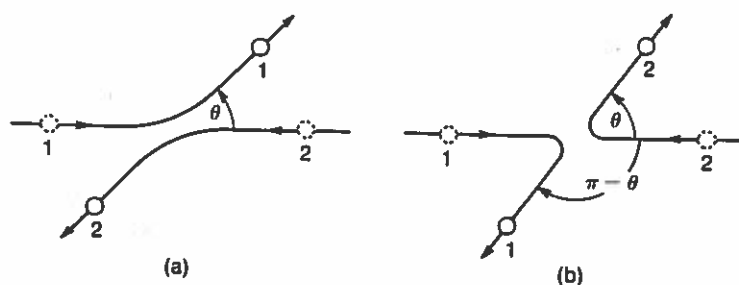


Fig. 13-3  
Collision processes which are indistinguishable if particles 1 and 2 are identical.



space function. The classical result, if expressed in terms of the squares of probability amplitudes, would be

$$P_{\text{classical}}(\theta) = |f(\theta)|^2 + |f(\pi - \theta)|^2$$

In the particular case of spinless particles, for which the combined spin function is necessarily symmetric, the results of the scattering will then reveal whether the space function is symmetric or antisymmetric, corresponding to the plus or minus sign in Eq. 13-6. Notice in particular that if we put  $\theta = \pi/2$ , then two very clear alternatives develop:

*For symmetric states:*

$$P\left(\frac{\pi}{2}\right) = 4\left|f\left(\frac{\pi}{2}\right)\right|^2$$

*For antisymmetric states:*

$$P\left(\frac{\pi}{2}\right) = 0$$

Fig. 13-4 Elastic-scattering cross section for alpha particles incident on  $\text{He}^4$ . The Rutherford theory is classical; the Mott theory is quantum-mechanical (1 barn =  $10^{-24} \text{ cm}^2$ ). [After N. P. Heydenburg and G. M. Temmer, *Phys. Rev.* 104, 123 (1956).]

